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Adhesion of Sol-Gel-Derived Organic-Inorganic Hybrid Coatings on Polyester

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Abstract. Inorganic coatings, including metal-oxide coatings, provide polymer surfaces with excellent abrasion and wear resistance, and protection against environmental degradation. However, one drawback associated with the incorporation of such ceramic coatings to polymeric materials is the adhesion characteristic at the ceramic-polymer interface. In this paper, two strategies for adhesion enhancement of ceramic coatings on polymer substrates were proposed: (1) formation of chemical bonds through surface condensation reactions, and (2) development of interlocked ceramic and polymeric networks through diffusion of alkoxide precursors. The current research has focused on the adhesion of sol-gel-derived organic-inorganic hybrid coatings on polyester by forming chemical bonds between the polymer substrate and the hybrid coatings, as well as developing interlocked polymeric and inorganic networks at the interface. Contact angle, wettability tests, and chemical analysis were done to verify the effectiveness of the adhesion of organic-inorganic hybrid coatings on polyester substrates. In addition, dry and wet thermal cycling tests were done to analyze the adhesion behavior of the hybrid coatings on polyester, followed by microscopy examination. It was found that although both approaches resulted in excellent adhesion of hybrid coatings on polyester, adhesion with interlocked ceramic and polymeric networks was far better than that with chemical bonds in the presence of water at elevated temperatures.

Keywords: adhesion, sol-gel processing, sol-gel coatings, hybrid coatings, organic-inorganic coatings, silica coatings, polyester, ceramic-polymer interface

Introduction

Polymers [1–5] have widespread applications in both everyday life and high technologies, and continue to gain increasing importance as technology advances because of its unique properties, including lightweight, optical transparency, electrical and mechanical properties, and ease in mass production. However, its relatively low abrasion and wear resistance and environmental degradation have hindered many important applications. One approach to overcome this limitation is to apply inorganic coatings onto polymer surfaces. Inorganic coatings, particularly metal oxide coatings, have been explored to enhance abrasion and wear resistance, and to prevent environmental degradation. The implementation of such ceramic coatings to polymers has gained considerable attention for the improvement of the mechanical properties. Polymers' readily scratched nature is often problematic for use in optical and structural applications. Therefore, to enhance its abrasion-resistance, ceramic or hybrid coatings are often applied to improve the surface properties.

A number of film deposition techniques have been employed to form inorganic coatings on polymers. Vapor phase techniques [6–8], such as evaporation, sputtering and CVD, produce high quality films (high density and high mechanical properties), but are expensive, require sophisticated vacuum equipment, and often require substrates to be maintained at high temperatures. In addition, uniform coatings of complex-shaped

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substrates are difficult with line-of-sight vacuum techniques. Solution deposition, such as biomimetic synthesis, is another approach for depositing oxide-based films. Biomimetic synthesis [9–13] has two important characteristics: (1) control of solution conditions, including ion concentration (supersaturation levels), pH, and temperature, and (2) 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 big drawback of this biomimetic approach is the need of a functionalized surface. Langmuir films and self-assembled monolayers (SAMs) are often applied to introduce functionality to the polymer surfaces.

One of the areas extensively studied for the deposition of oxide or oxide-based coatings on complex-shaped substrates involves various sol-gel techniques [14–24, 28]. Sol-gel processing offers easy manipulation of chemical composition and 100% usage of precursor materials. In addition, the substrate withdrawal rate can be controlled to obtain desired film thickness [24]. However, post deposition heat treatments at elevated temperatures are required to convert the porous structure to a dense film. Therefore, organically-modified oxide (also known as ormocer or ormosils) coatings have been extensively explored [14–18] or successfully commercialized in coatings for optical glass.[1] The organic components are introduced through hydrolysis and copolymerization of organic and inorganic precursors together during sol preparation. The unhydrolyzable organic ligands are incorporated into the oxide network through co-condensation. The oxide in the hybrid coating provides a backbone of the mechanical properties, while the organic components make the coating flexible in addition to reducing the mismatch of thermal expansion coefficients of the polymer substrate and the ceramic coating.

Extensive progress [6–28] has been made on developing coatings for various optical applications, but the instability of adhesive bonding at the interface between the coating and the polymer surface has hindered further advancement. Polymer surfaces prove technically difficult to deposit oxide or oxide-based coatings directly, leading to necessary surface treatment or modification for improved wetting behavior. As a result, a variety of surface treatment techniques [29–43]—mechanical scratching, Langmuir monolayers and surfactant assemblies, plasma etching, chemical synthesis, and primer or intermediate layer addition—have been studied to achieve good wetting and adhesion for deposition of oxide coatings by changing the polymer surface chemistry. Two techniques shown to be effective for modifying the polymer surface include oxygen plasma treatment [29–33] and wet chemical routes. Oxygen plasma has been widely used for polymer surface treatment for sol-gel-derived coatings [15, 16]. Functional groups such as carboxylic acids (—COOH) and hydroxyl groups (—OH) can be introduced, increasing the oxygen content on the polymer surface [44, 45]. Wet chemical routes are used to oxidize the polymer surface [34–43]. For example, etching polyethylene (PE) with dichromate/sulfuric acid solutions (chromic acid) is a simple method to introduce carboxylate groups [41]. Further surface modification or introduction of other functional groups can be achieved through the reactive carboxylate groups. Hydroxyl groups can react with alkoxide to form C—O—M (M: metal ion) bonds and terminate the surface with either metal or metal oxide. They can also be replaced by chlorine through contacting the treated polymer surface with PCl_5/Ether [38] or $SOCl_2$ [42]. Chlorinated polymer surfaces can be modified by replacing chlorine ions with amino groups so that various organic molecules can be attached to the polymer surface through stable C—N—C bonds. Hydroxyl groups also readily react with isocyanate groups in the presence of dibutyltin dilaurate in THF at room temperature, providing another chemical route to introduce other functional groups on polymer surfaces.

