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Nanoindentation and adhesion of sol-gel-derived hard coatings on polyester

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We investigated sol-gel-derived silica-based hard coatings on modified polyester substrates. The silica network was modified by incorporating an organic component and adding transition metal oxides. These modifications resulted in tailored thermal, optical, and mechanical properties of the coatings. Various low-temperature densification techniques were studied including sol-preparation procedure, enhanced solvent evaporation, ultraviolet irradiation, and low-temperature heating (below 150 °C). Oxygen plasma etching was applied to improve the adhesion of the sol-gel coatings on the plastic surface. Nanoindentation analysis revealed that the coatings have a surface hardness up to 2.5 ± 0.27 GPa and an elastic modulus up to 13.6 ± 0.4 GPa, approximately an order of magnitude higher than that of the plastic surface.

I. INTRODUCTION

The many desired features of plastics such as light weight, formability, high impact strength, and ductility have allowed them to be widely used in many optical applications. However, plastics have poor abrasion resistance, which means they are readily scratched, leading to decreased optical transparency. One approach is to apply abrasion-resistant coatings so as to improve their surface mechanical properties such as abrasion resistance. Vapor-phase techniques, such as evaporation, sputtering, and chemical vapor deposition (CVD) (e.g., Refs. 1–3), produce high-quality films with high density and high mechanical properties, but they are expensive, require sophisticated equipment, and often require substrates to be maintained at high temperatures. In addition, uniform coatings of complex-shaped substrates are difficult with such line-of-sight vacuum techniques.

Solution deposition is an alternative approach for applying oxide films to temperature-sensitive substrates. For example, the biomimetic synthesis (e.g., Refs 4–8) has two important characteristics: (i) control of solution conditions, including ion concentration (supersaturation levels), pH, and temperature; and (ii) the use of functionalized interfaces to promote mineralization at the substrate surface. By controlling the surface energy of the substrate along with the solution supersaturation, deposition conditions can be established that favor heterogeneous growth of the thin film on the substrate without bulk particle precipitation (homogeneous growth). The major drawback of this approach is the need of functionalized surface. Langmuir films and self-assembled monolayers (SAMs) are often applied to introduce functionality to the polymer surfaces.

Oxide or oxide-based coatings have been deposited on various substrate materials using the sol-gel techniques.[9–19] Protective-coating films derived by the sol-gel method can be potentially employed commercially for several reasons, including the method's low-cost coating equipment and precursors, room-temperature and standard pressure processing, complex-shape deposition, product homogeneity, and fast throughput. Moreover, because the sol-gel method is a liquid-phase process, large-area films can be made easily. Sol-gel processing also offers easy manipulation of chemical composition, precursor materials are recyclable, and the substrate withdrawal rate can be controlled to obtain desired film thickness.[19] However, postdeposition heat treatments at elevated temperatures are commonly required to convert the porous structure to a dense film. Organically modified oxide (also known as ormocer or ormosil) coatings have been studied extensively[9–13] and have been successfully commercialized as coatings for optical glasses (for example, Dow Corning ARC™ abrasion-resistant coatings). Organic components are introduced through hydrolysis and copolymerization of organic and inorganic precursors together during sol preparation. The unhydro-

lyzable organic ligands are incorporated into the oxide network through copolymerization. The oxide in the hybrid coatings provides a backbone for improved mechanical properties, and organic components make the coatings flexible and reduce the thermal expansion coefficient mismatch between polymer substrates and oxide coatings. A high coating density is necessary to ensure the mechanical properties required for protective coatings. However, highly dense inorganic coatings generally require a heat treatment at elevated temperatures (>500 °C) that readily damage key properties of the temperature-sensitive plastic substrates, such as optical properties and bioproperties.

This paper reports our recent study of sol-gel-derived hard coatings on modified polyester plastic substrates. Organic components were introduced into the film as a means to enhance film flexibility as well as to promote the collapse of the sol-gel network during drying so as to obtain a highly dense sol-gel coating. Transition metal oxides were also incorporated into the silica network to modify thermal, optical, and mechanical properties of the sol-gel coatings. Ultraviolet (UV) irradiation and low-temperature (below 200 °C) firing were applied for further densification of sol-gel-derived coatings. The coatings were characterized by means of ellipsometry and nanoindentation. The relationships among the chemical compositions, sol-gel processing conditions, low-temperature densification, and mechanical properties of the coatings are discussed. Also discussed are the adhesion of the sol-gel-derived coatings on modified polyester substrates and the effect of oxygen plasma treatments on the polyester substrates.

