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1 Independent Control of Adhesive and Bulk Properties of Hybrid 2 Silica Coatings on Polycarbonate

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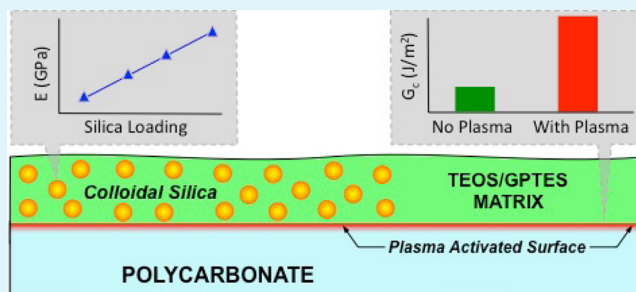
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8 **ABSTRACT:** Transparent polymers are widely used in many
9 applications ranging from automotive windows to micro-
10 electronics packaging. However, their intrinsic characteristics,
11 in particular their mechanical properties, are significantly
12 degraded with exposure to different weather conditions. For
13 instance, under humid environment or UV-irradiation,
14 polycarbonate (PC) undergoes depolymerization, leading to
15 the release of Bisphenol A, a molecule presumed to be a
16 hormonal disruptor, potentially causing health problems. This
17 is a serious concern and the new REACH (Registration,
18 Evaluation, Authorization and Restriction of Chemical
19 substances) program dictates that materials releasing Bisphenol A should be removed from the market by January 1st, 2015
20 (2012-1442 law). Manufacturers have tried to satisfy this new regulation by depositing atop the PC a dense oxide-like protective
21 coating that would act as a barrier layer. While high hardness, modulus, and density can be achieved by this approach, these
22 coatings suffer from poor adhesion to the PC as evidenced by the numerous delamination events occurring under low scratch
23 constraints. Here, we show that the combination of a N₂/H₂-plasma treatment of PC before depositing a hybrid organic-
24 inorganic solution leads to a coating displaying elevated hardness, modulus, and density, along with a very high adherence to PC
25 (> 20 J/m² as measured by double cantilever beam test). In this study, the sol-gel coatings were composed of hybrid O/I silica
26 (based on organoalkoxysilanes and colloidal silica) and designed to favor covalent bonding between the hybrid network and the
27 surface treated PC, hence increasing the contribution of the plastic deformation from the substrate. Interestingly, double-
28 cantilever beam (DCB) tests showed that the coating's adhesion to PC was the same irrespective of the organoalkoxysilanes/
29 colloidal silica ratio. The versatility of the sol-gel deposition techniques (dip-coating, spray-coating, etc.), together with the
30 excellent mechanical properties and exceptional adherence of this hybrid material to PC should lead to interesting new
31 applications in diverse fields: optical eye-glasses, medical materials, packaging, and so forth.

32 **KEYWORDS:** polycarbonate, sol-gel, hybrid silica, elastic properties, adhesion, plasma treatment, double cantilever beam



33 ■ INTRODUCTION

34 Polycarbonate (PC) is widely used commercially because of its
35 interesting characteristics such as transparency, lightness, high
36 impact resistance, along with an excellent quality/price ratio.
37 However, PC suffers from low scratch resistance and poor
38 stability in humid environment or UV exposure, leading to a
39 decrease in the material's lifetime and to the release of
40 Bisphenol A, a molecule highly suspected to be detrimental for
41 human health. As of today, two different approaches have been
42 mainly considered to mitigate these issues: formulating PC-
43 based copolymers,¹ or modifying the PC surface with a
44 protective coating.²⁻⁶ While the latter approach is more
45 challenging, it provides a very attractive solution to the
46 industry if the adhesion, the bulk mechanical properties, and
47 the barrier properties of such coatings could be precisely
48 controlled. Therefore, the research in this field has mainly
49 focused on the optimization of the coating's bulk mechanical

properties. In this regard, hybrid organic/inorganic silica
50 coatings prepared by sol-gel chemistry have received lots of
51 attention because of the possibility to enhance the mechanical
52 properties through the inorganic part while imparting other
53 specific properties for a given application with the organic
54 functionalities.⁷ The sol-gel route also presents several other
55 advantages such as, the availability of a large library of
56 precursors, implementability with low cost equipment, and
57 compatibility with PC's relatively low glass transition temper-
58 ature (143 °C).⁵⁹

