Hardness and Elastic Modulus Profiles of Hybrid Coatings

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Abstract. Instrumented-indentation testing (IIT) provided with a continuous stiffness measurement (CSM) technique was employed to measure hardness and elastic modulus profiles of thin organic/inorganic hybrid coatings on glass surfaces. Hybrids were synthesized by the hydrolytic condensation of (3-methacryloxypropyl) trimethoxysilane (MPMS) or vinyltrimethoxysilane (VMS), with 5–30 wt% tetraethoxysilane (TEOS), in the presence of formic acid. Coatings of 600–800 nm on glass substrates were obtained by dip-coating solutions of these hybrids with benzoyl peroxide (BPO) addition, and curing in an oven following a thermal cycle up to 120°C. Both hardness and elastic modulus showed a maximum value close to the surface, followed by a plateau and a significant increase at higher penetrations. Hybrids based on MPMS and 20–30 wt% TEOS exhibited a good combination of intrinsic values of hardness (0.50 GPa) and brittle index (0.06–0.07), that makes them suitable for coatings of plastic substrates.

1. Introduction

In a recent review of physical properties of sol–gel coatings [1], Mackenzie and Bescher discussed the need to quantify the relationship between hardness and elastic modulus of organically-modified silicates (Ormosils or Ormocers). When these hybrid materials are applied as coatings on organic polymeric sub-

strates, the usual interest is to enhance the abrasion resistance. This requires an increase in hardness while keeping a convenient low value of the brittle index, defined as the ratio of hardness to Young modulus. Hardness can be increased by the addition of colloidal silica or a tetraalkoxysilane to the initial formulation. However, this also results in an increase of brittleness. The optimum amount of silica to obtain a hard and tough coating for plastics, has not yet been analyzed [1].

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The Vickers hardness of some transparent polymeric materials is 0.15 GPa for polycarbonate (PC), 0.19 GPa for poly(methylmethacrylate) (PMMA), and 0.23 GPa for poly(ethyleneterephthalate) (PET) [2]. The brittle index is close to 0.06 for PC and PMMA, and 0.10 for PET [3]. This range of values is associated with an elastic brittle behavior, comparable with the properties of a soda-lime glass [3]. Hard ormosils based on silica modified with small amounts of poly(dimethylsiloxane) (PDMS), exhibit hardness values ranging from 0.86 GPa (10 wt% PDMS) to 1.57 GPa (3 wt% PDMS) [2, 4]. Corresponding values of the brittle index of these hybrid materials are, respectively, 0.066 and 0.084.

One interesting type of ormosils is based on the hydrolytic condensation of a tetraalkoxysilane with a trialkoxysilane bearing an organic moiety with a polymerizable group (epoxy, vinyl, etc.). In this kind of hybrid materials, two different types of networks may be formed: an organic network produced by the crosslinking of the polymerizable groups, and an inorganic network based on SiOSi bonds. The fraction of tetraalkoxysilane in the initial formulation will determine which is the prevalent network in the final structure. In turn, this will determine the resulting mechanical properties of the hybrid material.

The first aim of this study was to analyze the hardness and elastic modulus of coatings based on the hydrolytic condensation products of (3-methacryloxypropyl) trimethoxysilane (MPMS) or vinyltrimethoxysilane (VMS), with 5–30 wt.% tetraethoxysilane (TEOS). Vinyl groups present in both trialkoxysilanes can be polymerized by the addition of benzoyl peroxide as initiator [5]. However, the possibility of undergoing an organic polymerization should be lower for the short vinyl group than for the much larger (3-methacryloxypropyl) group, when they are covalently bonded to the silica network. Therefore, it may be expected that both types of coatings exhibit different mechanical properties.