II. EXPERIMENTAL

A. Sol preparation

Five types of silica sols were studied, including silica, organically modified silica, and transition metal-oxide-doped silica. The silica sol was prepared by an acid-catalyzed hydrolysis and condensation of tetraethylorthosilicate, $Si(OC_2H_5)_4$ (TEOS, 98%, Aldrich), dissolved in a mixture of ethanol (C_2H_5OH), water (H_2O), and nitric acid (HNO_3). The solution was under vigorous stirring at 60 °C for 90 min to yield a stable sol with a molar ratio of TEOS:C_2H_5OH:H_2O:HNO_3 of $1:3.8:5:4.8 \times 10^{-3}$. In addition to the SiO_2 sol, two different organic/inorganic hybrid sols were prepared using the same procedure described above. The hybrid sols were prepared with the addition of an organosilane precursor, 3-methacryloxy-propyl-trimethoxysilane, $H_2C=C(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$ (MPS, 98%, Aldrich), resulting in nominal molar ratios of TEOS:MPS:C_2H_5OH:H_2O:HNO_3 of $0.95:0.05:3.8:5:4.8 \times 10^{-3}$ and $0.67:0.33:3.8:5:4.8 \times 10^{-3}$ and referred to as SiO_2–5MPS and SiO_2–33MPS, respectively. Silica

sols doped with titania and zirconia were prepared with TEOS, titanium-isopropoxide, $Ti(OC_3H_7)_4$ (99%, Aldrich), and zirconium-isopropoxide, $Zr(OC_3H_7)_4$ (99%, Aldrich), as precursors using the following procedure. TEOS was first partially hydrolyzed with a deficient amount of water with a molar ratio of TEOS:H_2O = 1:1 at 60 °C for 90 min. After completely depleting the water, the titanium or zirconium precursor was added to the partially hydrolyzed TEOS solution. After titanium or zirconium alkoxide reacted with partially hydrolyzed TEOS, more water was added into the solution so that hydrolysis and condensation reactions could proceed further at 60 °C for another 30 min. The final sol had a nominal molar ratio of TEOS:$Ti(OC_3H_7)_4$:C_2H_5OH:H_2O:HNO_3 of $0.83:0.17:3.8:5:4.8 \times 10^{-3}$ (referred to as SiO_2–17TiO_2). The zirconia-doped silica sol had the same nominal molar ratio as SiO_2–17ZrO_2. Sols were diluted with ethanol with a volume ratio of sol:ethanol of 1:2, prior to dip-coating. Undiluted sols were stored in a freezer at −20 °C or sealed in plastic bottles for gelation at 60 °C. The resultant xerogels were later used for x-ray diffraction (XRD) and nitrogen sorption analysis at 77 K (Micromeritics ASAP 2000M).

B. Substrate preparation and deposition

Optical-grade modified polyester substrates, with a dimension of 1×4 cm, were cleaned with ethanol and subjected to oxygen plasma etching for 60 s with an oxygen pressure of 100 mtorr prior to sol-gel coating. Silicon wafers were also used for comparison studies and treated in a similar manner as that for polyester substrates. Sol-gel films were deposited by dipping the treated substrates into sols with ultrasonication for 1 min to remove possible gas bubbles at the substrate surface. They were then withdrawn at a speed of 3.5 cm/min in the presence of a dry air flow along the coating surfaces so as to enhance solvent evaporation. Some of the coatings were UV irradiated using a high-pressure Hg lamp (254 nm) at 2.4 mW/cm^2, immediately after withdrawal from the sols. The samples were kept approximately 3 cm from the lamp. Low-temperature heating was done on some of the coatings by exposing them to 150 °C for 3 h in air under ambient pressure.

