Qualitative evaluation of sol–gel SiO$_2$ as a protective layer for soft surfaces

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Abstract

In this paper, it is shown that SiO$_2$ sol–gel coatings deposited on glass and acrylic substrates (polymethyl methacrylate) considerably improved the mechanical resistance of the surface of these materials. We have used new methods to test the mechanical resistance and to measure the damage produced to the surface of the coated and bare substrates. The qualitative method employed to evaluate the mechanical resistance of the bare and coated surfaces consists of exposing the samples to the constant impacts and friction of zirconia balls. For that, the samples were fixed to the inner wall of a ball mill containing the zirconia balls. It is observed that during the mechanical treatment, the bare acrylic substrates lose their transparency, due to a large amount of surface defects created by the mechanical treatment. The presence of the defects is monitored measuring the transmitted light from a laser beam. Long exposure times to the mechanical test show that small amounts of materials are removed from the surface of the coating.

Keywords: [B] Abrasive test; [B] Atomic Force Microscopy; [D] Silicon oxide; [D] Polymethyl methacrylate

1. Introduction

The study of the mechanical properties of thin coatings has gained considerable interest in recent years. This is mainly due to the increasing number of applications of coatings to improve the surface properties of different materials. Among the desired mechanical properties of coatings are: good adhesion [1]; hardness [2]; and scratch/abrasion resistance [3]. In general, it is difficult to obtain a precise measurement of these properties for thin coatings whose thickness is of the order of 1 µm or less.

Mechanical impacts on the surface of soft materials such as polymers results in a loss of transparency, limiting their useful life. Thus, many transparent synthetic polymers, prepared with excellent optical transparency can only be used for a limited period, because the optical quality of their surface is easily and rapidly degraded by scratches or by mechanical impacts of ambient dust. To avoid this, several types of coatings have been developed to protect the surface of soft materials. These include coatings which are inorganic, prepared from the gas phase (CVD) or vacuum deposition (evaporation, sputtering). Although these coatings show good mechanical properties, they are expensive and often result in poor adhesion to polymer surfaces.

Wet chemical methods, such as sol–gel, have been extensively used to prepare coatings on different types of surfaces [4–9]. These methods have several practical advantages over the gas phase or vacuum techniques, such as low cost, room temperature preparation and low curing temperatures [10]. The properties of coatings prepared by wet chemical methods, employed to protect polymer surfaces, have been previously analyzed [4,5,7]. It has been shown that the abrasion resistance of the
SiO₂ sol–gel coating can be improved by the incorporation of nanoscaled particles [5].

In the present work, we have prepared sol–gel SiO₂ thin coatings on acrylic and Corning glass surfaces. The resistance to scratching and abrasion of these surfaces was evaluated after two types of coatings were applied to them. The two types of coatings analyzed were (i) pure SiO₂ and (ii) SiO₂ with embedded dye molecules. Coated and uncoated substrates were subjected to a mechanical test, which is described in the experimental methods section. After this test, the damage produced on the sample surface was analyzed, by measuring the transmitted laser light through the sample as a function of the mechanical treatment time. It is found that the mechanical test produces structural defects to the acrylic surface, which damage their optical quality. The light transmitted through this sample gradually decreases to approximately 10% of its original value after a few hours of mechanical treatment. When the acrylic surfaces are coated with a SiO₂ layer, the damage produced by the mechanical test is substantially reduced. The incorporation of dyes into the SiO₂ layer improves the hardness of these coatings.