Innocenzi et al. [3] reported mechanical properties of coatings based on the hydrolytic condensation products of 3-glycidoxypropyltrimethoxysilane (GPMS) and TEOS (7:3 molar ratio). In this case, the polymerization of epoxy groups was performed by the addition of either titanium butoxide or zirconium butoxide as initiators of the ring-opening polymerization. Hardnesses of the resulting coatings attained values in the range of 0.10–0.30 GPa, which are similar to those of usual plastic substrates. Brittle indices were located in the range of 0.07 to 0.08, close to values reported

for hard ormosils. Our first aim was to analyze if these range of values could be improved (increase in the hardness and decrease in the brittle index), by employing different types of trialkoxysilanes and varying the initial TEOS amount.

A second aim of this study concerns the determination of hardness and elastic modulus profiles along the coating thickness, by using a nano-indentation technique. Instrumented-indentation testing (IIT) has been developed over the last decade for the determination of mechanical properties of very thin films and coatings [6, 7]. At its most basic level, IIT employs a high-resolution actuator to force an indenter into a sample surface, and a high-resolution sensor to continuously measure the resulting penetration. As the indenter is withdrawn only the elastic portion of the displacement is recovered. This measurement may be used to determine an overall elastic modulus corresponding to the thickness affected by the initial loading.

The continuous stiffness measurement (CSM) technique, recently developed for nano-indentation testing, allows a continuous measurement of elastic modulus and hardness during loading [8]. This is accomplished by superimposing a small oscillation on the primary loading signal, and analyzing the resulting response of the system by means of a frequency-specific amplifier. In this way, elastic modulus and hardness can be obtained as a continuous function of penetration.

When using the CSM technique, the nano-indenter provides a continuous measurement of the displacement (h) and the contact stiffness (S), as a function of the applied load (P) [6–8]. The total displacement is the sum of the vertical distance along which contact is made, also called contact depth (h_c), and the displacement of the surface at the perimeter of the contact (h_s):

$$h = h_c + h_s \qquad (1)$$

For a three-sided pyramidal Berkovich indenter, which is the one used here, h_s may be estimated by [6]:

$$h_s = 0.75 P/S \qquad (2)$$

Therefore, the instantaneous value of the contact depth is given by:

$$h_c = h - 0.75 P/S \qquad (3)$$

The projected contact area (A) is the cross-sectional area of the indenter for a particular contact depth. For a perfect Berkovich indenter, it is given by:

$$A = 24.56\, h_c^2 \qquad (4)$$

However, indenters used in practical nanoindentation testing are not ideally sharp due to blunting of the tip. The actual function $A(h_c)$ was obtained with a calibration procedure, as described in the literature [6, 8].

The hardness (H) is defined as the mean pressure the material supports under load:

$$H = P/A(h_c) \qquad (5)$$

The reduced elastic modulus, E_r, may be calculated as [8]:

$$E_r = [\pi/A(h_c)]^{1/2} S/(2\beta) \qquad (6)$$

where β is a constant that depends on the geometry of the indenter; for a Berkovich indenter $\beta = 1.034$ [8]. E_r accounts for the fact that elastic deformation occurs in both the sample and the indenter. It is related to the elastic modulus of the sample (E) and the elastic modulus of the indenter material (E_i) by:

$$(1/E_r) = \left(1 - \nu_i^2\right)/E_i + (1 - \nu^2)/E \qquad (7)$$

where ν and ν_i are the Poisson's ratios of the sample and the indenter, respectively. For diamond which is the usual material of a Berkovich indenter, $E_i = 1141$ GPa and $\nu_i = 0.07$ [6].

The determination of local values of hardness and elastic modulus as a function of displacement enables to obtain intrinsic values of the hybrid material. Close to the surface a peak in mechanical properties may be recorded due to the pile-up effect [9–11]. There is also an effect of the substrate on load-displacement data when the indentation depth exceeds more than about 10% of the film thickness [6, 12, 13]. Therefore, there is a limited region where intrinsic properties of the coating may be determined.