C. Characterization

Nanoindentation on the sol-gel coatings were performed using a Hysitron™ Nano-Mechanical System attached to a Park CP™ Scanning Probe Microscope (SPM). A Berkovich diamond tip was used as both an indenter and imaging probe. Hardness and elastic modulus were determined from the unloading part of the force–depth (F–d) curve. The tip-area function is calibrated with fused silica according to the procedure reported in the literature.[20] Hardness was calculated as the maximum

applied load over the area of contact, which was calibrated as a function of contact depth up to 100 nm. The hardness measurements on the sol-gel coatings were performed with a load ranging from 10 to 300 μN, corresponding to a contact depth from 15 to 90 nm.

Thickness and refractive indices of the films on both the polyester and the silicon substrates were measured with a He–Ne laser ellipsometer ($\lambda = 632.8$ nm). The coatings were subjected to various thermal-cycling/adhesion tests. Dry thermal-shock tests were conducted by cycling between 150 °C on a hot plate for 55 min and –20 °C for 5 min for a total of 5 cycles. Wet thermal-shock tests were performed by (i) cycling between 100 °C for 55 min to 0 °C for 5 min in water for a total of 5 cycles and (ii) submerging in water at 100 °C for 7 h. The tested films were then analyzed by optical and scanning electron microscopy (SEM).

III. RESULTS AND DISCUSSION

XRD was used to analyze the xerogels; it was found that no crystalline phase was detectable in any of the five samples. Furthermore, SEM observations revealed that both the coatings and the xerogels had a homogeneous morphology with no phase segregation detectable. From these results we can infer the following: (i) the unhydrolyzable organic component is homogeneously dispersed within the silica network, and (ii) the titanium and zirconium oxides are incorporated into an amorphous silica network.

Table I shows the hardness and elastic modulus values of the different sol-gel coatings using a load of 50 μN except for SiO_2–$17ZrO_2$ coatings and the depth of penetration relative to coating thickness. The coatings were not subjected to any treatment; i.e., neither UV irradiation, nor low-temperature heating. The incorporation of organic components into silica coatings (the unhydrolyzable organic ligands in MPS precursors) resulted in a significant change in both hardness and modulus. With a 33 mol% concentration of MPS, the resultant coating exhibited much lower hardness and elastic modulus than

silica coatings. These results are in good agreement with the literature that the incorporation of organic components into the silica network makes the resultant coatings flexible and soft.[21,22] However, the addition of 5 mol% MPS resulted in an increase in both hardness and elastic modulus. Such an increase in mechanical properties might be attributable to a denser microstructure brought about by the addition of MPS.[23] The incorporation of ~17 mol% titania and zirconia also led to a reduction in hardness. It was anticipated that the incorporation of titanium and zirconium ions into a silica network would increase the connectivity due to the higher coordination numbers of Ti^{4+} and Zr^{4+} (larger than 6 as opposed to 4 for Si^{4+}). Thus, a higher hardness could be expected, similar to the addition of Ta^{5+} into a silica network.[24] The reduced hardness of both Ti- and Zr-doped silica coatings could be attributed to a relatively more porous structure of the coatings. It is well known that the addition of titanium or zirconium alkoxide into the silica sol greatly reduces the gelation time, because titanium or zirconium alkoxide has a catalytic effect on the condensation reaction;[25] a rapid condensation reaction would lead to a more porous structure. Nitrogen sorption analyses on xerogels confirmed this hypothesis.

Table II summarizes the gelation times, Brunauer–Emmett–Teller analysis (BET) surface areas, pore volumes, and average pore size for the five types of xerogels studied in the present work. This table shows that the incorporation of organic ligands into silica network resulted in a decrease in condensation reaction rate, which is reflected by a significant increase in gelation time. Xerogels for nitrogen sorption analyses were made by pouring the sols to petri dishes and drying at ambient conditions. After all the solvent was removed, xerogels were ground to fine powders and thoroughly degassed at 150 °C to remove any residual volatile components. Nitrogen sorption isotherms showed that the xerogels of silica and silica incorporated with MPS exhibited no detectable nitrogen sorption at 77 K (with BET surface areas less than 1 cm^2/g and pore volume less than 1×10^{-3} cm^3/g). Thus, these xerogels are considered to be dense.[26,27] However, nitrogen sorption revealed that

TABLE I. A composition and properties of sol-gel-derived silica-based coatings on modified polyester substrates. Neither UV irradiation nor low-temperature heating was applied.