In this paper, highly transparent hybrid silica coatings issued
60 from 3-glycidoxypropyltriethoxysilane (GPTES), tetraethylor-
61 thosilicate (TEOS), and colloidal silica prepared by the sol-gel
62

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63 route under acidic conditions and dip-coated on untreated and
 64 plasma pretreated PC are reported. This selection of precursors
 65 should ensure good mechanical properties for the bulk due to
 66 the silica network^{8,9} as well as an elevated interfacial fracture
 67 energy if plastic deformation within the PC could be activated.
 68 The effect of the precursor's ratio and the PC pretreatment on
 69 the bulk hardness, Young's modulus, and density, along with
 70 the adhesive fracture energy are thus investigated. As expected,
 71 both the hardness and the elastic modulus measured using
 72 nanoindentation and the density measured by X-ray reflectivity
 73 increased with increasing inorganic content, that is, colloidal
 74 silica. The coatings adhesive fracture energy (G_c) was quantified
 75 by a double cantilever beam (DCB) test, a newly adapted
 76 technique for polymeric substrates. To the best of our
 77 knowledge, it has never been reported for sol-gel hybrid silica
 78 films deposited on PC. The G_c values increased from less than 2
 79 J/m² to more than 20 J/m² when the PC surface was pretreated
 80 with a nitrogen based plasma. Moreover, the excellent film
 81 adhesive properties are maintained over long time storage as
 82 the same G_c values were obtained after aging for 1 year under
 83 atmospheric conditions. Surprisingly, the coatings fracture
 84 energy was not affected when the colloidal silica content varied
 85 from 10 to 50 wt %. Altogether, these results demonstrate that
 86 the bulk and the adhesive properties of such hybrid coatings
 87 can be independently controlled. It could be envisioned that
 88 with the proper pretreatment, precursors selection and sol-gel
 89 conditions, tunable optical, electrical, mechanical, and surface
 90 properties could be achieved while preserving the interfacial
 91 integrity of the coating to the polymeric substrate.

92 ■ EXPERIMENTAL METHODS

93 **Coating Preparation.** Coatings were prepared by the sol-gel route
 94 using TEOS and GPTES as alkoxysilanes and commercially available
 95 colloidal silica (Levasil 200E from AKZONOBEL, with an average
 96 particles size of 30 nm). Solutions with different alkoxysilanes/
 97 colloidal silica weight ratios ranging from 50/50 to 90/10 have been
 98 prepared. The coating deposition was realized after 36 h of sol aging
 99 by dip-coating at 1 mm/s, on both untreated and pretreated PC.
 100 Regarding the latter, a N₂/H₂ plasma treatment was performed by
 101 AcXys Technologies company (atmospheric pressure, 300 mm/s flow
 102 rate) on the PC surface prior to coating deposition. Atomic force
 103 microscopy (AFM) analysis performed after treatment did not indicate
 104 any change in terms of surface roughness. Finally, the coated samples
 105 were annealed under air in a ventilated oven at 135 °C for 1 h. Several
 106 micrometer-thick coatings were obtained. The coating preparation
 107 steps and deposition are fully described in reference 8.

108 **Characterization.** The density, ρ , of the coating was measured by
 109 specular X-ray reflectivity (XRR) using a diffractometer (X'Pert Pro
 110 MRD, Panalytical, Westborough, MA) with a ceramic X-ray tube ($\lambda =$
 111 0.154 nm) and high resolution horizontal goniometer (reproducibility
 112 = $\pm 0.0001^\circ$). The critical angle, θ_c , from the reflectivity data was
 113 obtained from the peak position of $I \times q^4$ versus q plot, where I is the
 114 reflected X-ray intensity, $q = (4p/\lambda) \times \sin \theta$, λ is the wavelength, and θ
 115 is the grazing angle of the X-ray beam. The coating density ρ was
 116 inferred from the electronic density ρ_e calculated using the equation

$$\rho_e = \frac{\theta_c}{\lambda} \times \frac{\pi}{r_e} \times \frac{A}{Z} \times N_A$$

117 where r_e is the classical electron radius, A the atomic mass number, Z
 118 the atomic number, and N_A the Avogadro number.

