

A Nanoscale Interface Improves Attachment of Cast Polymers to Glass

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ABSTRACT A novel interface was prepared on glass slides that stabilizes several cast polymers against delamination under conditions necessary for the study of cell surface interactions. This interface was synthesized by deposition of zirconium tetra(*tert*-butoxide) from the vapor phase onto the glass followed by mild thermolysis, which gives a surface-bound zirconium oxide coating. This oxide coating improved attachment of polymer coatings cast from formic acid or methylene chloride. Nylon, polyurethane, and polyhydroxybutyrate/polyhydroxyvalerate coatings were stable against delamination from the oxide-coated glass following sonication in ethanol for more than 30 min or immersion in water at pH 8 for at least 48 h.

KEYWORDS: polymer casting • polymer–glass interface • delamination inhibition • glass surface modification

INTRODUCTION

Surface derivatization of polymers is an increasingly important subject of research given the current scope of polymer-based applications, which ranges from biomedical implants (1) to flexible electronic devices (2). In this context, it is often expedient to support polymer films on a rigid substrate in order to optimize surface chemistry procedures, to improve surface characterization (including by imaging), or even to enable device applications. Glass is an inexpensive and readily available rigid substrate: In our studies of cellular response to surface-treated polymer scaffold materials (3, 4) we were often stymied by polymer substrate deformation, so we believed that coating the polymers on glass might be particularly useful to facilitate our research. However, polymer films cast from solution onto glass are notoriously unstable with regard to detachment when exposed to a range of solvent media (thin polymer films can be easily removed from glass support by immersion in warm water in as little as 30 min (5, 6). Indeed we found that delamination of polymer films cast from formic acid solution onto glass microscope slides was a persistent problem: Cast films of Nylon 6/6 had problems with lift-off and peeling when sonicated in ethanol, and cast films of polyurethane (Selectophore) peeled from its glass substrate within 5 h at pH 8. Films of biodegradable polyester polyhydroxybutyrate/polyhydroxyvalerate (PHBV) on glass delaminated in both ethanol and water. Thus we decided to examine methods for adhesion enhancement of these polymers to glass. Unfortunately, whereas silane coupling reagents (7–9) are well-known surface chemical treatments to improve the interface between glass and polymers, films of common reagents such as trialkoxysilanes can be problematic if they are cast too thick (10, 11); these films are also hydrolytically unstable under various pH

conditions (12) or if treated with aprotic solvents prior to polymer casting (8). Thus it was clear that significant improvement in glass–polymer interface methodology was warranted: The interface should enable polymer films to attach robustly to glass under the reaction conditions that are required for polymer surface chemical activation, surface analysis, and subsequent cell studies. We now report a novel metal oxide interface that is easy to prepare, significantly enhances polymer-to-glass adhesion, enables cast polymer films on glass to resist lift-off during sonication in ethanol, withstands reaction conditions necessary for surface derivatization, and provides stability under physiological conditions for at least 24 h.

EXPERIMENTAL SECTION

General. Soda-lime silicate slides (VWR, Cat. No. 48300–036; Daigger, Cat. No. EF15975A; Fisherbrand Plain, Cat., No. 12–549–3; and Fisherfinest, Cat. No. 12–544–1). Nylon 6/6 (Sigma Aldrich), polyurethane (Selectophore; Fluka), polyhydroxybutyrate (88 %)/polyhydroxyvalerate (12 %) (Goodfellows), formic acid (88 % ACS grade Reagent), methylene chloride (Fisher), zirconium tetra(*tert*-butoxide) (>95 %, Gelest), and absolute ethanol (Pharmaco-AAPER) were all used without further purification. Static water wetting contact angles were measured using a Tantec contact angle meter model CAM-micro. SEM and EDX measurements were made using FEI Quanta 200 Environmental-SEM equipped with an Oxford INCA Synergy 450 energy-dispersive X-ray microanalysis system with an X-Max 80 large area analytical silicon drift detector (SDD), and AFM images were recorded using a Digital Instruments Multimode AFM.