2. Experimental methods

Samples on Corning glass and commercial acrylic substrates were prepared using the sol–gel method. To do this, starting solutions were prepared using a mixture of TEOS Sigma–Aldrich (tetraethylorthosilicate), water and ethanol (Baker). The ethanol-to-TEOS and water-to-TEOS molar ratios were 4:1 and 11:1, respectively. Solutions with these compositions produce good quality SiO₂ coatings [11]. Some of the starting solution has been added with commercial dyes. To prepare these colored coatings, the dye was dissolved into the water and added to the ethanol–TEOS solution. We employed a yellow dye with the commercial name of Basic Yellow 2 (Productos Mardupol Dupont Co.), also called macrillon yellow with the color index 41 000. The dye/SiO₂ molar ratio was $5.4 \times 10^{-3}$. To catalyze the gelation–condensation reaction, $3.4 \times 10^{-4}$ moles of $o$-phosphoric acid (Baker) for each mole of TEOS were added to all solutions. Samples of pure SiO₂ were prepared by the dipping method on glass and acrylic substrates from the starting solutions with the composition mentioned above. The dipping method was performed at room temperature with a dipping speed of 8 mm/s; more experimental details are presented by Díaz-Flores et al. [6]. Some of the sol–gel starting solutions containing the dye were placed in a ball mill and milled for several hours. According to previous results, it is possible to improve the dye dispersion when the solutions are subjected to a ball milling process [12]. In other words, with this process it is possible to break up dye aggregates to achieve solutions in which the dye is much better dispersed. The ball mill employed was a home-made system, with a cylindrical plastic vial with a 8-cm internal diameter and 10-cm length. Zirconia balls with a diameter between 1 and 2 mm were used and the balls-to-solution volume ratio was approximately 2:1. Good dye dispersion was obtained after 4 h of milling at 55 rev./min; this speed corresponds to 0.36 of $V_c$ [13], where $V_c$ is the critical speed of the mill. In this study, the coatings with dye molecules, obtained from solutions without the milling process, are denoted as WOM and those obtained from solutions subjected to the milling process as WM. All coatings had a thickness of approximately 600 nm and all were subjected to heat treatment in air at 100°C for 1 h. The thickness of each sample was obtained from optical reflectance and transmittance measurements.

In order to evaluate some mechanical properties of the bare and coated substrates, they were subjected to a mechanical test, which provides qualitative information about the hardness, the resistance to scratch, abrasive resistance, etc. of the samples. To do that, the samples were fixed to the inner wall of a ball mill, similar to the one described above used for the dye dispersion. In this way, during the ball mill operation, the bare or the coated substrates were exposed to the constant impacts and friction of the zirconia balls. This mechanical test was done in a dried ambient condition, i.e. no liquids were added during the test. The ball mill operation conditions for this mechanical test were: 100 cm³ of zirconia balls and 65 rev./min, which corresponds to 0.42 of $V_c$.

The optical absorption spectra of the coatings were obtained in an UV–VIS Perkin–Elmer spectrophotometer Lambda 2. The sample/substrate transmitted light intensity from a solid-state laser ($\lambda = 650$ nm) was measured at different times of exposure to the mechanical resistance test. This monochromatic light source was selected because the colored sample are basically transparent at 650 nm, therefore, the transmittance measurements are more sensitive to the scattering centers generated by the mechanical treatment, such as micro cracks, surface roughness, etc. Images of the surface topography of coated and uncoated substrates were obtained using the SPC-400 Atomic Force Microscope (AFM), fabricated by Park Instruments.

3. Experimental results and discussion

Fig. 1 shows the optical density, in the range of 300–700 nm, for the WOM and WM coatings. The measurements were taken before any mechanical resistance test. As can be seen, the effect of milling in the starting solutions is clearly observed in the spectra. The spectrum corresponding to the WOM coatings has two absorption bands, whereas the spectrum obtained for the WM has only one absorption band at approximately 415 nm. The
presence of a structured absorption band in the WOM samples has been previously associated with dye agglomerates [12]. The position of the 650-nm laser line, used in the transmission measurement, is indicated with an arrow. As mentioned above, the colored coating is basically transparent to this laser light; therefore, the transmission measurement will be more sensitive to any type of light dispersion from the laser beam, caused by the formation of cracks, holes and surface roughness produced by the mechanical test on the surface of the samples.