119 Quasi-static nanoindentation measurements were performed on a
 120 commercial nanoindenter, Hysitron Model TI-950, with a diamond
 121 cube corner (three-sided pyramid) probe of 40 nm end radius. To
 122 eliminate adsorbed moisture that could complicate measurements of
 123 mechanical properties, nanoindentation was carried out under a
 124 positive pressure of dry nitrogen in the closed indenter enclosure.

Freshly loaded samples were allowed to equilibrate with dry nitrogen
 for at least 12 h that also allows for thermal equilibrium. The cube
 corner probe was calibrated on a quartz sample with a modulus of 70
 GPa. As the probe was indenting the sample, both contact depth (h)
 and applied load (P) were monitored. Seven different loads ranging
 from 7 nN to 25 nN with 7 runs per load were carried out on each
 sample. At the maximum indentation depth, the load was kept
 constant for 5 sec. A load versus contact depth curve was then
 generated from the collected data. The reduced Young's modulus E_r
 and hardness H were further calculated based on their relationship
 with the contact area A_c and the sample stiffness S using the following
 equations:

$$H = \frac{P_{\max}}{A_c}$$

$$E_r = \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \times \frac{S}{\sqrt{A_c}}$$

The effective contact area A_c was calculated from the contact depth
 and the tip geometry using the Oliver and Pharr method.¹⁰ The
 stiffness was obtained from the slope of the unloading curve (dP/dh).

The Young's modulus, E_p , was then calculated from the reduced
 modulus E_r , taking into account elastic displacements from both the
 film and the indenter, using the equation

$$\frac{1}{E_r} = \frac{(1 - \nu_i^2)}{E_i} + \frac{(1 - \nu_f^2)}{E_f}$$

where E_i is the indenter Young's modulus (1140 GPa), ν_i the indenter
 poisson's ratio (0.07), and ν_f the film poisson's ratio (assigned as 0.25).

The coatings adhesion energy on PC was quantified using the
 symmetric Double Cantilever Beam (DCB) test. The specimens were
 prepared by bonding a blank (uncoated) substrate of 2 mm- thickness
 onto a coated substrate of the same thickness. The in-plane
 dimensions of the specimen were 9 mm \times 70 mm. The fracture
 tests were conducted on a micromechanical adhesion test system
 (DTS Delaminator Test System, DTS Company, Menlo Park, CA) in
 displacement control mode. The specimens were loaded at a
 displacement rate of 5 μ m/sec in tension to produce controlled
 crack growth, followed by unloading. The load was measured
 simultaneously and the adhesion energy G_c (J/m²) was calculated
 from the critical value of the strain energy release rate using the
 Kanninen corrected equation¹¹

$$G_c = \frac{12 \times P_c^2}{E \times B^2 \times h} \times \left(\frac{a}{h} + 0.64 \right)^2$$

where P_c is the load when the load–displacement curve deviated from
 linearity until initial crack extension, E the plane strain Young's
 modulus of the substrate, B the substrate width, a the crack length, and
 h the substrate thickness.

X-ray photoelectron spectroscopy (XPS) [Physical Electronics Inc,
 Chanhassen, MN] was used to characterize the atomic composition of
 the DCB fracture surfaces throughout the bulk. An Al-K α (1486 eV)
 X-ray source with a spot size of \sim 1 mm was used in conjunction with
 an argon ion beam to sputter off the material at a rate of 4 nm/min for
 the silica coatings, with the setting of 1 kV, 0.5 μ A, and 1 mm \times 1 mm
 sputter spot. The angle between the detector and the sample surface
 was 45°. The scan range for the binding energy was 0 to 1000 eV.

119 ■ RESULTS AND DISCUSSION

Four different sol-gel solutions with alkoxysilanes/colloidal
 silica weight ratios of 50/50, 70/30, 80/20, and 90/10 were
 studied. The alkoxysilanes contribution comes from a mixture
 of GPTES and TEOS with a constant TEOS/GPTES molar
 ratio of 1.65. Regarding the coatings' thermal treatment, the
 low annealing temperature of the samples (set at 135 °C to stay
 below the T_g of PC) should prevent the formation of highly

179 densified silica. Therefore, pre-condensed colloidal silica was
180 added to the solutions to strengthen the final coating. As
181 described previously,⁸ sol-gel solutions were aged for 36 h
182 before deposition, to ensure completion of the hydrolysis
183 reaction while condensation is still at an early stage.¹² This
184 should lead to maximum bonding between the coating and the
185 substrate during film deposition and curing.