Cleaning of Soda-Lime Silicate Slides. Slides were first rinsed with deionized water with gentle rubbing of the surface with gloved fingers to remove loosely bound debris. After drying under a stream of nitrogen, slides were immersed in a 10 % KOH solution in methanol and were incubated for 2 h. Slides were then rinsed copiously with deionized water until it beaded off the surface and no

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schlieren lines were observed. The slides were then dried in a stream of nitrogen, stored at room temperature, and used within 3 days.

Vapor Deposition and Thermolysis of Zirconium Tetra(*tert*-Butoxide) (1**) (13, 14).** Clean slides were placed in a glass deposition chamber equipped with two stopcocks for exposure to either vacuum or to vapor of **1**; liquid **1** was contained in a 10 mL reservoir. The chamber was evacuated to 1×10^{-3} Torr, and the glass slides were exposed to vapor of **1** with external evacuation for 30 s. The stopcock to the vacuum was closed, and the slides were exposed for 5 min without external evacuation. This cycle was repeated once; the stopcock to the reservoir of **1** was then closed, and heating tape was applied to the chamber. The chamber was heated to 80 °C and held at this temperature for 10 min. The tape was removed; the chamber was allowed to cool to room temperature and was placed under active vacuum to clear the chamber. In most cases, surfaces were completely thermolyzed to ZrO_2 , which was confirmed by contact angle measurement. If fully thermolyzed, the measurement indicated full wetting; if only partially thermolyzed, the contact angle was $>20^\circ$, in which case the coating was hydrolyzed to ZrO_2 by soaking in deionized water for 3 h. Under these conditions, approximately 6–9 monolayers of ZrO_2 are formed on the glass surface.

Polymer Casting. Solutions of polymers were made in 88% formic acid or methylene chloride. Nylon was cast from a 0.05 g/mL formic acid solution, and polyurethane was cast from a 0.02 g/mL formic acid solution. PHBV was cast from a 0.02 g/mL methylene chloride solution. Zirconium complex-coated and clean slides were spin coated with dynamic dispensing using 10 drops of the polymer solution for 40 s at 4000 rpm. Samples were then heated at 120 °C for 10 min to set the polymer layers by solvent evaporation. Slides were cooled to room temperature before testing for stability.

Ethanol Stability Testing. Polymer-coated slides (with and without the interfacial layer of ZrO_2) were placed in beakers of ethanol and were sonicated. Every 5 min, samples were removed and dried under a stream of nitrogen to test for peeling. Samples were tested over a 30 min range; a test was deemed successful if no peeling occurred after this period.

Water Stability Testing. Polymer-coated slides (with and without the interfacial zirconium oxide layer) were placed in beakers of water adjusted to pH 8 using 1N NaOH. Every hour, samples were removed and dried under a stream of nitrogen to test for peeling. Samples were tested over a 48 h range; a test was deemed successful if no peeling occurred after this period.

RESULTS AND DISCUSSION

We hypothesized that the polymer–glass interface could be improved by the inclusion of an interlayer that could interact, even by noncovalent bonds, with both the substrate and the polymer coating. Zirconium oxide deposited on various polymer surfaces by vapor phase treatment