Composition	Hardness[a]	Elastic modulus[a]	Contact depth[a]	Thickness
SiO_2	1.45 ± 0.08 GPa	10.7 ± 0.3 GPa	20 ± 1 nm	128 nm
SiO_2–5MPS	1.77 ± 0.08 GPa	12.5 ± 0.4 GPa	20 ± 1 nm	188 nm
SiO_2–33MPS	0.20 ± 0.01 GPa	2.0 ± 0.2 GPa	40 ± 2 nm	250 nm
SiO_2–$17ZrO_2$	0.95 ± 0.05 GPa[b]	13.6 ± 0.4 GPa[b]	43 ± 2 nm[b]	190 nm
SiO_2–$17TiO_2$	1.30 ± 0.08 GPa	11.5 ± 0.2 GPa	15 ± 1 nm	120 nm

[a]Both hardness and modulus were determined using a load of 50 μN.
[b]These two data were measured using a load of 100 μN.

TABLE II. Composition, gelation time, and microporous structure of silica-based xerogels.

Composition	Gelation time	Pore volume	BET surface area	Average pore size
SiO_2[a]	36 h	<10^{-3} cm^3/g	<1 m^2/g	N/A[b]
0.5 MPS–SiO_2[a]	88 h	<10^{-3} cm^3/g	<1 m^2/g	N/A
0.33 MPS–SiO_2	>500 h	<10^{-3} cm^3/g	<1 m^2/g	N/A
0.17 ZrO_2–SiO_2	20 min	37×10^{-3} cm^3/g	70 m^2/g	2.0 nm
0.17 TiO_2–SiO_2	60 min	7×10^{-3} cm^3/g	11 m^2/g	2.5 nm

[a]Nitrogen sorption produces typical type-VI isotherms, which is typical for dense materials.
[b]N/A = not available.

both SiO_2–$17TiO_2$ and SiO_2–$17ZrO_2$ xerogels were porous with pore volumes of 7 and 37×10^{-3} cm^3/g, respectively (data shown on Table II). It is noticed that both the pore volume and BET surface area of SiO_2–$17ZrO_2$ xerogel are significantly higher than that of SiO_2–$17TiO_2$ xerogel, which is in good agreement with the gelation time. Bulk xerogels generally exhibit a different microstructure than that of thin films or coatings due to the significantly different drying process, with thin films or coatings having a much denser structure. The general trend obtained in the xerogels would provide a good indication for the thin films or coatings. Significantly porous structure of both SiO_2–$17TiO_2$ and SiO_2–$17ZrO_2$ xerogels may indicate a more porous structure in both SiO_2–$17TiO_2$ and SiO_2–$17ZrO_2$ coatings in comparison with the microstructures of silica and silica–MPS coatings and, thus, explain the relatively low hardness and elastic modulus of the former.

Figure 1 depicts the dependence of the hardness and elastic modulus of sol-gel coatings on contact depth, which is directly related to the indentation load; i.e., an increased load results in a greater contact depth. For all coatings, both the hardness and elastic modulus de-crease with increasing contact depth. The reduction in coating hardness and elastic modulus could be due to the density gradient of the sol-gel coatings. The sol-gel-derived coatings may have a density gradient with density decreasing from the surface toward the interface between the coating and the substrate.[14] The density gradient could be due to the more restricted shrinkage and a slower drying rate at the interface compared with the relative free shrinkage and rapid solvent evaporation at the surface. However, our ellipsometry analysis did not produce convincing data in supporting or opposing the hypothesis of whether a density gradient exists in the coatings.