186 To assure the substrate's integrity over time, it was highly
187 important to assess the coatings bulk properties with regards to
188 raw PC, and also to evaluate the coatings' adhesion to the
189 substrate, a critical component of the coating's lifetime. Those
190 two characteristics were studied separately. The bulk
191 mechanical properties (Young's modulus and hardness) and
192 density were measured by nanoindentation, and by X-ray
193 reflectivity, respectively. The coatings fracture energy was
194 obtained from symmetric DCB tests.

195 **Bulk Properties.** First, we measured the coatings densities
196 by X-ray reflectivity as a function of the colloidal silica content
197 (Figure 1). In the range of 10 to 50 wt % colloidal silica, the

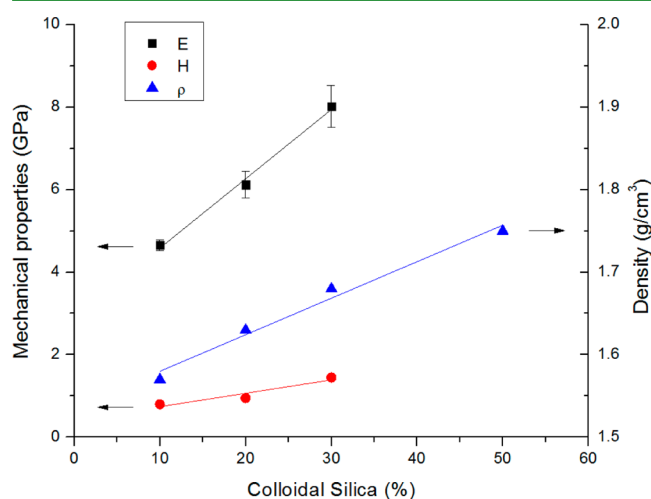


Figure 1. Coatings Young's modulus (E), hardness (H), and density (ρ) as a function of colloidal silica percentage as measured by nanoindentation. Hardness standard deviation was always smaller than 0.1 GPa and is not represented here. Pure silica Young's modulus hardness and density from literature respectively are 72 GPa, 8 GPa, and 2.2 g/cm³.

198 density increased linearly from 1.57 g/cm³ to 1.75 g/cm³. As
199 expected, the addition of pre-densified silica nanoparticles leads
200 to a significant change in film bulk properties. Interestingly, by
201 extrapolating the density data to 100 wt % colloidal silica, one
202 would obtain a density of 1.94 g/cm³, a value close to the one
203 of dense silica coatings (2.2 g/cm³) deposited by gas phase
204 deposition techniques.¹³ The results above indicate that the
205 intrinsic density of the nanoparticles is around 1.94 g/cm³ and
206 that they are well dispersed throughout the main bulk of the
207 film. Moreover, the absence of porosity, as indicated by
208 ellipsometric measurements,⁸ suggests that the intimate mixing
209 of the nanoparticles within the hybrid network was successfully
210 achieved.

211 Next, nanoindentation experiments were conducted on the
212 different coatings to study the influence of the silica
213 nanoparticle loading on the bulk Young's modulus and
214 hardness (Figure 1). The contact depth measured at the
215 different loads for coatings with up to 30 wt % silica
216 nanoparticles was always smaller than a tenth of the total film