with zirconium alkoxides followed by mild heating (13, 14), has been shown to activate these surfaces through the coordination of oxygen and nitrogen functional groups (3, 4, 13). We proposed that glass slides could be similarly activated by vapor deposition of zirconium alkoxides, in which the metal alkoxide could coat the surface by coordinating both hydroxyl and μ -oxo groups at the glass surface to the Zr. A thin cross-linked Zr oxide layer would be formed on the surface through mild thermolysis by analogy with ZrO_2 prepared on other hydroxylated metal surfaces in ultrahigh vacuum where temperature-dependent thermolysis of the surface deposited tetraalkoxide showed sequential loss of organic groups (15). This oxide would then interface with spin-coated polymers through dative bonding of their nitrogen and oxygen functional groups to the Zr of the oxide layer (3, 4, 13). Indeed, the first part of this hypothesis was substantiated by a sequence in which cleaned glass slides were first treated with vapor of **1** and then by thermolysis to give thin layers of zirconium oxide on the glass surface. This process could be monitored by contact angle (Θ) measurements for water wetting. On partial thermolysis, this contact angle was $>20^\circ$ (attributed to remaining *tert*-butoxy groups (IR spectra show $\nu_{\text{C-H}} = 2976 \text{ cm}^{-1}$, indicative of these groups (13)); at full thermolysis, or by hydrolysis with deionized water, to ZrO_2 , contact angle measurement indicated complete surface wetting ($\Theta < 5^\circ$), and IR shows no signal for *tert*-butoxy ligands (13). The thickness of the deposited zirconium oxide layer was determined using the method we previously reported (13, 14), in which the relationship between deposition and heating times of surface-deposited **1** and layer thickness was probed via quartz crystal microgravimetry (QCM) using a silicon QCM crystal surrogate for glass. The change in the crystal frequency following deposition (at approximately 1×10^{-3} Torr) and heating (at ca. 80 °C) is related to the mass of the adhesion layer that has been deposited on the crystal. Layer thicknesses can be estimated assuming that the ZrO_2 layer packs with a density similar to zirconia and were calculated as the quotient of the measured aerial surface density of zirconia on the QCM crystal (in ng/cm^2) and the known density of zirconia ($5.89 \times 10^9 \text{ ng/cm}^3$). By direct QCM measurement here, frequency changes for deposition of **1** onto glass ranged from 713 to 1258 Hz, which correspond to 3 to 4.7 nm or 6 to 9 monolayers thickness of deposition. EDX analysis of a representative sample showed the entire glass surface to be covered with Zr (see the Supporting Information). SEM showed an even surface texture for the ZrO_2 -coated glass (Figure 1); AFM images (see the Supporting Information) indicated the ZrO_2 rms roughness to be about 1.4 nm.

To test the critical polymer adhesion aspect of the hypothesis, representative films of three polymer classes, polyamides, polyurethanes, and polyesters were examined. Nylon 6/6, polyurethane (Selectophore), and polyhydroxybutyrate/polyhydroxyvalerate (PHBV), were cast from formic acid or methylene chloride solutions onto zirconium alkoxide/oxide-treated slides. Control samples were also cast from

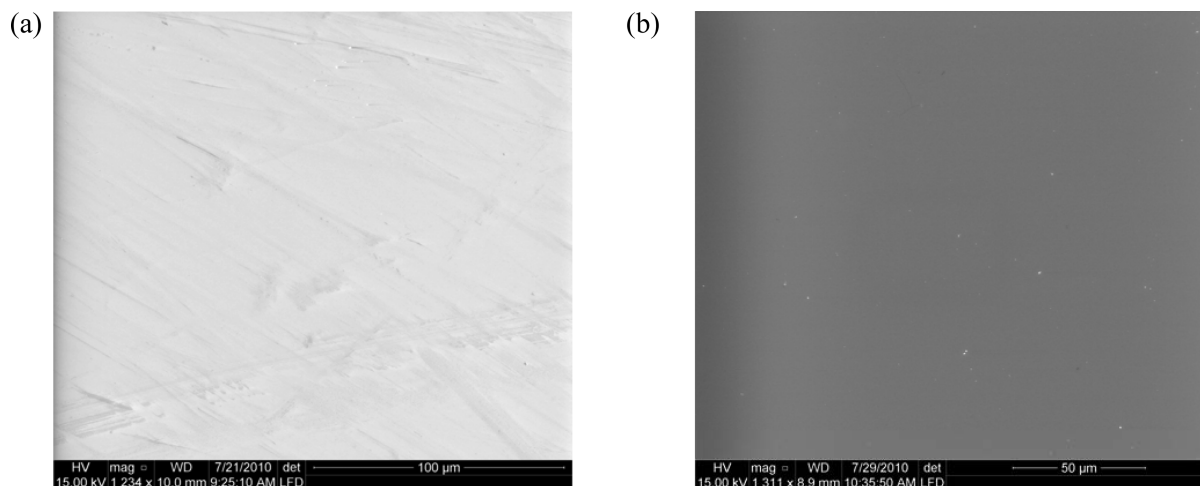


FIGURE 1. SEM images of (a) clean glass (1234x); (b) ZrO_2 -treated glass (1311x). Scale bars are (a) 100 μm and (b) 50 μm .