A variety of mechanisms can be responsible for the adhesion between two materials. These range from covalent bonding to van der Waals attraction, and include capillary adhesion, electrostatic attraction, and mechanical interlocking [46–50]. With the possible exception of mechanical interlocking, these mechanisms are each dependent upon the chemistry and composition of the interface. For oxide or oxide- based coatings on polymers, stable adhesive bonding is desired. Stable bonding at the interface between vapor phase deposited coatings and polymers is achieved through depositing a very thin (a few atomic layers) metallic buffer layer on the polymer substrate [7]. This is done by initially depositing a metallic layer in an oxygen-depleted environment, followed with partial oxidation, and then continued with deposition of metal oxide film. In this way, the metal oxide film has M—O—M bonds linked to the metal buffer layer that attach to the polymer

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substrate through M—C bonds, and thus forms stable adhesive bonding at the interface. However, bonding of sol-gel-derived oxide or oxide-based coatings on polymers is achieved, in general, through formation of C—O—M bonds. Bonds with C—O—M formation, similar to alkoxide precursors, are subjected to hydrolysis under certain conditions. Consequently, when exposed to moisture or water, sol-gel-derived oxide or oxide-based coatings may delaminate and lose adhesion from the polymer surface. Therefore, it is desired to develop a general strategy to form stable, unhydrolyzable bonds at the interface between sol-gel-derived oxide or oxide-based coatings and polymers.

Our studies explore the adhesion characteristics of sol-gel-derived hybrid coatings on polyester by comparing the effects of using two surface modification techniques. Polyester surfaces were modified through interfacial chemical bonding and through interpenetrated networking. Oxygen plasma or wet chemical etching treatment is a rapid way to prepare the surfaces of polyester substrates for bonding hybrid coatings [29–33] by introducing hydroxyl groups and increasing the oxygen content on the polymer surface [44, 45]. Silica impregnation is another efficient method to modify the surface of polyester substrates for the incorporation of hybrid coatings by introducing an interlocking silica network within the polymer matrix. The effectiveness of each surface preparation technique was verified through contact angle and wettability tests for plasma-modified polyester and through Electron Spectroscopy for Chemical Analysis (ESCA) for impregnated polyester. Furthermore, the adhesion behavior of the hybrid coating on polyester was analyzed by thermal cycling and tape test methods, followed by optical microscopy examination.

Experimental

Surface Preparation

Prior to applying sol-gel-derived hybrid coatings, optical grade polyester substrates (Korry Electronics Co., Seattle, WA) were subjected to surface modification or treatment. Three different modification or treatment techniques were attempted: oxygen (O_2) plasma etching, hydrogen peroxide-sulfuric acid (H_2O_2-H_2SO_4) solution etching, and silicon alkoxide impregnation. Both O_2 plasma and H_2O_2-H_2SO_4 solution etching were used to hydroxylate the polyester surface, whereas silicon alkoxide impregnation was used to form an interpenetrating silica network within the polyester substrate. Polyester substrates that were used in this study were initially cleaned and rinsed with ethanol and deionized water. Substrates modified by etching were subjected to O_2 plasma etching [28] for 60 seconds with an O_2 pressure of 100 mtorr. Surface modification could also be done by immersing the polyester substrates in a 30:70 ratio of 30%H_2O_2:H_2SO_4 solution [51] at 90°C for 30 minutes, but this study emphasizes results from O_2 plasma etching. Polyester substrates modified by impregnation were immersed in a 50:50 tetramethylorthosilicate (TMOS, $Si(OCH_3)_4$):EtOH solution at 90°C for 5 hours. Heating was used to enlarge or open the polymer structure so that silicon alkoxide could diffuse in. The substrates were then rinsed again with ethanol and deionized water to remove excess etchant on the surface and allowed to air dry.

