



Hardness and Elastic Modulus Profiles of Hybrid Coatings

LIJIANG HU

Department of Applied Chemistry, Harbin Institute of Technology (HIT), Box 713, Harbin 15001, China

XINGWEN ZHANG

Department of Environmental Engineering, Harbin Institute of Technology (HIT), Box 713 Harbin 15001, China

YI SUN

Department of Mechanics, Harbin Institute of Technology (HIT), Box 713, Harbin 15001, China

ROBERTO J.J. WILLIAMS*

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), J.B. Justo 4302, 7600 Mar del Plata, Argentina

williams@fi.mdp.edu.ar

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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.

Keywords: hybrid coatings, ormosils, hardness, elastic modulus, brittle index, instrumented-indentation testing (IIT), continuous stiffness measurement (CSM)

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].

*To whom all correspondence should be addressed.

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42 The Vickers hardness of some transparent polymeric
43 materials is 0.15 GPa for polycarbonate (PC), 0.19 GPa
44 for poly(methylmethacrylate) (PMMA), and 0.23 GPa
45 for poly(ethyleneterephthalate) (PET) [2]. The brittle
46 index is close to 0.06 for PC and PMMA, and 0.10 for
47 PET [3]. This range of values is associated with an elas-
48 tic brittle behavior, comparable with the properties of a
49 soda-lime glass [3]. Hard ormosils based on silica mod-
50 ified with small amounts of poly(dimethylsiloxane)
51 (PDMS), exhibit hardness values ranging from 0.86
52 GPa (10 wt% PDMS) to 1.57 GPa (3 wt% PDMS) [2,
53 4]. Corresponding values of the brittle index of these
54 hybrid materials are, respectively, 0.066 and 0.084.

55 One interesting type of ormosils is based on the
56 hydrolytic condensation of a tetraalkoxysilane with
57 a trialkoxysilane bearing an organic moiety with a
58 polymerizable group (epoxy, vinyl, etc.). In this kind
59 of hybrid materials, two different types of networks
60 may be formed: an organic network produced by the
61 crosslinking of the polymerizable groups, and an inor-
62 ganic network based on SiOSi bonds. The fraction of
63 tetraalkoxysilane in the initial formulation will deter-
64 mine which is the prevalent network in the final struc-
65 ture. In turn, this will determine the resulting mechan-
66 ical properties of the hybrid material.

67 The first aim of this study was to analyze the hardness
68 and elastic modulus of coatings based on the hydrolytic
69 condensation products of (3-methacryloxypropyl)
70 trimethoxysilane (MPMS) or vinyltrimethoxysilane
71 (VMS), with 5–30 wt.% tetraethoxysilane (TEOS).
72 Vinyl groups present in both trialkoxysilanes can
73 be polymerized by the addition of benzoyl perox-
74 ide as initiator [5]. However, the possibility of un-
75 dergoing an organic polymerization should be lower
76 for the short vinyl group than for the much larger
77 (3-methacryloxypropyl) group, when they are cova-
78 lently bonded to the silica network. Therefore, it may
79 be expected that both types of coatings exhibit different
80 mechanical properties.

81 Innocenzi et al. [3] reported mechanical properties
82 of coatings based on the hydrolytic condensation prod-
83 ucts of 3-glycidoxypropyltrimethoxysilane (GPMS)
84 and TEOS (7:3 molar ratio). In this case, the polymer-
85 ization of epoxy groups was performed by the addi-
86 tion of either titanium butoxide or zirconium butoxide
87 as initiators of the ring-opening polymerization. Hard-
88 nesses of the resulting coatings attained values in the
89 range of 0.10–0.30 GPa, which are similar to those
90 of usual plastic substrates. Brittle indices were located
91 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 hard-
ness and decrease in the brittle index), by employing
different types of trialkoxysilanes and varying the ini-
tial TEOS amount.

A second aim of this study concerns the determina-
tion of hardness and elastic modulus profiles along the
coating thickness, by using a nano-indentation tech-
nique. 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 deter-
mine an overall elastic modulus corresponding to the
thickness affected by the initial loading.

The continuous stiffness measurement (CSM) tech-
nique, 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 ob-
tained as a continuous function of penetration.