2. Experimental

2.1. Sol Preparation

Two different trialkoxysilanes were used: (3-metacryloxypropyl)trimethoxysilane (MPMS, Dow Corning Z-6030) and vinyltrimethoxysilane (VMS, Sigma T 5051). The trialkoxysilane was placed in a beaker together with a variable amount of tetraethoxysilane (TEOS), ranging from 0 to 30 wt%. Ethanol (99.7 wt%) was used as a solvent, in a 3:1 molar ratio with respect to Si. The polycondensation was carried out in the presence of formic acid (88 wt%), added in a 3 : 1 molar ratio with respect to Si. Reactions taking place in the presence of formic acid have been described in the literature [14, 15]. The beaker was sealed with a plastic film and the reaction was carried out for 3 days at 35°C. Then, needle-size holes were made in the plastic film and the reaction was continued for another 3 days at the same temperature. After this period, the plastic film was removed and the reaction continued for 7 days at 35°C.

2.2. Coatings on Glass Substrates

The resulting TEOS-modified silsesquioxane was diluted with ethanol (99.7 wt%), in a weight ratio 1:30, and benzoyl peroxide (BPO) was added to the solution in a weight ratio 1:100 with respect to the trialkoxysilane. Dip-coating was performed on glass substrates (76.4 × 25.2 × 1.2 mm), at 270 mm/min. The coated glasses were cured in an oven at 80°C for 6 h, followed by 2 h at 120°C. Coatings derived from MPMS and TEOS will be denoted as SMT, and those derived from VMS and TEOS will be indicated as SVT.

2.3. Thickness

The thickness of the different coatings was determined by scanning electron microscopy (SEM, Hitachi S-570).

2.4. Instrumented-Indentation Testing (IIT)

Hardness and elastic modulus profiles of different coatings were determined using a Nano-Indenter device (XP, MTS Systems), provided with the continuous stiffness measurement (CSM) technique, and a triangular pyramid Berkovich indenter. Several (3-4) load vs. displacement curves were obtained for every type of coating.

Local vales of hardness (H) and elastic modulus (E) were calculated for every load vs. displacement curve using Eqs. (5) and (7), respectively. The Poisson ratio of

the hybrid coatings was estimated as $\nu = 0.225$ [7]. Due to the fact that it enters as $(1 - \nu^2)$ in the calculation of E, an error in the estimation of the Poisson ratio does not produce a significant effect on the resulting value of the elastic modulus. Using the set of experimental curves obtained for every type of coating, average values of H and E as a function of displacement were generated, together with the corresponding standard deviations.

3. Results and Discussion

The thickness of the different coatings was comprised in the range of 600 to 800 nm, as observed from SEM micrographs.

Figures 1 and 2 show typical load-unload cycles for SVT and SMT coatings containing different TEOS
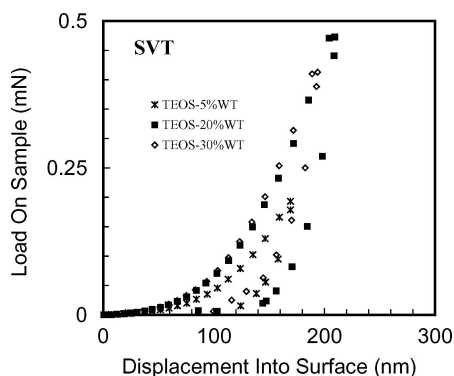

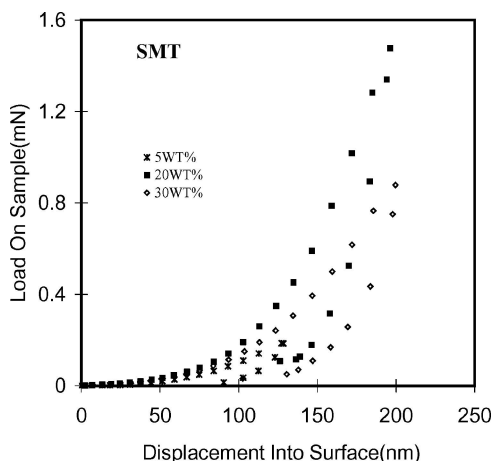*Figure 1.* Load—unload cycles for SVT coatings containing different TEOS amounts.