There is, however, another possible mechanism. The reduction of both hardness and elastic modulus of the sol-gel coatings could be attributable to substrate effect, because the plastic substrates are much softer (with a hardness of approximately 0.29 ± 0.04 GPa under a load of 200 μN) than the coating materials. Such an influence of soft substrates is a well-known phenomenon in the literature.[29] Figure 2 compares the depth dependence of both hardness and elastic modulus of sol-gel-derived
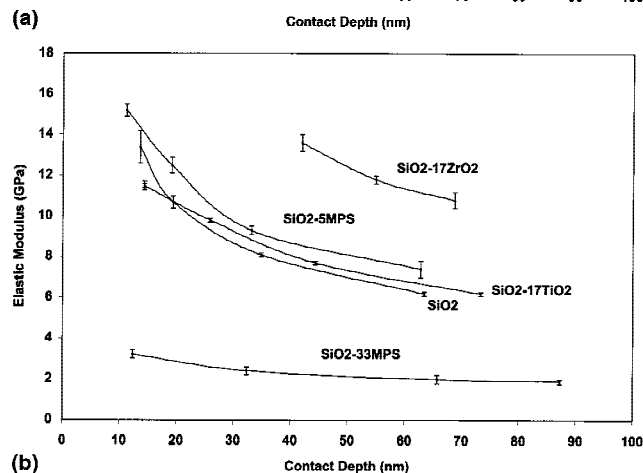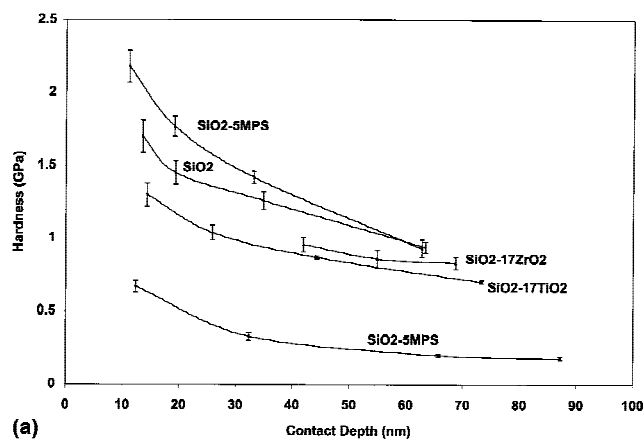

FIG. 1. (a) Hardness and (b) elastic modulus of various ambient dried sol-gel coatings deposited on modified polyester substrates as a function of the contact depth.
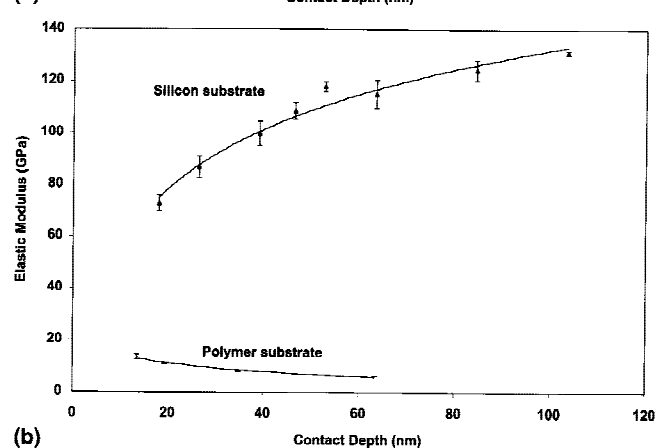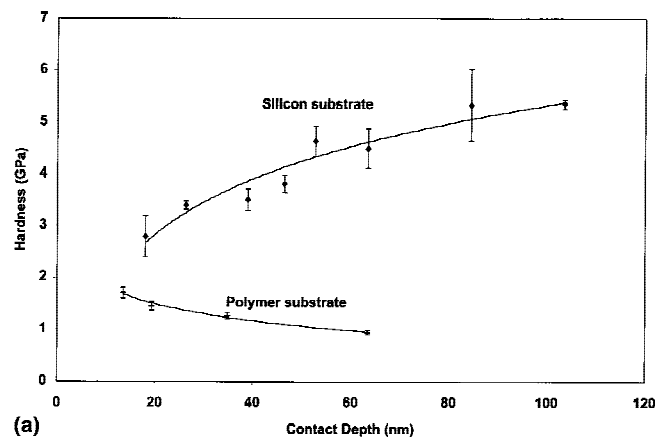

FIG. 2. (a) Hardness and (b) elastic modulus of sol-gel-derived silica coatings on modified polyester and silicon substrates. The coatings were made from the same batch of sol, coated with the same procedure, and ambient dried prior to nanoindentation tests.

silica coatings on polyester and silicon substrates. All of the chemical compositions and the processing conditions were kept the same. The silicon wafer has a significantly higher hardness (approximately 12.2 ± 0.04 GPa) and elastic modulus in comparison to that of sol-gel derived silica coating. Nanoindentation measurements indeed revealed that both hardness and elastic modulus of sol-gel coatings on silicon wafer increased as contact depth increased. Opposite results were obtained for the same coating on polyester substrates. Thus, the above results support that both hardness and elastic modulus are indeed dependent on the mechanical properties of the substrates.