Sol Preparation

The silica-based organic-inorganic hybrid sol used to coat the polyester substrates was prepared with an acid-catalyzed, two-step hydrolysis-condensation process. The hybrid sol was prepared by admixing a silica precursor, tetraethylorthosilicate (TEOS, $Si(OC_2H_5)_4$), and an organic precursor, 3-methacryloxypropyltrimethoxysilane (MPS, $H_2CC(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$), in the presence of ethanol (EtOH), deionized water (DI-H_2O), and hydrochloric acid (HCl). Silica (SiO_2)-based hybrid sol containing 10 mol% MPS with a TEOS:MPS ratio of 90:10 was prepared for this study. An initial stock solution was made by dissolving specific amounts of TEOS and MPS in a mixture of ethanol (EtOH), deionized water (DI-H_2O), and 1 N hydrochloric acid (HCl), which acts as the catalyst in the reaction. The stock solution contained a TEOS:MPS:EtOH:DI-H_2O:HCl nominal molar ratio of $0.90{:}0.10{:}3.8{:}5{:}4.8 \times 10^{-3}$. The combined mixture was vigorously stirred at a rate of 500 RPM for 90 minutes at a temperature of 60°C to obtain a stable sol. Further processing of the sol required an additional 3.6 mL 1 N HCl and 1.2 mL DI-H_2O to 30 mL of stock solution. The sol was then vigorously stirred again at a rate of 500 RPM for 60 minutes at a temperature of 60°C. Prior to use, ethanol was added to dilute the sol in order to obtain a volume ratio of 2:1 ethanol to solution. The mixture was stirred for 1 minute and unused portions were stored at freezing temperature (−20°C) to stabilize the reaction; undiluted sols were also stored at −20°C.

Film Deposition

The incorporation of the hybrid coating to the polyester substrates involved a simple dip-coating process. After surface preparation and sol preparation, film deposition of the hybrid coating onto the substrate surface was performed. The polyester substrates modified by O_2 plasma etching were dipped at a constant rate of 3.5 cm/min into the sol with ultrasonication for approximately 1 minute and then were withdrawn at the same rate in the presence of dry air flow to enhance solvent evaporation [28]. The polyester substrates modified by silicon alkoxide impregnation were dipped in the sol at a constant rate of 14 cm/min for approximately 1 minute, withdrawn at the same rate, and then air-dried for approximately 15 minutes. Following deposition, the substrates were exposed to low-temperature heating at a temperature of 150°C for 30 minutes up to 3 hours at a heating and cooling rate of 5°C/min to ensure densification of the gel network.

Characterization

Contact angle analysis using DI-H_2O was used to verify the presence of hydroxylation reactions on the polyester surface after O_2 plasma etching. Angle-resolved Electron Spectroscopy for Chemical Analysis (ESCA, SSX-100 or S-Probe system) using a monochromatized Al K_α x-ray source was performed over a voltage range of 0–1100 eV. Survey scans at 0, 55, and 80 degree angles were used to verify the presence of silicon at a depth of 100, 57, and 17 angstroms within the polymer matrix after silicon alkoxide impregnation, respectively. The characterization of the adhesion behavior of the hybrid coating on each surface-modified polyester substrate was performed using various thermal cycling and adhesion tests [38–42]. Dry thermal cycling tests were conducted by cycling between a 150°C furnace oven for 55 minutes and a −20°C freezer for 5 minutes for a total of 5 cycles. Wet thermal cycling tests were performed by cycling between 100°C for 55 minutes and 0°C for 5 minutes in deionized water for a total of 5 cycles. After thermal cycling tests were performed, optical microscopy was used to analyze the hybrid coatings on each polyester substrate.

Results and Discussion

Adhesion Through Interfacial Chemical Bonding

Surface modification by way of O_2 plasma etching (or H_2O_2-H_2SO_4 solution etching) resulted in the hydroxylation of the polyester surface. Figure 1(a) schematically shows the formation of hydroxyl groups on the surface of a polyester substrate after etching. In this

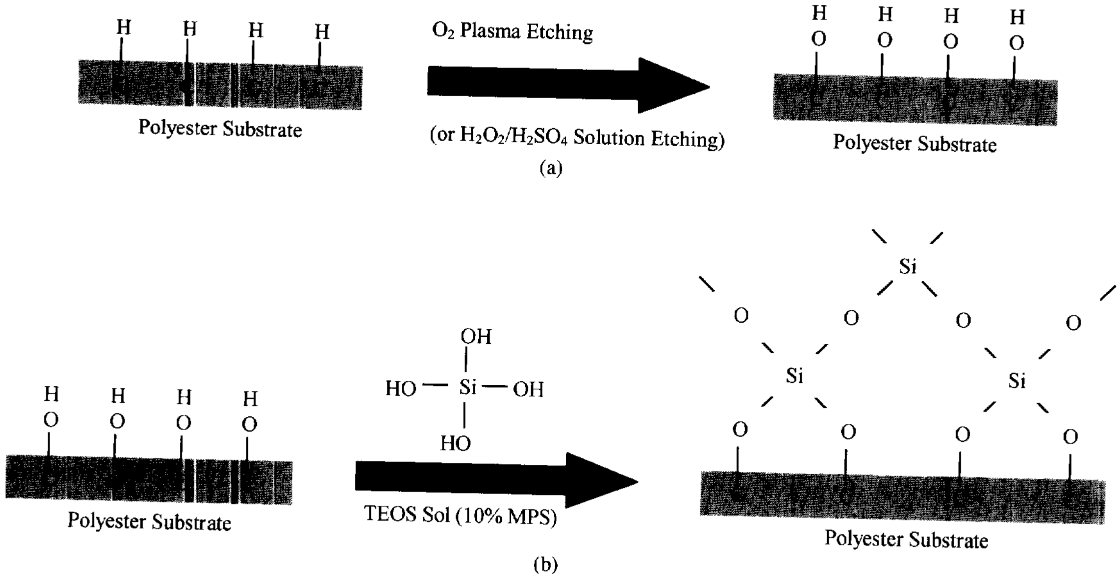

Figure 1. Schematic of (a) surface hydroxylation of polyester by way of oxygen plasma etching or hydrogen peroxide and sulfuric acid wet chemical etching, and (b) subsequent attachment of sol-gel-derived hybrid coating on polyester after surface preparation.