Fig. 2 shows the relative transmittance measurements as a function of the time, $t_m$, of the samples exposed to the mechanical test. The transmission was measured for $t_m$ in the range of 0–600 min. The light transmitted by the substrate without coating at $t_m$ equal zero was considered as the 100% transmission. Fig. 2a shows the behavior of the optical transmittance vs. $t_m$ for the bare and for the coated Corning glass substrates: substrate without coating (solid circles), pure or non-colored SiO$_2$ coating (solid squares), WOM coating (open circles) and WM coating (open triangles). From Fig. 2a, it can be observed that, for $t_m$ in the range of 0 to approximately 550 min, the bare Corning glass substrate, the SiO$_2$ and the WM coatings on Corning glass, practically do not show any changes in their transmittance values. For the WOM coating, the optical transmission starts at approximately 60% and it decreases to approximately 30% for $t_m$ longer than approximately 300 min. The explanation of this result will be clear once the AFM images are discussed in next paragraph.

Fig. 2b shows similar transmittance plots for the bare and for the coated acrylic substrates: the acrylic substrate without coating (solid squares), with the SiO$_2$ coating (open triangles) and with the WM coating (solid circles). In this case, all transmission curves decrease with $t_m$. The transmission curve corresponding to the acrylic substrate covered with the WM coating has the least decrease of all. After $t_m$ of approximately 550 min, the transmission has only decreased to approximately 80% of its original value. For the same $t_m$ value, the transmission through the acrylic substrate coated with the pure SiO$_2$ and that through the bare acrylic substrate decreases to a value below 40% and 20% of its original value, respectively.

AFM images of the surface topography for the Corning glass coated and uncoated substrates were obtained. Due to the fact that the acrylic surfaces are rougher than the Corning glass surface, AFM images are not very reliable and, therefore, they are not shown. Fig. 3 shows the AFM surface images in an area of $10 \times 10$ $\mu$m$^2$ for the Corning glass substrates without coating at different $t_m$ values: (a) $t_m=0$; (b) $t_m=300$; (c) $t_m=420$; and (d) $t_m=540$ min. In the figure, each division in the vertical scale corresponds to 100 Å. As can be observed, the surface morphology of the glass substrate does not show appreciable change with $t_m$.

Fig. 4 shows the AFM surface images, in an area of $10 \times 10$ $\mu$m$^2$, for the WOM coatings on Corning glass substrate at the $t_m$ intervals of 0, 120, 300, 420 and 540 min. In this case, each division in the vertical scale corresponds to 1000 Å. The large features on the surface of the colored coating (image a) have been identified as particles of agglomerated dye, which were not dissolved in the sol–gel starting solutions [12]. As can be seen, the mechanical treatment in the ball mill gradually produces micron size holes. The appearance of these holes is attributed to the removal of some of the weakly bound dye aggregates.
Fig. 3. AFM images in an area of $10 \times 10 \, \mu \text{m}^2$ for the bare and coated substrates for $t_m$ values of: (a) 0; (b) 300; (c) 420; and (d) 540 min.

Fig. 4. AFM images in an area of $10 \times 10 \, \mu \text{m}^2$ for the WOM samples on a Corning glass substrate at different $t_m$ values: (a) 0; (b) 120; (c) 300; (d) 420; and (e) 540 min.
Fig. 5 shows the AFM surface images, in an area of $10 \times 10 \mu m^2$, for the WM coatings on Corning glass substrate taken at the $t_m$ intervals of 0, 120, 300, 420 and 540 min. In these images, each division in the vertical scale corresponds to 100 Å. For these coatings, the surface features do not show an appreciable change as a function of $t_m$ and they are considerably smaller than the observed in the WOM samples. The latter indicates that a much better dye dispersion was achieved using the ball milling process of these sol–gel starting solutions.