Low-temperature heating and UV irradiation promote surface condensation and structural relaxation, and thus lead to denser sol-gel coatings. Table III compares the layer thickness, refractive index, and hardness and elastic modulus of sol-gel silica coatings with various treatments. The thickness of the coatings was reduced noticeably with either UV irradiation or heat treatment. The coating hardness and elastic modulus increased accordingly. The reduction in thickness following UV irradiation and thermal treatment suggests increased film density or reduced film porosity. One might expect that a density increase would result in a higher refractive index. However, the refractive indices of the coatings measured by ellipsometry showed a different trend. The coating without any treatment had the highest refractive index, whereas both UV-irradiated and heat-treated sol-gel coatings had relatively lower refractive indices. One might anticipate that both UV irradiation and low-temperature heat treatment promoted evaporation of residual water or organic solvent from sol-gel coatings, whereas a relatively large amount of residual water could be present in the coating without any treatment. It is noticeable, however, that both UV irradiation and low-temperature heat treatment did not improve the hardness of silica coatings as significantly as reported in the open literature.[23,29] A possible explanation is that the sol-gel silica coating without any treatment was already relatively dense. For more porous coatings such as zirconia-

doped silica films, low-temperature heat treatment or UV irradiation resulted in a much more significant improvement.

Figure 3 compares the hardness and elastic modulus of sol-gel SiO_2–$17ZrO_2$ coatings before and after a low-temperature heat treatment at 150 °C as a function of contact depth. Figure 3(a) shows that the hardness of the coatings increased significantly, although the elastic modulus did not have an appreciable increase. For example, the hardness (measured with a load of 100 μN) of sol-gel SiO_2–$17ZrO_2$ coatings increased from 0.96 ± 0.05 GPa to 1.80 ± 0.04 GPa with a heat treatment at 150 °C, whereas the elastic modulus remained almost the same. After the low-temperature heat treatment, the same contact depth dependence of hardness and elastic modulus was found. It is also worth noting that there was no appreciable difference in hardness and modulus between using UV irradiation and low-temperature heating. Preliminary abrasion-resistance tests showed that both SiO_2 and SiO_2–5MPS coatings were not damaged by the 2.5-lb eraser rub test described in MIL-C-675.

TABLE III. The variation of layer thickness, refractive indices, hardness, and elastic modulus of silica coatings on modified polyester substrates with different treatments.[a]

Treatment	Layer thickness	Refractive index	Hardness	Elastic modulus
No treatment	128.0 nm	1.437	1.11 ± 0.11 GPa	5.6 ± 0.1 GPa
UV irradiation	114.5 nm	1.432	1.23 ± 0.15 GPa	6.7 ± 0.4 GPa
Heating at 150 °C	108.8 nm	1.436	1.37 ± 0.11 GPa	9.0 ± 0.2 GPa

[a]Both hardness and elastic modulus were determined by a load of 30 μN, which corresponds to a penetration depth (or contact depth) of approximately 15 nm.
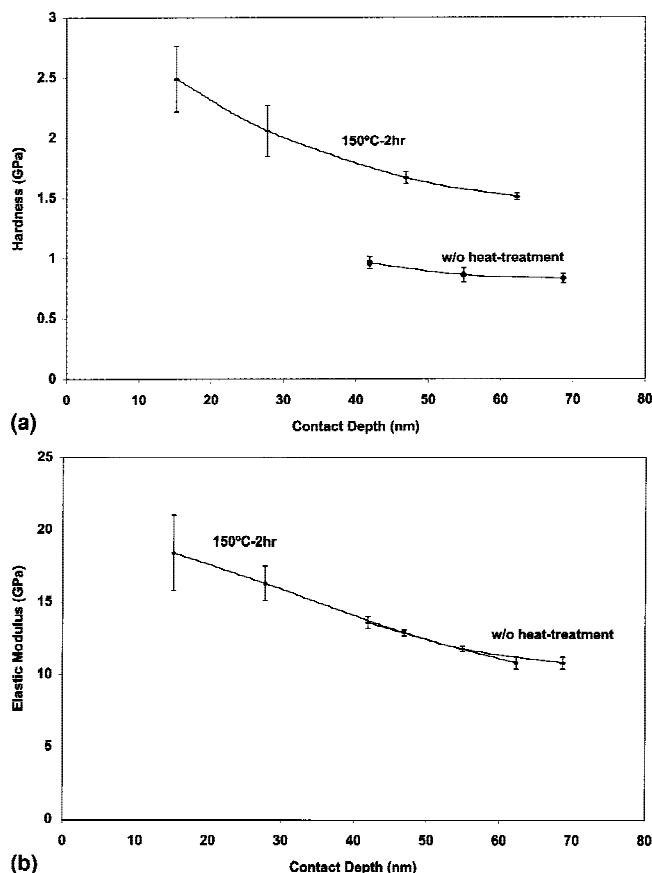