thickness (2–3 μm), minimizing the substrate effect.¹⁴ 217
218 Conversely, nanoindentation data indicated a strong substrate
219 contribution for 50 wt % colloidal silica content coatings,
220 because of the lower film thickness (1.2 μm) combined with
221 the substrate plasticity and consequently they are not reported
222 here. Both Young's modulus and hardness were found to
223 increase when the colloidal silica percentage was varied from 10
224 to 30 wt %. The Young's modulus almost doubled, increasing
225 from 4.7 GPa to 8.0 GPa while the hardness changed by more
226 than 80 %, from 0.8 GPa to 1.5 GPa. In comparison, the
227 Young's modulus and hardness of PC are respectively 2.5 GPa
228 and 0.17 GPa.¹⁵ These data clearly demonstrate the mechanical
229 benefits obtained by depositing such coatings onto PC. These
230 values are also similar to the ones reported for silica particle
231 doped sol-gel coatings on different substrates. Depending upon
232 both the silica particle content and the alkoxy silanes nature,
233 moduli between 1 and 15 GPa and hardness of 0.2 to 2 GPa
234 have been obtained by nanoindentation.^{2,3,16–21} Altogether,
235 this confirms that the addition of pre-densified silica enables the
236 toughening of a broad range of organosilicate films. Moreover,
237 the linear increase of the film mechanical properties is in good
238 agreement with the one observed for the density over the same
239 colloidal silica range. These results support that the silica
240 nanoparticles are homogeneously distributed within the hybrid
241 network. Finally, it demonstrates that such a toughening
242 strategy can be applied when low thermal requirements need to
243 be satisfied.

Film/PC Interfacial Adhesion. The adhesive fracture
244 energy (G_c) of the various coatings was obtained by symmetric
245 DCB. This technique specifically measures the adhesion
246 between a coating and a substrate independently of any other
247 mechanical characteristics. This is fundamentally different from
248 the scratch test technique where the samples are stressed both
249 normally and tangentially at the same time. In this case, the
250 lower force at which cracking occurs ($Lc1$) is a function of both
251 bulk mechanical properties and interfacial adhesion. Never-
252 theless, this technique has been widely utilized for the
253 qualitative characterization of protective coatings on PC.^{9,19,22}
254 Conversely, DCB was only recently adapted to polymeric
255 substrates,^{11,23} permitting quantitative measurements of the
256 adhesive fracture energy. Coatings with different composition
257 deposited both on untreated and N₂/H₂ plasma pretreated PC
258 were studied. The G_c values measured on untreated and plasma
259 treated PC as a function of composition are plotted in Figure 2. 260

261 All coatings display similar behavior: the plasma treatment
262 leads to a significant increase in G_c from 1–2 J/m² to more
263 than 20 J/m², and the adhesion of the sol-gel film to the
264 substrate is unaffected by the colloidal silica loading. It is worth
265 noting that the fracture occurred at the hybrid film to PC
266 interface as indicated by the X-ray photoelectron spectroscopy
267 (XPS) surface analysis results shown in Figure 3. The low
268 interfacial fracture energy measured for the pristine PC is not
269 surprising as the hydrophilic coating should have little
270 interaction with the hydrophobic PC surface. In this case,
271 adhesive debonding occurs at low applied stress at the interface
272 and consequently little energy can be dissipated in the PC
273 substrate. After the plasma treatment the PC surface becomes
274 hydrophilic, that is, the water contact angle drops from 82°
275 to less than 40°. The formation of polar bonds, such as, C–OH
276 and C–NH₂ has already been evidenced by XPS,⁸ it not only
277 renders the PC surface more hydrophilic but it also most likely
278 leads to covalent bonding with both organic and inorganic
279 moieties from the hybrid network.²⁴ The interaction between 279

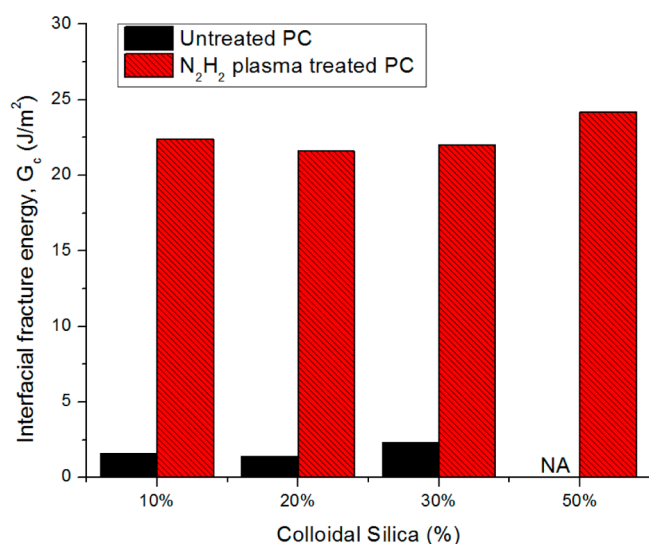


Figure 2. Coatings adhesive fracture energy as a function of colloidal silica ratio on untreated or N_2/H_2 plasma treated PC as measured by DCB.