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case, hydroxyl groups form on the polymer surface allowing for subsequent exposure of the surface in silica-based sol to initiate a condensation reaction with partially hydrolyzed and/or condensed TEOS. Figure 1(b) shows the incorporation of the hybrid coating to the surface of the polyester substrate. The reaction of the hydroxyl groups at the surface with the partially hydrolyzed and/or condensed TEOS sol would form Si—O—C bonds attaching the hybrid coating with the polymer substrate at the interface. Contact angle tests using DI-H_2O verified that hydroxyl groups were present on the polymer surface. The advancing DI-H_2O contact angle of the polyester substrates was altered from greater than 90° to less than 2° before and after O_2 plasma etching [28]. This technique for the modification of the surface chemistry by generating hydroxyl groups on the polymer surface resulted in improved wettability and polarity, thereby enhancing the adhesion characteristics. Initial analysis found that dry thermal shock cycling did not have an effect on the coating. In addition, the coating stayed intact after performing tape test analysis. The coating remained stable, where neither cracking nor delamination was observed, indicating that very good film adhesion was achieved.

Adhesion Through Interpenetrated Networking

Silica impregnation by reaction of a polyester substrate with TMOS diluted in ethanol at an elevated temperature of 90°C for approximately 5 hours resulted in the incorporation of silicon alkoxide within the polyester substrate. Subsequently, silicon alkoxide would undergo hydrolysis and condensation processes with water from ambient conditions inside the polymer matrix, forming a silica network that interpenetrates within the polymer structure. The silica network would extend to the surface of the polyester and form Si—O—Si bonds with the sol-gel-derived coating. Figure 2 schematically shows the reaction of a polyester substrate with TMOS solution, and the formation of the hybrid coating on the surface. Silicon alkoxide would initially diffuse and interpenetrate the polyester substrate, forming an interpenetrated silica network within the polymer matrix. Further hydrolysis-condensation reactions would form Si—O—Si bonds at the interface, followed by strong bonding of the coating through surface condensation. The elevated temperature would allow silicon alkoxide to better diffuse to the interior of the polymer matrix where interlocking Si—O—Si networks would form, leaving attached hydroxyl groups at the surface. The "chemical" similarity of the surface groups with partially hydrolyzed and/or condensed TEOS in the sol would initiate surface condensation and thus form chemical bonds with the hybrid coating.

Using ESCA analysis, the presence of silicon within the polyester substrate after silica impregnation was verified at various depths. Figures 3(a)–(c) represent ESCA plots for obtaining the amount of silicon within the top layer of a polyester substrate. From the plots, it can be seen that the amount of silicon increased as the depth of analysis decreased from 100 to 57 to 17 angstroms. Through closer analysis and calculations, the amount of silicon increased from 3.54 to 4.87 to 6.54 atomic percent at 100, 57, and 17 angstrom depths, respectively. This showed that traces of silicon were present within the top 100 angstroms of the polymer matrix, indicating that silicon alkoxide diffused to the interior of the polyester substrate forming networks of Si—O—C and Si—O—Si bonds within the structure. Initial analysis involving dry thermal shock cycling and tape test analysis indicated that the coating remained stable, where neither cracking nor delamination was observed. It was shown that very good film adhesion was also achieved by using this surface treatment method.

Comparison of Adhesion at the Interface

The adhesion behavior of the hybrid coating to the O_2-plasma-modified and silica-impregnated polyester substrates was further analyzed and compared by way of wet thermal shock cycling. In contrast to the results from dry thermal shock cycling, wet thermal shock cycling had an effect on the hybrid coating bonded to the plasma-modified substrate. Figures 4(a) and 4(b) are optical micrographs of the hybrid coating after wet thermal cycling of the plasma-modified polyester substrate [28]. It can be seen that cracks formed and delamination occurred from thermally cycling with water. The coatings were severely cracked and delaminated with large delaminated fragments shown to be re-deposited onto the substrate, indicating film cohesion at the surface. The adhesion between the hybrid coating and the polymer surface is generally strong due to the C—O—M bonding. However, in this case, the presence of water or moisture [52–55] resulted in the hydrolysis of these bonds, which may have been the cause for delamination and separation of the hybrid coating from the polyester surface. This problem is more alarming for sol-gel-derived hybrid coatings because sol-gel coatings are