Figure 2. Load—unload cycles for SMT coatings containing different TEOS amounts.
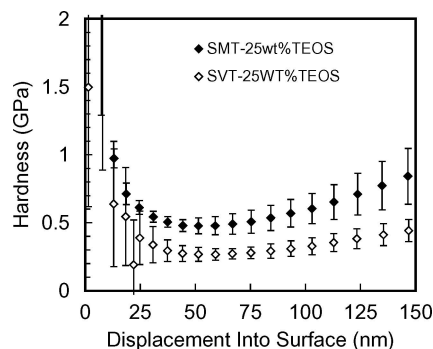

Figure 3. Average hardness profiles showing standard deviations, for SMT and SVT coatings containing 25 wt% TEOS.

amounts. The hysteresis (area between load and unload curves) is a measure of the plastic deformation produced during the loading part of the cycle.

Figure 3 shows average hardness profiles for SMT and SVT coatings containing 25 wt% TEOS. The high value measured close to the surface is an experimental artifact due to a pile-up effect [9–11]. The effect of the substrate is apparent from about 70 nm, where a continuous increase in the hardness value was recorded. The effect starts at a penetration close to 10% of the coating thickness [6, 12, 13]. Therefore, intrinsic values of hardness were determined in the plateau region, from about 40 nm to 70 nm, for every type of coating.

The hardness of the SMT coating containing 25 wt% TEOS is about twice the one of the SVT coating with the same composition. This probably arises from the fact that the organic polymerization was more effective in the former system due to the larger size of organic branches covalently bonded to the silica network. Methacryloxy groups should be able to approach one to each other to participate in the free-radical crosslinking process. This should be much more difficult for the short vinyl groups present in the SVT coating.

Figure 4 shows profiles of average elastic modulus for SMT and SVT coatings containing 25 wt% TEOS. In this case there is a small pile-up effect close to the surface and a strong effect of the substrate, evidenced at very small displacements. The influence of the substrate on the modulus measurement (elastic behavior) is much stronger than the one on the hardness determination (elasto-plastic behavior) [16]. Therefore, a true plateau value of the elastic modulus might eventually not be obtained for very thin films. Characteristic values of elastic modulus were taken at the plateau located at about 20–25 nm displacement. The elastic modulus
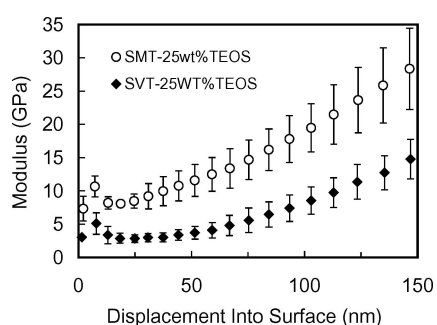
Figure 4. Average elastic modulus profiles showing standard deviations, for SMT and SVT coatings containing 25 wt% TEOS.

of the SMT coating containing 25 wt% TEOS is about three times larger than the one of the SVT coating with the same TEOS amount. This might be explained by a larger conversion of C=C bonds during the organic polymerization, generating a hybrid network with a higher cohesive energy density.

Average values of hardness and elastic modulus of the different coatings are shown in Table 1, together with standard deviations. An analysis of these data must be made with care due to the significant values of standard deviations. Even with this remark, there are some definite trends arising from the Table. For every TEOS concentration, SMT coatings exhibit higher values of hardness and elastic modulus than SVT coatings, as discussed in connection with Figs. 3 and 4.

The hardness of SVT coatings increases with the TEOS amount but values lie in the range of those of coatings based on the hydrolytic condensation products of 3-glycidoxypropyltrimethoxysilane (GPMS) and TEOS [3], and of polymers like polycarbonate, poly(methylmethacrylate) and poly(ethyleneterephthalate). Therefore, SVT coatings are not useful to increase the hardness of plastic substrates. As the elas-

tic modulus of these coatings did not show any significant variation with the TEOS amount, within experimental error, the brittle index, defined as the H/E ratio, increases with the TEOS concentration.

SMT coatings exhibit a different behavior. Although any trend in the variation of hardness with the TEOS amount cannot be ascertained due to the significant standard deviation of experimental values, formulations containing 20 to 30% TEOS showed values of hardness that are 2 to 3 times larger than those of usual plastic substrates. For these formulations, brittle indices are in the range of 0.06–0.07, that are similar to those of plastics. Therefore, SMT coatings exhibit mechanical properties of interest for practical applications.