280 the hybrid coating and the PC is therefore increased.
 281 Furthermore, plasma treatments are known to roughen the
 282 polymer surface creating a larger contact surface between the
 283 two materials.^{25,26} These two factors are responsible for the 10
 284 fold increase in interfacial fracture energy after plasma
 285 treatment: the higher energy input required to overcome the
 286 stronger interaction between the coating and the substrate
 287 results in a higher stress state at the vicinity of the crack tip, and
 288 more energy is dissipated in the substrate and coating because
 289 of plastic deformation. While the plasma treatment time was
 290 not optimized for this specific coating, it is unlikely that a low
 291 molecular weight layer (LMWL) due to PC over-exposure was

formed in our case. Indeed, the presence of a LMWL on PC
 292 leads to a rapid decay of the adhesive fracture energy with G_c
 293 values <10 J/m² for silica coatings deposited by atmospheric
 294 plasma.¹¹

The colloidal silica content seems to have little or no effect
 296 on the adhesion to PC. While surprising at first, this can be
 297 rationalized if there is no segregation of silica nanoparticles at
 298 the interface and if the plastic properties of the hybrid network
 299 do not significantly change. It has been shown in the case of
 300 polymeric nanoparticles that segregation at the substrate
 301 interface occurs with hydrophilic surfaces and is a function of
 302 the nanoparticles' loading.²⁷ We believe that the use of a water
 303 based sol-gel solution minimizes this segregation phenomenon
 304 as all the hydrolyzed silicate species will maintain strong
 305 interaction with the Si-OH surface covered silica nanoparticles
 306 after film deposition. This is in good agreement with the XRR
 307 and nanoindentation data, which indicated a homogeneous
 308 composition throughout the film thickness. XPS depth profiling
 309 analysis of the beams after G_c measurement confirmed that the
 310 fracture occurred at the film to PC interface and that its
 311 composition was identical to the bulk. An example of such
 312 profile is shown in Figure 3 for the 30 wt % loading colloidal
 313 silica sample. Despite the high carbon content initially detected
 314 (coming from both atmospheric contamination and polymeric
 315 residues after fracture) and removed with 30 sec of sputtering,
 316 the concentration of carbon, silicon, and oxygen atoms is
 317 constant from the fractured interface into the bulk.

Regarding plastic deformation of the hybrid network, it can
 319 only be influenced by the GPTES amount if polymeric chains
 320 are formed through epoxide opening.²⁸ Even at 10 wt %
 321 colloidal silica loading (i.e. maximum GPTES content), the low
 322 G_c value measured on untreated PC indicates that there is little
 323 or no hybrid network plastic deformation. In this case,
 324 increasing the stiffness of the hybrid network with the addition
 325 of more silica nanoparticles would certainly not add plasticity to
 326