FIG. 3. The change of (a) hardness and (b) elastic modulus of sol-gel-derived zirconia-doped silica coatings with a low-temperature firing at 150 °C for 2 h in air.

Silica-based sols can be readily applied to coat-modified polyester substrates by either dip- or spin-coating; a thin (~100 nm in thickness) uniform film is formed. However, peel testing using Scotch™ tape revealed that the sol-gel-derived coatings can readily be peeled off completely from the modified polyester substrates, indicating that the adhesion of sol-gel coatings on modified polyester substrates is very weak. In the current study, oxygen plasma etching was thus applied to modify the surface chemistry of the substrates, so as to improve the adhesion of sol-gel coatings on modified polyester.

After oxygen plasma etching, the advancing DI–H_2O contact angle of the plastic substrates changed from >90° to <2° and tape testing showed that the sol-gel coatings had very good adhesion on the plastic substrates. Oxygen plasma etching introduced various oxygen-containing species into the plastic surface, including carboxylates and hydroxyl groups[30,31] possibly leading to the formation of Si–O–C bonds at the interface between the coating and the plastic substrate. As a result, very good film adhesion was achieved. The sol-gel coatings that were subjected to the dry thermal-cycling tests remained very stable; neither crack nor delamination was observed. However, coatings that were thermally cycled with water or continuously submerged in boiling water developed cracks and delamination; no appreciable difference was observed between continuous submersion in boiling water and thermal cycling with water. Figure 4 shows optical micrographs of the silica sol-gel coatings on plastic substrates after 5 cycles of 55 min in boiling water (100 °C) and 5 min in ice water (0 °C). The coatings were severely cracked and delaminated. It is interesting to note that large delaminated fragments have been redeposited onto the substrate. Therefore, the adhesion between the plastic and the coating is reversible and subject to degradation when exposed to boiling water or ice water cycling, while the film cohesion remains quite strong. Although adhesion mechanisms can be complex and difficult to infer without careful surface analysis, one possible failure mechanism can be explained by the hydrolytic instability of the Si–O–C bonds between the coating and the plastic substrate. Figure 5 schematically shows a suggested "chemistry" evolution of the surface of modified polyester substrates and/or the interface between substrates and coatings. Oxygen plasma etching resulted in the formation of hydroxyl groups on the polymer surface, albeit a small fraction.[30] These hydroxyl groups would react with partially hydrolyzed TEOS, resulting in the formation of Si–O–C bonds. Such chemical bonds link sol-gel-derived coatings with the polymer substrates and result in a strong adhesion. However, the Si–O–C bonds formed at the interface between the sol-gel coating and plastic substrate may undergo hydrolysis reaction with water at elevated temperatures catalyzed by
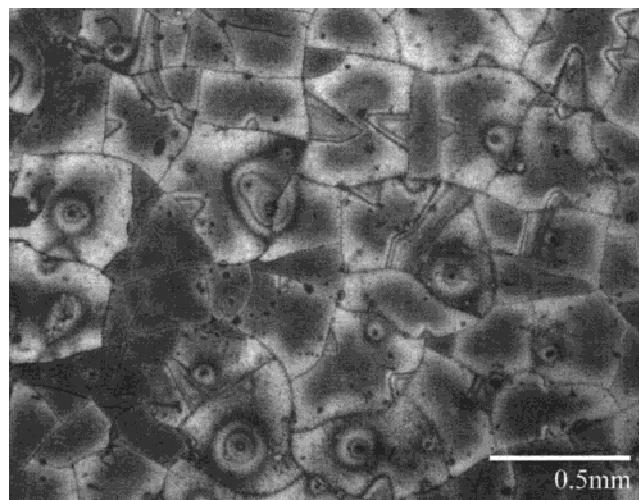