Looking at the AFM images (Fig. 4), the decrease in the laser light transmission for the WOM coatings on glass as a function of $t_m$ (Fig. 2a) can be clearly attributed to the loss of laser light due to dispersion by the holes left when some dye aggregates are removed during the mechanical test. However, the fact that the transmission through the bare glass substrate through the SiO$_2$ coating on glass and through the WM coating does not change significantly means that no drastic changes have been produced at the surface of these samples during the mechanical test. In other words, no cracks, no holes or other light scattering centers have appeared during the mechanical test. This is confirmed by the AFM images (Figs. 3 and 5), which shows that the surface morphology has approximately the same roughness, regardless of $t_m$. The situation is different for samples on acrylic substrates (Fig. 2b), where the transmission decreases for all shown cases. The largest loss in the transmitted laser light is for the bare acrylic substrate and the lowest for the acrylic with the WM coating. Acrylic substrates coated with a SiO$_2$ layer have intermediate transmission values. The drastic loss in transmission for the bare acrylic substrate is attributed to the large amount of micro-cracks and micro-holes formed during the constant impacts and friction of the zirconia ball. These defects scatter part of the laser beam, producing the decrease in transmission. The defects at the surface of the acrylic are clearly observed by an optical microscope and the transparency of the acrylic is basically lost for a $t_m$ of approximately 550 min. It is also clear that the SiO$_2$ coating provides some
protection to the fragile acrylic substrates. However, some defects are still produced at the surface of these substrates, resulting in some scattering of the laser beam. Using the above described mechanical resistance test, the coating which proves to be the best protective layer for the acrylic surface is the WM coating. It increases the mechanical resistance of the acrylic surface by more than a factor of five. It is interesting to notice that the three transmission curves in Fig. 2b have similar behavior: they first have a sharp decrease in transmission ($t_m \sim 100$ min), then it goes up, and at $t_m \sim 300$ min it gradually goes down. As mentioned above, we were unable to do the AFM measurements for the coatings on acrylic substrates due to the large surface roughness of their surfaces; therefore, we do not have an explanation for the observed transmission behavior.

So far, we have shown that bare acrylic surfaces are damaged by the constant impacts of the zirconia balls and that SiO$_2$ layers prevent some of this damage; however, the effects produced by this mechanical test on the SiO$_2$ coating could not be established from the data shown so far. To explore this issue, we have exposed a SiO$_2$ coating on a Corning glass substrate to a mechanical test in a ball mill, in which small zirconia balls were constantly hitting and frictioning the surface of the sample. It is observed that this mechanical test produced defects at the surface of the sample. It can be used as a sensitive method to determine very slow abrasive effects on very thin films. The use of this method is particularly attractive when the coated surfaces are soft, where other methods such as the Taber test [14] are difficult to use. Nevertheless, further investigations are in progress to establish the proper calibrations, which could allow us to use the method, presented in this work as a quantitative abrasive resistant test.

4. Conclusions

The sol–gel method has been used to prepare SiO$_2$ based coatings on glass and acrylic substrates. Two types of coatings were made: one of pure SiO$_2$ and the other of SiO$_2$ with added dispersed molecular dyes. These coated samples and bare substrates were subjected to a mechanical test in a ball mill, in which small zirconia balls were constantly hitting and/or frictioning the surface of the samples. It is observed that this mechanical test produced defects at the surface of the uncoated acrylic and removes small amounts of material from the surface of the SiO$_2$ coatings. The surface defects can be detected, monitoring the transmitted light at a fixed laser wavelength. The observed decrease in the transmitted laser beam intensity is due to the fact that some of the laser light is dispersed by the surface defects. It is also observed that SiO$_2$ coatings increase the surface hardness of the surface, thus maintaining its transparency for much longer times. Long exposures of glass coated with SiO$_2$ layers show that during the mechanical treatment, small amounts of material from
the surface of the coating are removed at very slow rates.

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