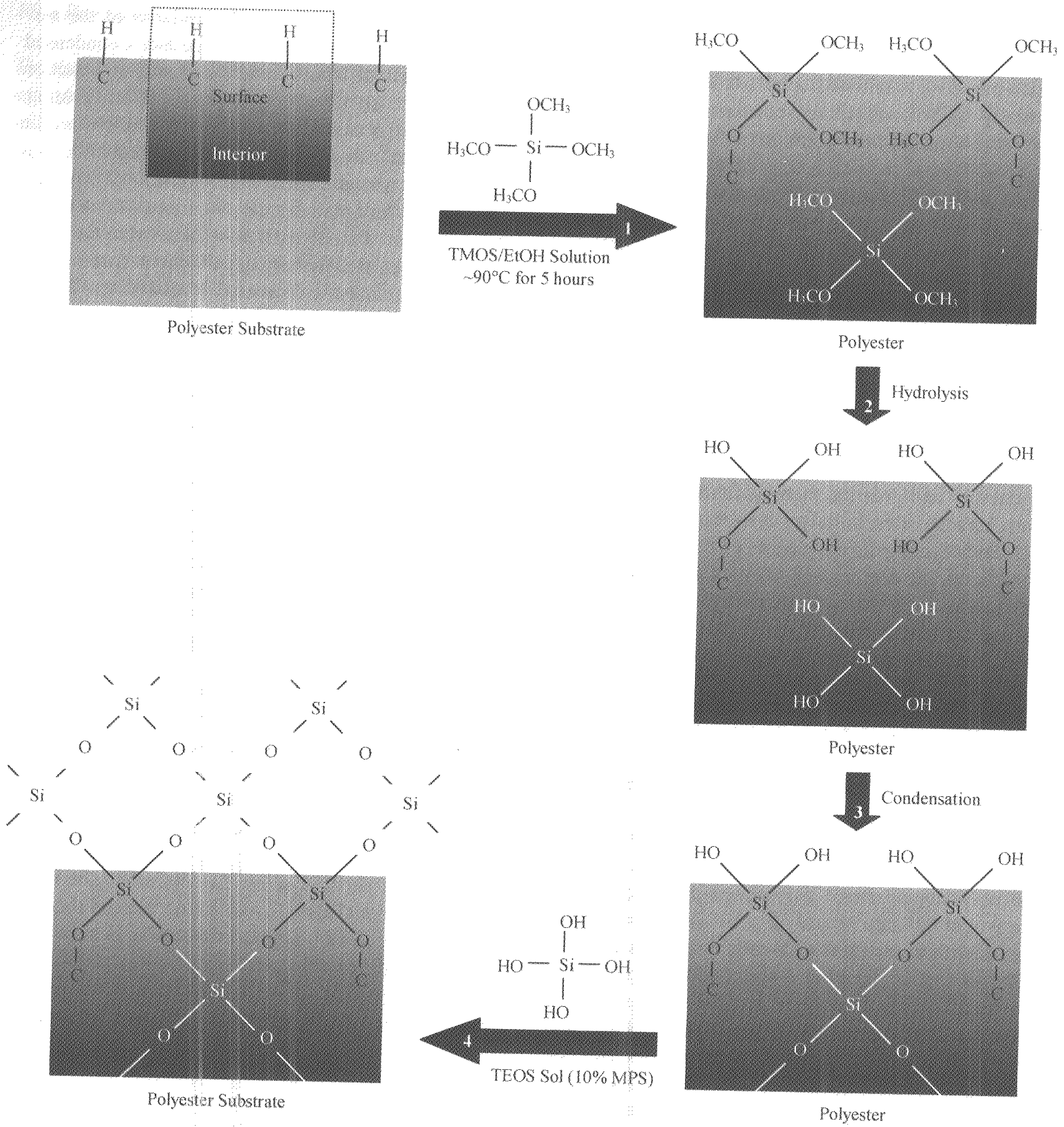


Figure 2. Schematic depicting (1) the diffusion and interpenetration of silicon alkoxide within the polyester structure, (2) the initial formation of hydroxyl groups through hydrolysis reactions, (3) the succeeding formation of an interlocking silica network through condensation reactions, and (4) the subsequent bonding of sol-gel-derived hybrid coating on the surface.

generally porous without heat-treatment at high temperatures (>400°C), which allows water or moisture to easily penetrate through the coating to the interface.

In contrast to the results found from plasma-modified polyester, wet thermal shock cycling did not have an effect on the hybrid coating bonded to the silica-impregnated polyester substrate, further indicating the stability of the interfacial bonding of the coating applied to polyester containing an interpenetrating silica network. Figures 5(a) and 5(b) are optical micrographs