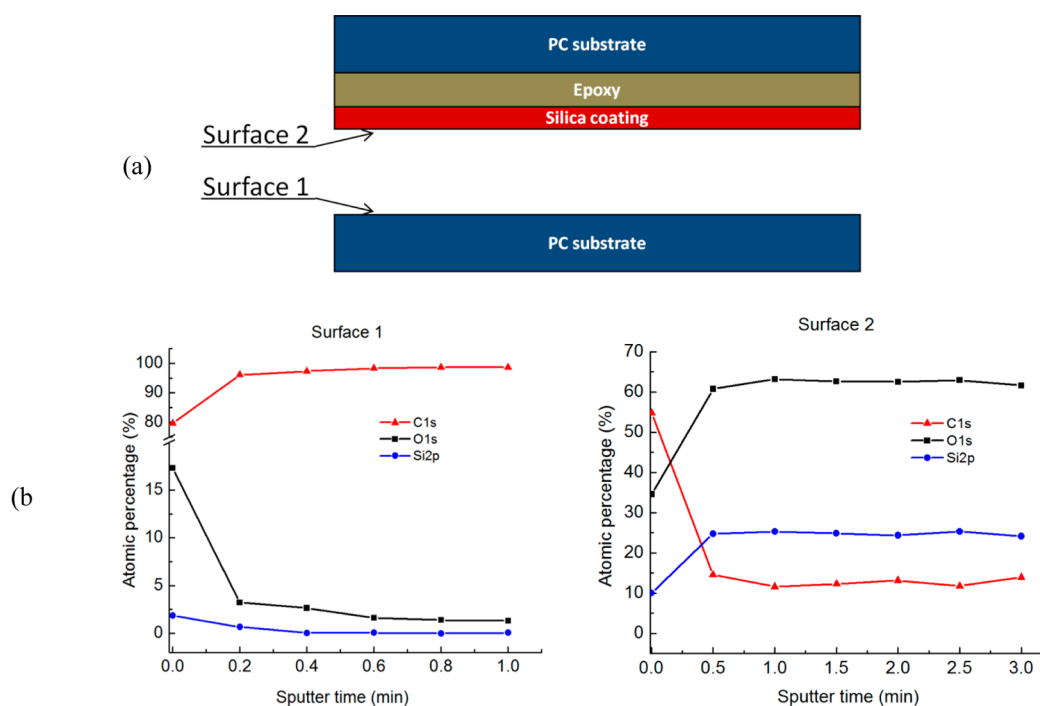


Figure 3. (a) Scheme of ideal XPS analyzed surfaces (after DCB fracture) and (b) XPS depth profile of the interfacial layer between the PC substrate (surface 1) and the 30 wt % loading colloidal silica coating (surface 2).

the coating. Conversely, for plasma treated PC, the high G_c values measured indicate that plastic deformation has been activated in both the PC substrate and the hybrid network. However, the lack of change in G_c values when decreasing the coating organic content suggests that the contribution of the hybrid network plastic deformation is minimal compared to that in PC.

Finally, 10, 20, and 30 wt % colloidal silica loading samples were prepared the same day but their interfacial fracture energy was measured after 1 year interval to probe the robustness of the film towards environmental conditions. The results presented in Table 1 demonstrate that the interfacial fracture

Table 1. Interfacial Fracture Energy Measured in the Wake of Coating Deposition (Test 1) and after Aging for 1 Year (Test 2)

colloidal silica %	G_c (J/m ²)	
	test 1	test 2
10 wt %	24.9 ± 2.1	19.8 ± 2.9
20 wt %	20.2 ± 2.1	23.0 ± 2.4
30 wt %	20.1 ± 2.8	23.9 ± 2.5

energy is not affected by the coating aging time. Consequently, these sol-gel hybrid films could be potential candidates for development toward industrial applications.

CONCLUSION

In conclusion, we have demonstrated that the bulk properties and the interfacial adhesion of PC protective coatings based on sol-gel chemistry can be independently controlled. The use of pre-condensed silica nanoparticles to toughen the hybrid network while respecting the thermal requirements due to the low glass transition temperature of the PC substrate was successfully achieved. DCB was used for the first time to quantitatively measure the interfacial fracture energy of sol-gel hybrid silica films deposited on PC. For these films, the adhesion was only a function of the PC plasma surface pretreatment and independent of the silica content. With nanoparticle loadings ranging from 30 to 50 wt %, the Young's modulus was >8.0 GPa and the adhesive fracture energy G_c was found to be >20 J/m². These values remained unchanged after aging at ambient conditions for 1 year, making this protective coating very attractive for further development. The protective coating mechanical properties are currently under investigation under environmental conditions known to degrade PC: UV exposure and high humidity. If the correlation between these properties and PC degradation can be established, it might provide a novel way to assess BPA release in applications where PC toxicity is a concern.

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Notes

The authors declare no competing financial interest.

ABBREVIATIONS

PC, polycarbonate; O/I, organic/inorganic; DCB, double-cantilever beam; GPTES, 3-glycidoxypropyltriethoxysilane;

TEOS, tetraethylorthosilicate; XRR, X-ray reflectivity; XPS, X-ray photoelectron spectroscopy; Tg, glass transition temperature; LMWL, low molecular weight layer

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