4. Conclusions

Organic-inorganic hybrid coatings derived from poly-condensation products of MPMS with 20–30 wt% TEOS, heated to 120°C in the presence of benzoyl peroxide, exhibit good mechanical properties, higher than those of transparent organic glasses. A hardness close to 0.50 GPa associated with a brittle index of 0.06-0-07, makes them suitable to increase the abrasion resistance of these plastics.

Instrumented-indentation testing (IIT) provided with a continuous stiffness measurement (CSM) technique constitutes an appropriate method to determine intrinsic mechanical properties of thin film coatings. There is a plateau region where hardness and elastic modulus could be determined. However, the range for the elastic modulus was very narrow due to the significant influence of the substrate, even at very low penetrations.

References

1. J.D. Mackenzie and E.P. Bescher, J. Sol–Gel Sci. Technol. **19**, 23 (2000).

Table 1. Average values of hardness, *H* (GPa), and elastic modulus, *E* (GPa), of SMT and SVT coatings containing different TEOS amounts.

wt% TEOS	SMT		SVT	
	H (GPa)	*E* (GPa)	*H* (GPa)	*E* (GPa)
5	0.35 ± 0.15	4.7 ± 2.4	0.14 ± 0.01	2.2 ± 0.2
15	0.39 ± 0.13	4.9 ± 1.5	0.18 ± 0.03	2.8 ± 0.7
20	0.50 ± 0.04	8.4 ± 1.0	0.20 ± 0.03	2.1 ± 0.7
25	0.48 ± 0.05	8.3 ± 1.0	0.27 ± 0.04	2.8 ± 0.7
30	0.43 ± 0.04	6.0 ± 1.0	0.27 ± 0.02	2.7 ± 0.7

2. T. Iwamoto and J.D. Mackenzie, J. Sol–Gel Sci. Technol. **4**, 141 (1995).

3. P. Innocenzi, M. Esposto, and A. Maddalena, J. Sol–Gel Sci. Technol. **20**, 293 (2001).

4. J.D. Mackenzie, Q. Huang, and T. Iwamoto, J. Sol–Gel Sci. Technol. **7**, 151 (1996).

5. M.A. Fanovich, S.A. Pellice, P.G. Galliano, and R.J.J. Williams, J. Sol–Gel Sci. Technol. **23**, 45 (2002).

6. W.C. Oliver and G.M. Pharr, J. Mater. Res. **7**, 1564 (1992).

7. J. Malzbender, J.M.J. den Toonder, A.R. Balkenende, and G. de With, Mater. Sci. Eng. R **36**, 47 (2002).

8. X. Li and B. Bhushan, Mater. Charact. **48**, 11 (2002).

9. R. Saha and W.D. Nix, Mater. Sci. Eng. A **319–321**, 898 (2001).

10. A. Bolshakov, W.C. Oliver, and G.M. Pharr, Mat. Res. Soc. Symp. Proc. **436**, 141 (1997).

11. T.Y. Tsui, W.C. Oliver, and G.M. Pharr, Mat. Res. Soc. Symp. Proc. **436**, 207 (1997).

12. T.Y. Tsui, C.A. Ross, and G.M. Pharr, Mat. Res. Soc. Symp. Proc. **473**, 57 (1997).

13. R. Saha and W.D. Nix, Acta Mater. **50**, 23 (2002).

14. K. Sharp, J. Sol–Gel Sci. Technol. **2**, 35 (1994).

15. P. Eisenberg, R. Erra-Balsells, Y. Ishikawa, J.C. Lucas, H. Nonami, and R.J.J. Williams, Macromolecules **35**, 1160 (2002).

16. M. Tabbal, P. Merel, M. Chaker, M.A. El Khakani, E.G. Herbert, B.N. Lucas, and M.E. O'Hern, Surf. Coat. Technol. **116–119**, 452 (1999).