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

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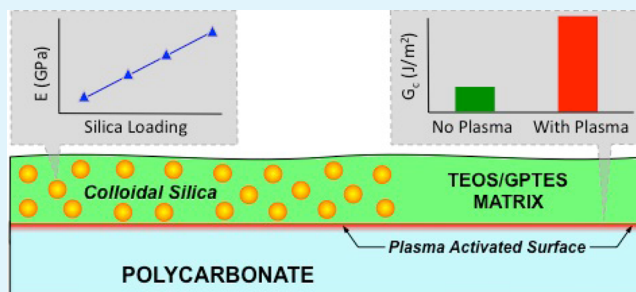
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8 **ABSTRACT:** Transparent polymers are widely used in many  
9 applications ranging from automotive windows to micro-  
10 electronics packaging. However, their intrinsic characteristics,  
11 in particular their mechanical properties, are significantly  
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 N<sub>2</sub>/H<sub>2</sub>-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/m<sup>2</sup> 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,<sup>1</sup> or modifying the PC surface with a  
44 protective coating.<sup>2-6</sup> 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.<sup>7</sup> 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).<sup>59</sup>

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<sup>8,9</sup> 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/m<sup>2</sup> to more than 20 J/m<sup>2</sup> 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 alkoxy silanes and commercially available  
 95 colloidal silica (Levasil 200E from AKZONOBEL, with an average  
 96 particles size of 30 nm). Solutions with different alkoxy silanes/  
 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 N<sub>2</sub>/H<sub>2</sub> 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,  $\rho$ , 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,  $\theta_c$ , 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,  $q = (4p/\lambda) \times \sin \theta$ ,  $\lambda$  is the wavelength, and  $\theta$   
 115 is the grazing angle of the X-ray beam. The coating density  $\rho$  was  
 116 inferred from the electronic density  $\rho_e$  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.<sup>10</sup> 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),  $\nu_i$  the indenter  
 poisson's ratio (0.07), and  $\nu_f$  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  $\mu$ m/sec in tension to produce controlled  
 crack growth, followed by unloading. The load was measured  
 simultaneously and the adhesion energy  $G_c$  (J/m<sup>2</sup>) was calculated  
 from the critical value of the strain energy release rate using the  
 Kanninen corrected equation<sup>11</sup>

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

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 $\alpha$  (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  $\mu$ 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.

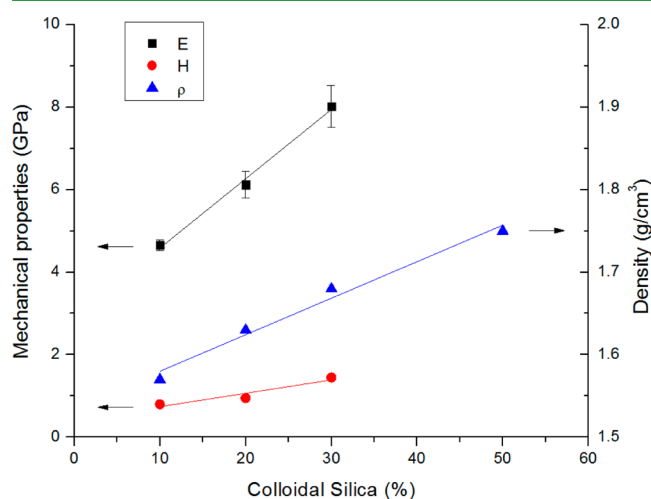
## 119 ■ RESULTS AND DISCUSSION

Four different sol-gel solutions with alkoxy silanes/colloidal  
 silica weight ratios of 50/50, 70/30, 80/20, and 90/10 were  
 studied. The alkoxy silanes 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

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

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

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



**Figure 1.** Coatings Young's modulus ( $E$ ), hardness ( $H$ ), and density ( $\rho$ ) 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/cm<sup>3</sup>.

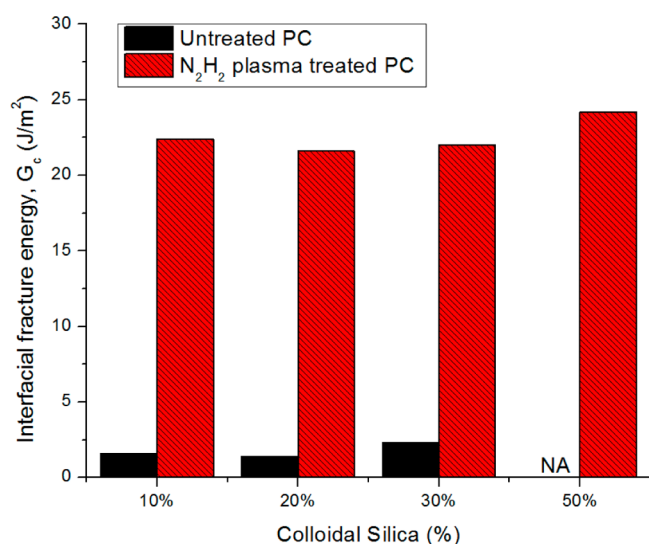
density increased linearly from 1.57 g/cm<sup>3</sup> to 1.75 g/cm<sup>3</sup>. As expected, the addition of pre-densified silica nanoparticles leads to a significant change in film bulk properties. Interestingly, by extrapolating the density data to 100 wt % colloidal silica, one would obtain a density of 1.94 g/cm<sup>3</sup>, a value close to the one of dense silica coatings (2.2 g/cm<sup>3</sup>) deposited by gas phase deposition techniques.<sup>13</sup> The results above indicate that the intrinsic density of the nanoparticles is around 1.94 g/cm<sup>3</sup> and that they are well dispersed throughout the main bulk of the film. Moreover, the absence of porosity, as indicated by ellipsometric measurements,<sup>8</sup> suggests that the intimate mixing of the nanoparticles within the hybrid network was successfully achieved.