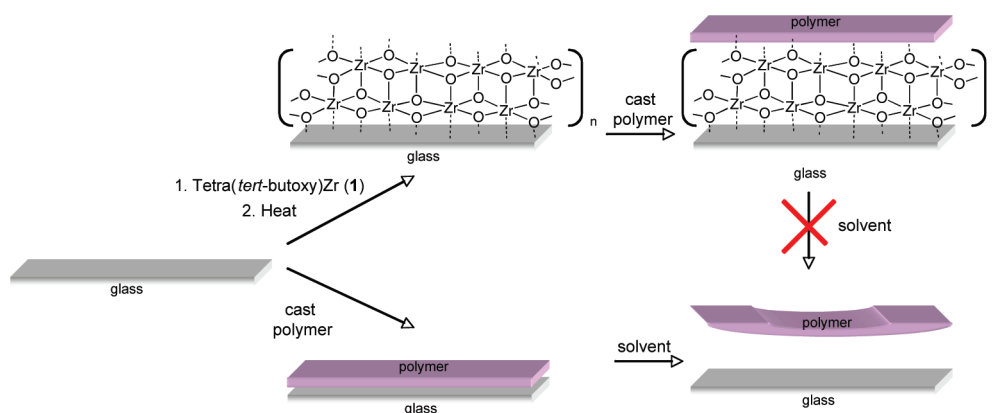


FIGURE 2. Cartoon showing delamination of a cast polymer in the absence of the zirconium oxide interface; the interface provides stability against such delamination.

formic acid or methylene chloride solutions onto clean glass slides. The polymer films were set by heating to drive off any water and residual solvent. Water wetting contact angles of the films were consistent with reported values (nylon, $\Theta = 40^\circ$; polyurethane, $\Theta = 66^\circ$; PHBV, $\Theta = 69^\circ$).

Stability of the cast films to peel off was first measured by sonication in ethanol. Polymer coated slides (with and without the underlying zirconium oxide layer) were placed in beakers of ethanol and sonicated. Every 5 min, samples were removed and dried under a stream of nitrogen. The nylon 6/6 films cast on to control glass slides began peeling and lifting off after less than 5 min. The nylon 6/6 films cast on the glass slides coated with the zirconium oxide showed no signs of peeling after 15 min, and only after 30 min of sonication did films begin to curl at the edges; most of the film remained intact and usable after this time. Likewise, the PHBV films cast onto control glass slides were completely removed after 5 min of sonication; however the PHBV films cast on the glass slides treated with zirconium oxide were completely intact after 30 min. In contrast, all slides cast with polyurethane, regardless of the presence of the zirconium oxide layer, were stable to sonication in ethanol, showing no signs of peeling after 30 min.

Stability to water was then measured. Polymer coated slides (with and without the underlying zirconium oxide interface) were placed in beakers of water adjusted to pH 8. Samples were removed every hour and dried under a stream of nitrogen to test for peeling. The nylon 6/6 films cast on to control glass slides began peeling and lifting off after 20 h. The nylon 6/6 films cast on the glass slides equipped with the zirconium oxide interface showed no signs of peeling, even after 48 h. The polyurethane films cast on control glass slides became white and brittle after only 2 h and began to lift off the glass after 5 h. In contrast, the polyurethane films cast on the glass slides treated with the zirconium oxide interface showed no signs of peeling even after 48 h. The PHBV films cast on control glass slides began peeling at the edges after 2 h and were unusable after 24 h due to significant peeling over the entire surface. In contrast, the PHBV films cast on zirconium oxide treated glass showed no signs of peeling after 48 h. Water wetting contact angles of intact films remained unchanged (nylon, $\Theta = 40^\circ$; polyurethane, $\Theta = 66^\circ$; PHBV, $\Theta = 69^\circ$); where the polymer film had peeled, the contact angle of the residual surface was fully wetting ($\Theta < 5^\circ$) (Figure 2). In no cases were any