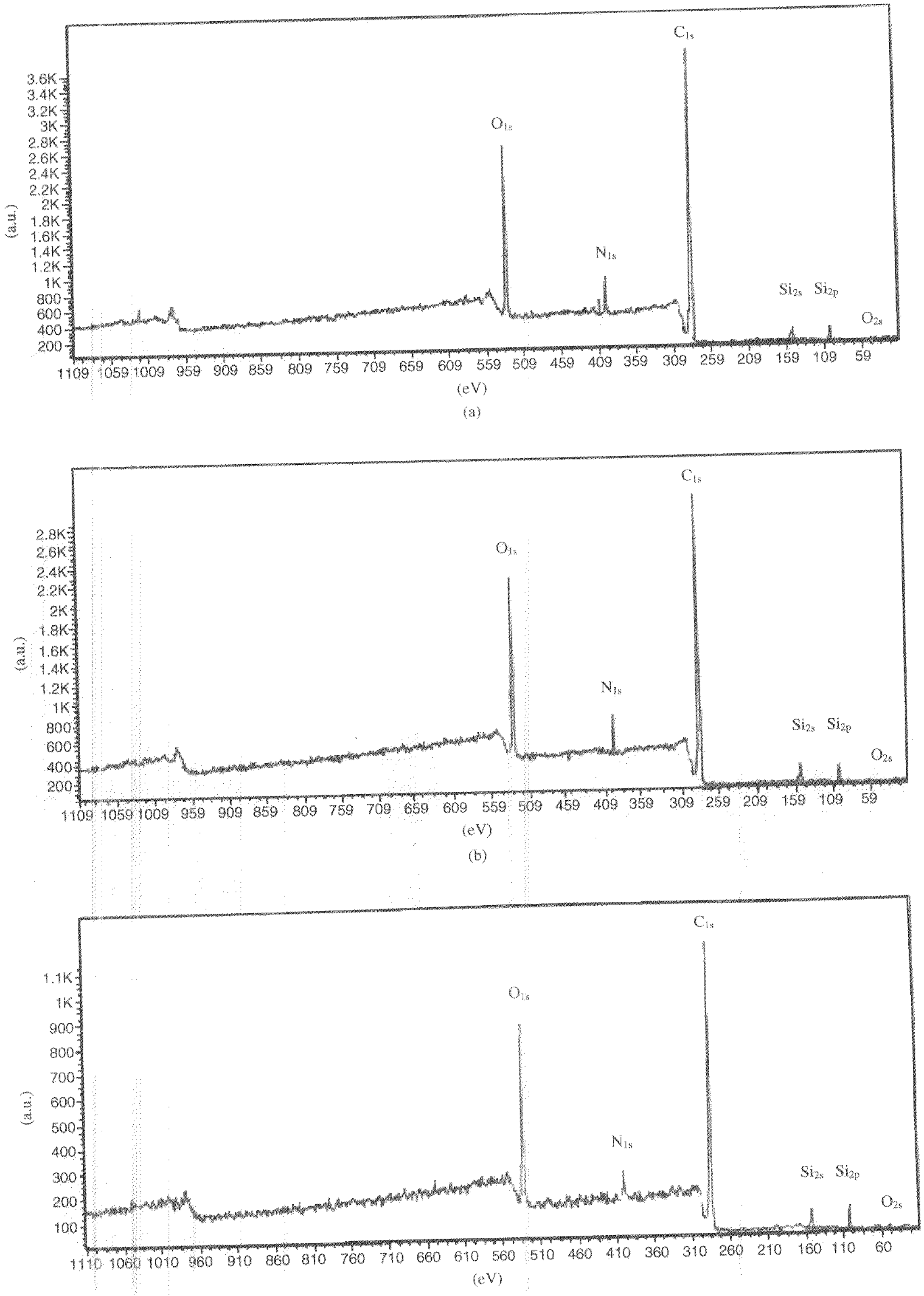
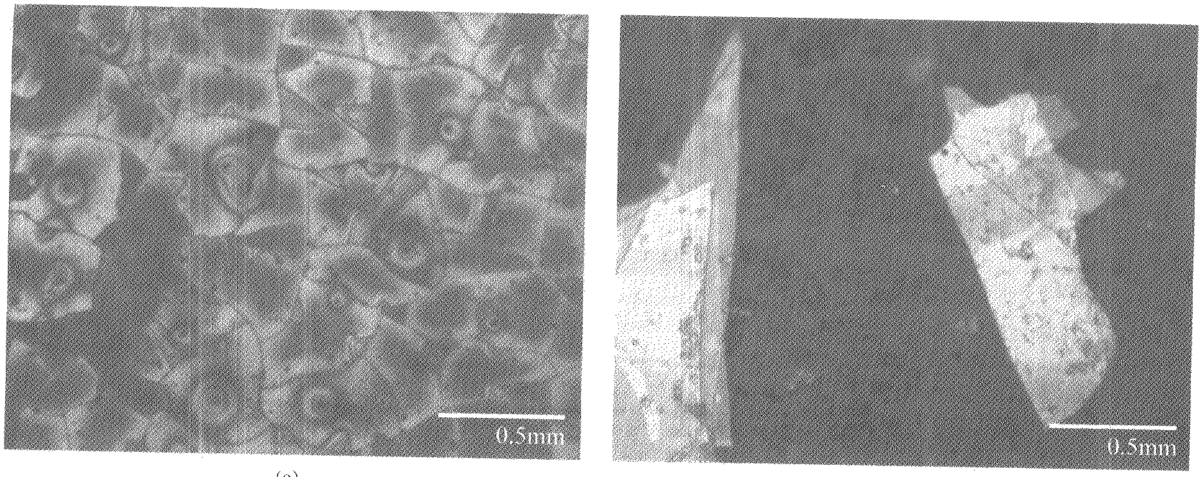


Figure 3. ESCA plots representing the amount of silicon at (a) 100 angstrom depth (0° scan), (b) 57 angstrom depth (55° scan), and (c) 17 angstrom depth (80° scan) within the structure of polyester.