When using the CSM technique, the nano-indenter
provides a continuous measurement of the displace-
ment (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 dis-
placement of the surface at the perimeter of the contact
(h_s):

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

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

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

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

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

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

$$A = 24.56 h_c^2 \quad (4)$$

136 However, indenters used in practical nanoindentation
137 testing are not ideally sharp due to blunting of the tip.
138 The actual function $A(h_c)$ was obtained with a calibra-
139 tion procedure, as described in the literature [6, 8].
140 The hardness (H) is defined as the mean pressure
141 the material supports under load:

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

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

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

144 where β is a constant that depends on the geometry
145 of the indenter; for a Berkovich indenter $\beta = 1.034$
146 [8]. E_r accounts for the fact that elastic deformation
147 occurs in both the sample and the indenter. It is related
148 to the elastic modulus of the sample (E) and the elastic
149 modulus of the indenter material (E_i) by:

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

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

154 The determination of local values of hardness and
155 elastic modulus as a function of displacement enables
156 to obtain intrinsic values of the hybrid material. Close
157 to the surface a peak in mechanical properties may be
158 recorded due to the pile-up effect [9–11]. There is also
159 an effect of the substrate on load-displacement data
160 when the indentation depth exceeds more than about
161 10% of the film thickness [6, 12, 13]. Therefore, there
162 is a limited region where intrinsic properties of the coat-
163 ing may be determined.

164 2. Experimental

165 2.1. Sol Preparation

166 Two different trialkoxysilanes were used: (3-
167 metacryloxypropyl)trimethoxysilane (MPMS, Dow

Corning Z-6030) and vinyltrimethoxysilane (VMS, 168
Sigma T 5051). The trialkoxysilane was placed 169
in a beaker together with a variable amount of 170
tetraethoxysilane (TEOS), ranging from 0 to 30 wt%. 171
Ethanol (99.7 wt%) was used as a solvent, in a 3:1 172
molar ratio with respect to Si. The polycondensa- 173
tion was carried out in the presence of formic acid 174
(88 wt%), added in a 3 : 1 molar ratio with respect to 175
Si. Reactions taking place in the presence of formic 176
acid have been described in the literature [14, 15]. 177
The beaker was sealed with a plastic film and the 178
reaction was carried out for 3 days at 35°C. Then, 179
needle-size holes were made in the plastic film and 180
the reaction was continued for another 3 days at the 181
same temperature. After this period, the plastic film 182
was removed and the reaction continued for 7 days at 183
35°C. 184

2.2. Coatings on Glass Substrates 185

The resulting TEOS-modified silsesquioxane was di- 186
luted with ethanol (99.7 wt%), in a weight ratio 1:30, 187
and benzoyl peroxide (BPO) was added to the solution 188
in a weight ratio 1:100 with respect to the trialkoxysi- 189
lane. Dip-coating was performed on glass substrates 190
(76.4 × 25.2 × 1.2 mm), at 270 mm/min. The coated 191
glasses were cured in an oven at 80°C for 6 h, followed 192
by 2 h at 120°C. Coatings derived from MPMS and 193
TEOS will be denoted as SMT, and those derived from 194
VMS and TEOS will be indicated as SVT. 195

2.3. Thickness 196

The thickness of the different coatings was deter- 197
mined by scanning electron microscopy (SEM, Hitachi 198
S-570). 199

2.4. Instrumented-Indentation Testing (IIT) 200

Hardness and elastic modulus profiles of different coat- 201
ings were determined using a Nano-Indenter device 202
(XP, MTS Systems), provided with the continuous stiff- 203
ness measurement (CSM) technique, and a triangula- 204
r pyramid Berkovich indenter. Several (3–4) load vs. 205
displacement curves were obtained for every type of 206
coating. 207

Local vales of hardness (H) and elastic modulus (E) 208
were calculated for every load vs. displacement curve 209
using Eqs. (5) and (7), respectively. The Poisson ratio of 210

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

219 **3. Results and Discussion**

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

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

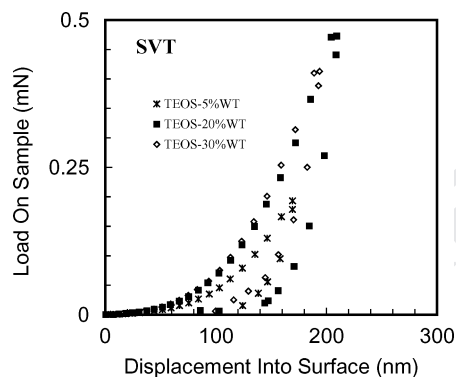


Figure 1. Load—unload cycles for SVT coatings containing different TEOS amounts.