(a)
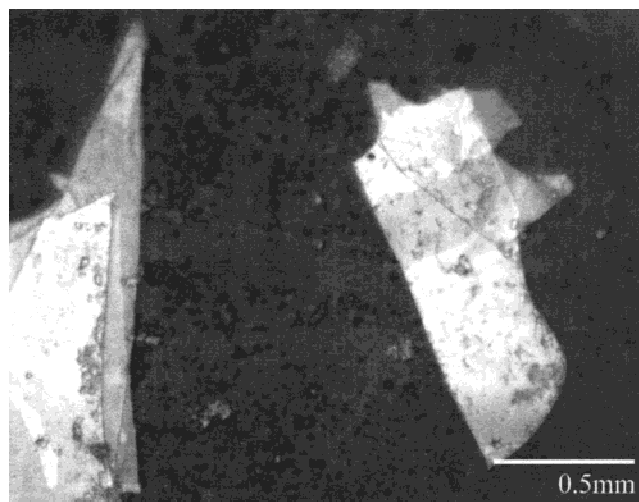
(b)

FIG. 4. (a) Formation of cracks and (b) delamination of sol-gel-derived silica coatings on modified polyester substrates after thermal cycling (water-boiling test) at 100 °C for 55 min and 0 °C for 5 min in water for 5 h in total.

the interfacial stress, induced from the mismatch of the thermal expansion coefficients of sol-gel-derived coatings and modified polyester substrates, resulting in dissociation of sol-gel coatings from plastic substrates. The above discussion is highly speculative and will be a subject of future investigation.
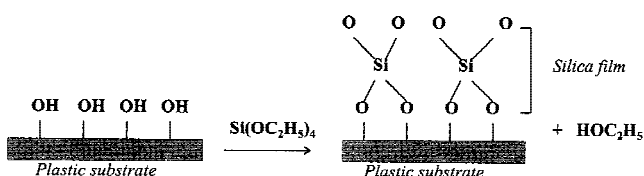
IV. SUMMARY

Five types of sol-gel coatings have been studied. Relatively dense sol-gel-derived coatings were obtained with low-temperature densification methods including UV irradiation and low-temperature heating. The incorporation of organic component resulted in an increased density.

SURFACE MODIFICATION:
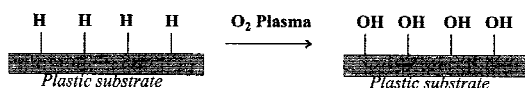
SOL-GEL COATINGS:

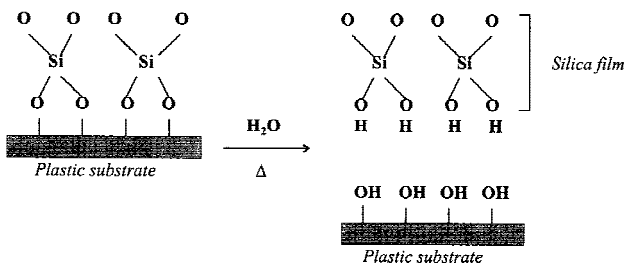## HYDROLYSIS AND DELAMINATION:

FIG. 5. A suggested schematic diagram showing the possible chemistry evolution of the polymer surface and/or the interface between the sol-gel coating and polymer substrate under various treatments.

We have found that the hardness and elastic modulus of a coating may be enhanced with a small amount of organic component or reduced with a large amount of organic component. The introduction of transition metal oxides led to a coating with reduced hardness. Presumably, the reduced hardness resulted from a porous structure brought about by rapid condensation reactions due to the catalytic effect of transition metal oxides. UV irradiation and low-temperature heating effectively enhanced the density and hardness of transition metal-oxide-doped silica coatings. Oxygen plasma etching was proven effective in improving the adhesion of sol-gel coatings on plastic substrates. Nevertheless, the adhesion between the plastic substrate and the coating degrades severely when exposed to boiling water.

ACKNOWLEDGEMENTS

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