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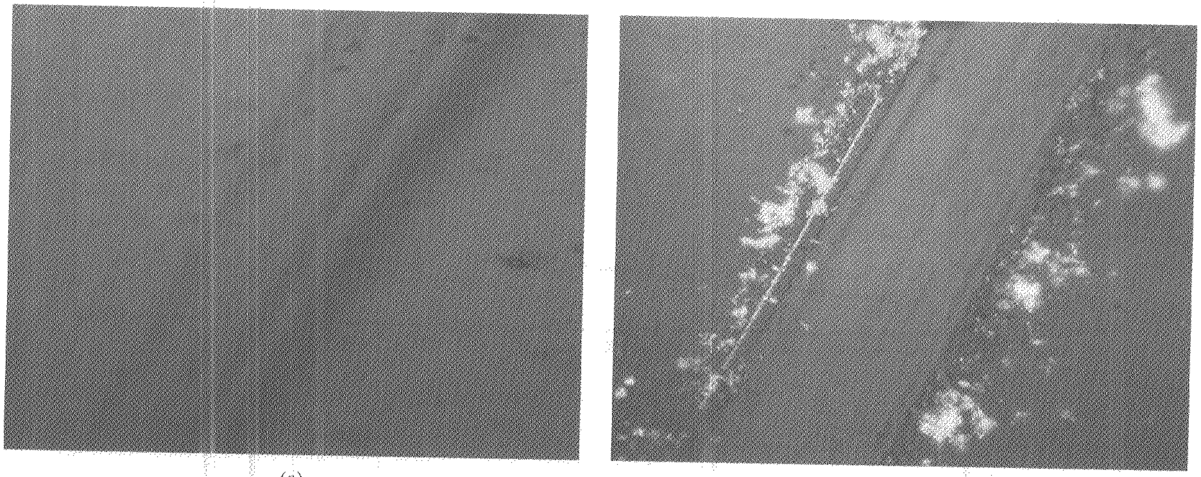
(b)

Figure 4. Optical images of the formation of (a) cracks and (b) delamination of the sol-gel-derived hybrid coating bonded to polyester modified by oxygen plasma etching after wet thermal cycling.



(a)

(b)

Figure 5. Optical images of a scratch on (a) bare polyester, and (b) coated polyester after wet thermal cycling of the sol-gel-derived hybrid coating bonded to polyester modified by silicon diffusion reactions.

verifying the presence of the hybrid coating after wet thermal cycling of the impregnated polyester substrate. It was found that without scratching the coating, the presence of the hybrid coating was difficult to detect due to the transparency and smoothness of the coating surface. In addition, no signs of cracking and/or delamination was present to indicate the existence of the coating. For these reasons, a deep scratch was administered on the surface to identify whether the coating remained stable after thermal cycling in water. By comparing the scratch of a bare polyester substrate to that of the coated polyester substrate, it can be seen that the coating remained on the surface. Closer imaging indicated that the scratch displaced the coating, leaving particles near the edge that were not seen on the bare polyester substrate. This indicated that wet thermal cycling caused neither cracking nor delamination in the coating, and that the coating remained intact.

The difference in the adhesion behavior of the hybrid coating bonded to O_2-plasma-modified and silica-impregnated polyester substrates can be explained by the bonding characteristics at the ceramic-polymer interface. For the plasma-modified polyester substrate, water cycling at extreme temperatures was shown to

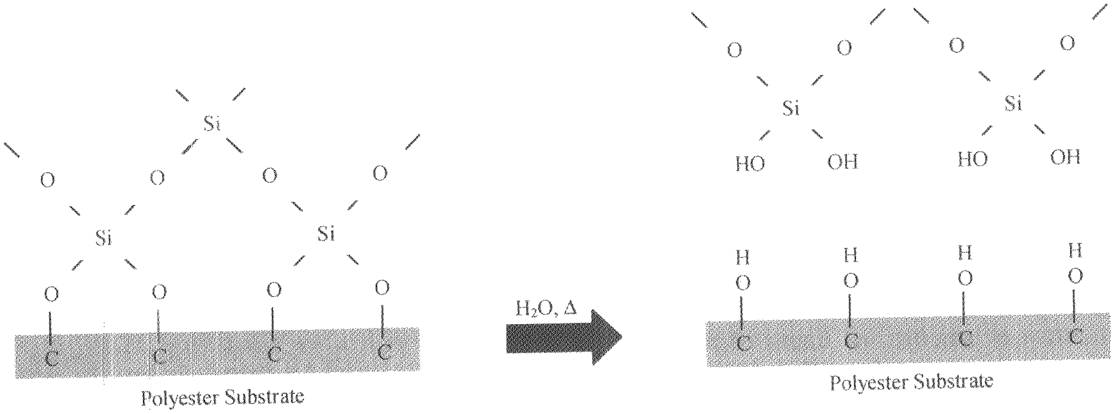


Figure 6. Schematic of hydrolysis reactions at the interface of plasma-modified polyester, causing detachment of the hybrid coating from the surface after wet thermal cycling.

affect the bonding at the ceramic-polymer interface. Figure 6 shows the detachment of the hybrid coating from the polyester substrate surface after wet thermal cycling. Upon forming the hybrid coating, bonds formed at the interface are hydrolyzable, resulting in delamination and loss of adhesion of the coating on the polymer substrate when water was present. The hydrolytic instability of the Si—O—C bonds between the coating and the polyester substrate would cause the detachment of the coating after cycling in water since the Si—O—C bonds formed at the interface may undergo hydrolysis reactions with water at elevated temperatures, catalyzed by interfacial stress. For this reason, it is more desirable to achieve stable unhydrolyzable bonding at the ceramic-polymer interface.