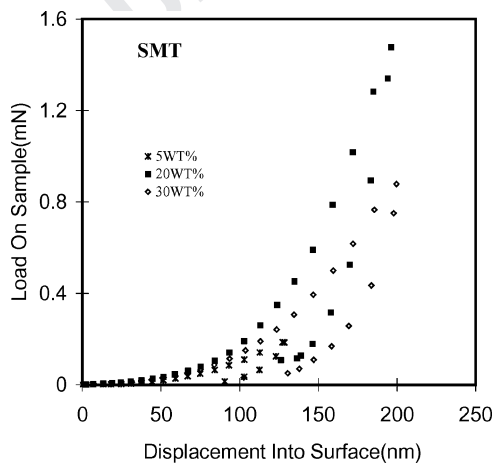


Figure 2. Load—unload cycles for SMT coatings containing different TEOS amounts.

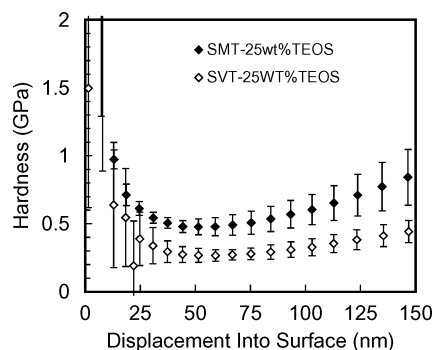


Figure 3. Average hardness profiles showing standard deviations, for SMT and SVT coatings containing 25 wt% TEOS.

amounts. The hysteresis (area between load and un- 225
 load curves) is a measure of the plastic deformation 226
 produced during the loading part of the cycle. 227

Figure 3 shows average hardness profiles for SMT 228
 and SVT coatings containing 25 wt% TEOS. The high 229
 value measured close to the surface is an experimental 230
 artifact due to a pile-up effect [9–11]. The effect of 231
 the substrate is apparent from about 70 nm, where a 232
 continuous increase in the hardness value was recorded. 233
 The effect starts at a penetration close to 10% of the 234
 coating thickness [6, 12, 13]. Therefore, intrinsic values 235
 of hardness were determined in the plateau region, from 236
 about 40 nm to 70 nm, for every type of coating. 237

The hardness of the SMT coating containing 25 wt% 238
 TEOS is about twice the one of the SVT coating with 239
 the same composition. This probably arises from the 240
 fact that the organic polymerization was more effec- 241
 tive in the former system due to the larger size of or- 242
 ganic branches covalently bonded to the silica network. 243
 Methacryloxy groups should be able to approach one 244
 to each other to participate in the free-radical crosslink- 245
 ing process. This should be much more difficult for the 246
 short vinyl groups present in the SVT coating. 247

Figure 4 shows profiles of average elastic modulus 248
 for SMT and SVT coatings containing 25 wt% TEOS. 249
 In this case there is a small pile-up effect close to the 250
 surface and a strong effect of the substrate, evidenced 251
 at very small displacements. The influence of the sub- 252
 strate on the modulus measurement (elastic behavior) 253
 is much stronger than the one on the hardness determi- 254
 nation (elasto-plastic behavior) [16]. Therefore, a true 255
 plateau value of the elastic modulus might eventually 256
 not be obtained for very thin films. Characteristic val- 257
 ues of elastic modulus were taken at the plateau located 258
 at about 20–25 nm displacement. The elastic modulus 259

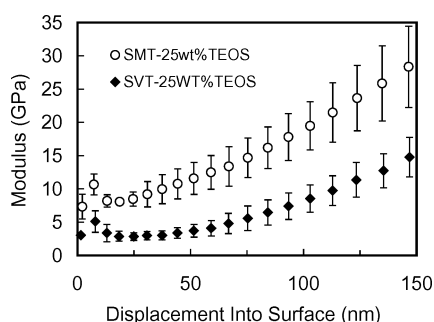


Figure 4. Average elastic modulus profiles showing standard deviations, for SMT and SVT coatings containing 25 wt% TEOS.

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-

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

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 polycondensation 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.

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