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

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

**Film/PC Interfacial Adhesion.** The adhesive fracture energy ( $G_c$ ) of the various coatings was obtained by symmetric DCB. This technique specifically measures the adhesion between a coating and a substrate independently of any other mechanical characteristics. This is fundamentally different from the scratch test technique where the samples are stressed both normally and tangentially at the same time. In this case, the lower force at which cracking occurs ( $Lc1$ ) is a function of both bulk mechanical properties and interfacial adhesion. Nevertheless, this technique has been widely utilized for the qualitative characterization of protective coatings on PC.<sup>9,19,22</sup> Conversely, DCB was only recently adapted to polymeric substrates,<sup>11,23</sup> permitting quantitative measurements of the adhesive fracture energy. Coatings with different composition deposited both on untreated and N<sub>2</sub>/H<sub>2</sub> plasma pretreated PC were studied. The  $G_c$  values measured on untreated and plasma treated PC as a function of composition are plotted in Figure 2.

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



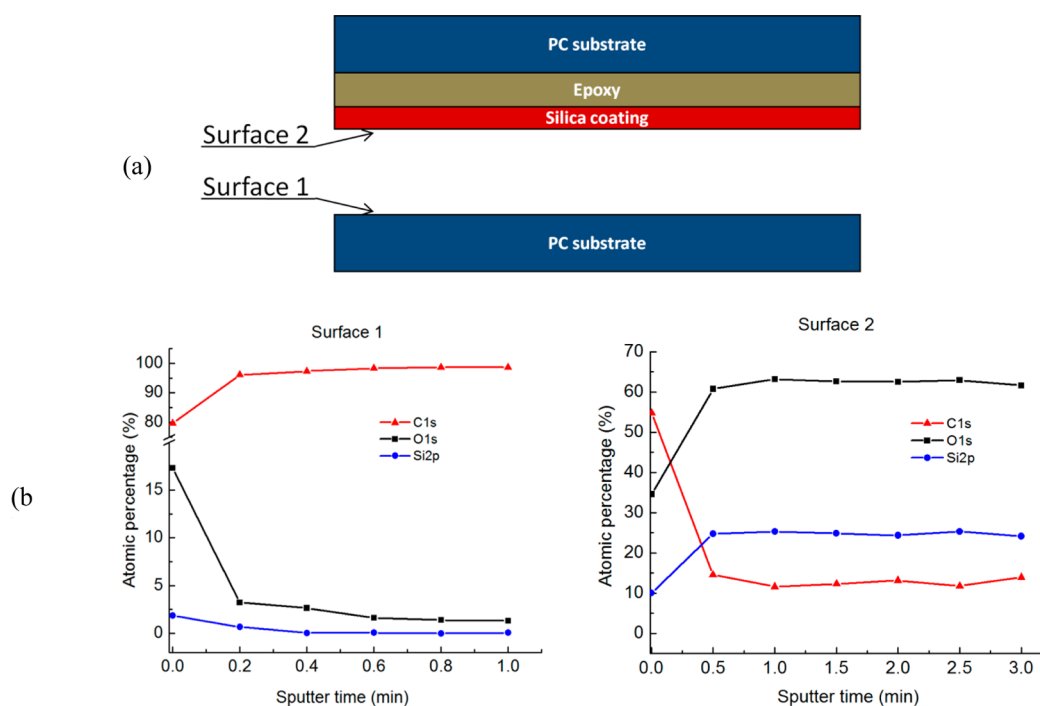
**Figure 2.** Coatings adhesive fracture energy as a function of colloidal silica ratio on untreated or  $N_2/H_2$  plasma treated PC as measured by DCB.

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

formed in our case. Indeed, the presence of a LMWL on PC leads to a rapid decay of the adhesive fracture energy with  $G_c$  values  $<10$  J/m<sup>2</sup> for silica coatings deposited by atmospheric plasma.<sup>11</sup>

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

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



**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 <sup>2</sup> )	
	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/m<sup>2</sup>. 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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