For the polyester substrate containing an interlocking silica network, water cycling at extreme temperatures was shown to not affect the bonding at the interface. Figure 7 depicts the absence of coating removal due to the linking mechanism of the hybrid coating to the polyester substrate after diffusion, interpenetration, and hydrolysis-condensation reactions. The interaction of the hydroxyl groups at the surface with the partially hydrolyzed and/or condensed TEOS sol would form Si—O—Si bonds that would link the hybrid coating to the polyester substrate at the interface after

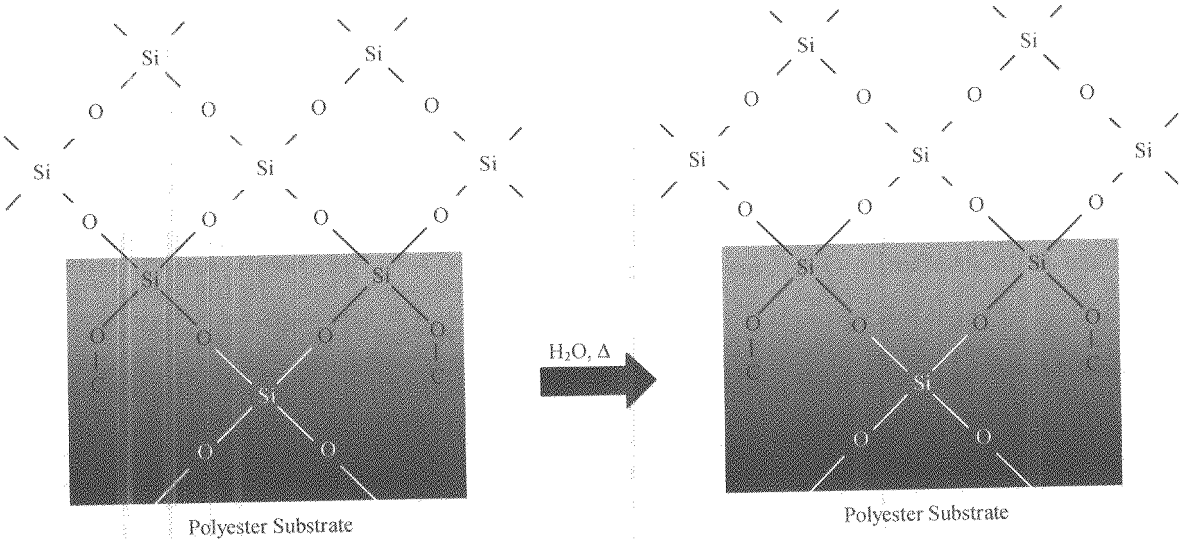


Figure 7. Depiction of the adhesion stability on impregnated polyester after wet thermal cycling, resulting in no detachment of the hybrid coating from the surface.

interaction with the surface groups. Silicon alkoxide would undergo a hydrolysis and condensation process inside the polymer matrix and form a silica network that would interpenetrate with the polymer network. The silica network would then extend to the polymer surface and form Si—O—Si bonds with subsequent deposition of the coating at the interface through co-condensation. This interlocking Si—O—Si bonding network within the polymer matrix, in addition to the Si—O—Si bonding network at the interface, would result in stronger bonding and improved adhesion at the ceramic-polymer interface. Therefore, any possible hydrolysis reactions at the interface would be hindered, preventing any dissociation of the coating at the surface.

Conclusions

It was found that the adhesion of sol-gel-derived hybrid coatings on polyester is strongly dependent on the bonding characteristics at the ceramic-polymer interface, dictated by surface modification techniques. Both oxygen plasma etching and wet chemical etching are effective methods to introduce hydroxyl groups onto the polymer surface. These hydroxyl groups react with the sol through surface condensation, forming chemical bonds between the sol-gel coating and the polymer substrates. Such bonding is proven to provide excellent adhesion between inorganic coatings on polymers; however, delamination and cracking of inorganic coatings occur when subjected to wet thermal cycling. Delamination and cracking are attributed to the hydrolyzable nature of the chemical bonds at the interface. The adhesion behavior of hybrid coatings on polyester with silica impregnation was found to be far better when subjected to wet thermal cycling. The good adhesion at the interface of silica-impregnated polyester can be attributed to the interlocking silica network fused into the polymer structure of polyester, which is not found at the interface of O_2-plasma-modified polyester.

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Note

1. For example, Dow Corning ARC^{TM} abrasion resistant coatings.

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