Vickers Crack Nucleation of Glass Sheets Coated by Thin Silica Gel Layers

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Silica gel layers of different thickness have been deposited on glass sheets by dipping from gelling solutions with different concentrations of silicon alkoxide. Some mechanical properties of the coated samples such as hardness (H), elastic modulus (E), crack formation tendency, and tensile stress in the film (σ) have been measured by microindentation techniques and slide deflection. SiO₂ films deposited from more dilute solutions had lower H, E, and σ values, accounting for the observed higher resistance to crack nucleation in comparison with that found for samples prepared from more concentrated solutions. [Key words: sol–gel, coatings, mechanical properties, silica, hardness.]

Among the various exploitations of the sol–gel method, one of the most important and popular applications remains the deposition of thin layers over glass sheets to improve their physical and chemical features. In these cases the dip-coating method appears the most suitable for the thickness and uniform composition of the deposited layers.

More recently, interest in research on this topic has been extended to the mechanical properties of the coating systems: a marked reduction in both crack propagation and crack nucleation has been found in comparison with uncoated substrates.

The thickness of the coatings was evaluated by a commercial profilometer, testing five samples for each treatment.

Crack formation was evaluated by a Vickers diamond pyramid hardness test. Above the threshold load, well-defined radial cracks extended from the indentation corners. The number of corners with cracks increased with loading from zero to a maximum of four. The crack-formation tendency can be expressed by the crack propensity index (CPI) defined as the number of developed cracks divided by 4. For individual indents this index can have values of 0, 0.25, 0.5, 0.75, or 1 depending on whether or not zero, one, two, three, or four cracks emanate from indent corners. CPI values for each load were averaged over 30 indentations. For each samples CPI values were measured at least three different loads, allowing the drawing of crack propensity index vs indentation load curves. Vickers tests were performed in air with a constant loading time of 15 s. The number of developed radial cracks was evaluated 15 s after the withdrawal of the indenter.

Vickers hardness was evaluated together with elastic modulus measurements resulting from Knoop indentation tests with a load of 0.25 N. The diagonals of the impressions for both tests were measured by using SEM facilities.

The intrinsic stress field in the film was evaluated by measuring the inflection of thin (0.15 mm thick) glass sheets coated on only one face. The intensity of the stress in the coating was determined by applying the formulation

\[ \sigma = 4E\beta f / (3(1 - \nu)L^2b) \]

where E and ν are, respectively, Young's modulus and the Poisson coefficient of the substrate, B its thickness, L its length, b the film thickness, and f the measured deflection of the coated beam, considered simply supported at the ends. As the sheets were not perfectly flat, the effective inflection was evaluated by the difference of the same uncoated sheet as the average value of three different width measurements.

RESULTS AND DISCUSSION

Table I reports hardness H and elastic modulus E for some selected samples, as determined from Vickers and Knoop indentation experiments. Considering that our measurements result from mechanical properties of the gel layer and glass substrate, the lower load available was used to enhance the contribution of the thin gel film. While gel coatings generally lower both H and E values in comparison with the glass substrate, a marked difference was observed as the film deposition parameter changed. Thus, sample 3, with the same thickness as sample 1, displays considerably lower H and E values which must be directly related to intrinsic differences in the H and E values of the film only. This fact can be explained by the chemical procedure used, the consequence being that the coating obtained from the
more diluted solution displays more "plastic," i.e., less stiff, behavior than that prepared with higher concentrations of SiO$_2$.

Table II reports tensile stress $\sigma$ values, together with the thickness of the layers for some samples studied here. Our data, obtained from strictly mechanical experiments, are in agreement with those calculated by the indirect optical approach. 3 Samples prepared from different solutions at different concentrations display residual tensile stress fields in the silica gel layer, the intensity of which is inversely dependent on solution concentration. On the other hand, a net increase in $\sigma$ was observed by increasing the temperature from 60° to 400°C. The layer thickness effect seems to play a minor role in determining $\sigma$ values, in agreement with literature reports. 4 The presence of a permanent stress field in the coating is due to gel shrinkage as a consequence of solvent evaporation and density increase. The latter may be explained by physical or chemical factors such as pore elimination or Si-OH group condensation. Solvent evaporation is more favored at lower temperatures, whereas pore reduction requires more drastic firing. The intensity of the tensile stress field in the coatings depends on the degree of shrinkage and its elastic modulus; it seems reasonable that the deformation and densification of the coating improves resistance against crack nucleation, since the sample approaches the CPI response of bulk gels, which is 1 order of magnitude lower than that of bulk glass. 5 This fact explains the CPI improvement observed for the double-layer samples, in comparison with the thinner monolayer ones, in spite of their similar $H$, $E$, and $\sigma$ values. The observed negative effect of the temperature increase is consistent with the concomitant increase of $H$, $E$, and $\sigma$ in these samples.

The conclusions of the present work may be exploited for dip-coating applications of sol-gel processes in which higher concentrations of the solution are used to increase coating thickness. As concentrations are increased, the obtained coatings are chemically and physically different from those obtained by subsequent deposits from more diluted solutions. As far as mechanical properties are concerned, these experimental results indicate that coatings obtained from more concentrated solutions display higher values of hardness, elastic modulus, and residual tensile stress, affording lower improvement against crack formation in comparison with coatings from more diluted solutions.
REFERENCES