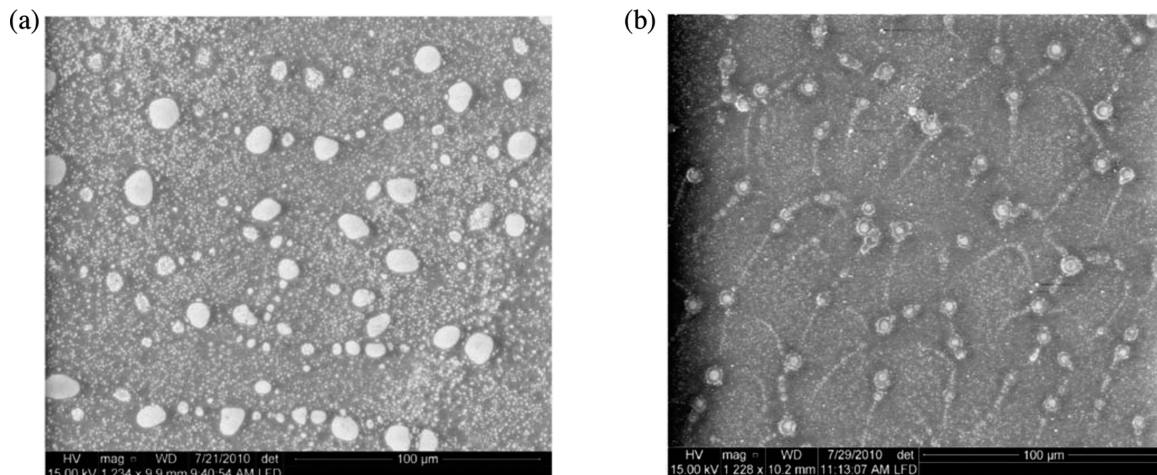


FIGURE 3. SEM images of PHBV cast on (a) clean glass (1234x); (b) ZrO_2 -treated glass (1228x). Scale bars are 100 μm .

ostensible differences in adhesion to the glass slides noted for zirconium oxide thickness that ranged from 6 to 9 monolayers. It is interesting that although SEM analysis of PHBV cast on clean glass showed a rough surface covered with “blisters” (see Figure 3), SEM of the polymer cast on the ZrO_2 adhesion layer showed it to be more surface conforming, consistent with our proposal of polymer attachment to that layer. Polymers cast on glass using the ZrO_2 interface were used for cell studies, which have been reported elsewhere (3, 4, 13).

CONCLUSIONS

Surface-bound zirconium oxide layers, which are readily synthesized through vapor deposition and heating on the surface of glass slides, are effective interfaces to improve attachment of polymer coatings that are cast from formic acid or methylene chloride. Nylon, polyurethane, and biodegradable polyester (PHBV) coatings were shown to be stable to delamination following sonication in ethanol for more than 30 min or immersion in water at pH 8 for at least 48 h. Because our activation process likely involves initial, simple coordination of the Zr *tert*-butoxide complex to oxygen functionality at the glass surface (which could also involve any adventitious residual water), this method should be applicable to a wide range of oxide-terminated surfaces such as on silicon, aluminum, or titanium. Because interface adhesion also likely involves coordination to Zr, this activation method should be applicable to a variety of polymer coatings including

polyimides, polyureas, or natural polyamides, such as collagen or silk.

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Supporting Information Available: EDX image showing Zr coverage of the glass slide; AFM images of PHBV on clean glass vs ZrO_2 -treated glass (PDF). These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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