Poly(aryl-ether-ether-ketone) (PEEK) is emerging as an important biomaterial for use in trauma, orthopedic, and spine applications.1 It has distinct advantages over metallic implant materials in that it can be combined with carbon fiber to have mechanical properties that more nearly replicate those of bone, and it is radiolucent, which facilitates radiographical analysis of tissue surrounding implanted devices. Paradoxically, it suffers compared to metals in that the PEEK surface is quite bioinert, so much so that even desired cell growth on it is severely limited. Indeed, it is this low ability of PEEK to foster surface cell growth that has limited its application to devices where tissue fixation is critical. To this end, considerable efforts have been made to create composites of PEEK and hydroxyapatite (HA) in attempts to combine the beneficial mechanical properties of the plastic with possible osseoconductive properties of HA.1 Unfortunately, these efforts have resulted in trade-offs between desirable cell surface and materials mechanical properties. Common chemical surface treatments have also failed to yield materials displaying both beneficial mechanical and cell growth properties. We have reported that polymers with functional groups that can be acidified, such as N—H groups of polyamides2 or polyurethanes,3 can be surface activated for cell adhesion by treatment with vapor of zirconium or titanium alkoxides followed by ligand replacement reactions with organics that can be used to bond cell adhesive peptides. This process is not, however, applicable to PEEK, which is simply a polyether polyketone.1 We now report that an adhesion layer can be prepared on PEEK from these alkoxides in a process reminiscent of deposition and partial thermolysis of metal alkoxides on oxide surfaces:4 a thin film of the alkoxide is vapor deposited onto the PEEK surface, and the metal complex is bound through simple ligation. Controlled thermolysis of the alkoxide coating gives a mixed alkoxide—oxide “adhesion layer,” which is then used to attach organophosphonates or carboxylates through methods comparable to those we have described for native metal oxide surfaces.5

We had observed that deposition of zirconium tetra(tert-butoxide) (1) onto metal oxide surfaces followed by mild thermal treatment (ca. 50 °C) in UHV gave a surface bound Zr species with stoichiometry consistent with a mixed alkoxide—oxide.5 We hypothesized that carbonyl or ether groups at the surface of polyesters, polyethers, or polyketones could similarly serve as coordinating groups to enable deposition of a metal alkoxide complex onto the polymer surface, and that mild thermolysis would give an analogous mixed metal alkoxide—oxide layer that would be bound to the polymer through coordinative interactions between these surface ether or carbonyl groups and the metal centers.

In typical experiments coupons of PEEK (Goodfellow) were treated with the vapor of 1 or titanium tetra(tert-butoxide) (2) at 10⁻³ Torr with external evacuation for 30 s followed by 5 min exposure without external evacuation. They were next heated to 75 °C and then sonicated for 1 min in dry acetonitrile to give 3a. A similar sequence done on a 0.5 mm thick film of poly(ethylene terephthalate) (PET), but with sonication in THF, gave 3b, which was imaged by atomic force microscopy (AFM). IR spectra of 3a and 3b showed νC—H = 2976 cm⁻¹, indicative of tert-butoxide groups.6 The static water contact angle (90°) measured for 3a decreased to 35° as the tert-butoxy ligands were cleaved by exposure to ambient water. Samples of 3a and 3b were treated with octadeclphosphonic acid (ODPA) via the T-BAG method,7 which gave phosphonate adducts 4a and 4b (water contact angle = 95°; IR, vCH₂asym = 2920 cm⁻¹, vCH₂sym = 2849 cm⁻¹, characteristic of disordered alkyl chains8). X-ray photoelectron spectroscopy of coated 4a showed Zr (3d) and P (2p) peaks with Zr/P = 2:1 (see Supporting Information), consistent with a model in which the Zr alkoxide—oxide forms a bilayer and only the topmost layer reacts with the phosphonic acid (Scheme 1). A sample of 4b was vigorously flexed and wiped with a Kimwipe. AFM analysis of the resulting material showed a film thickness of 3–4 nm (determined from pin holes in the film; Figure 1); since the phosphonate is about 2 nm long, this suggests that the adhesion layer is 1–2 nm thick, consistent with the XPS data.

The relationship between deposition and heating times of 1 and adhesion layer thickness was probed via quartz crystal microgravimetry (QCM) using a silicon QCM crystal surrogate placed in the deposition chamber alongside samples of PET and PEEK. The change in the crystal frequency following deposition (at 10⁻³ Torr) and heating (at ca. 50 °C) is related to the mass of the adhesion layer (3c) that has been deposited on the crystal.5,9 Layer thicknesses were estimated assuming that the adhesion layer packs with a density similar to that of zirconia and were calculated as the quotient of the measured aerial surface density of 3c on the QCM crystal (in ng/cm²) and the known density of zirconia (5.89 × 10⁹ g/cm³) (Table 1).

PEEK was cut into 1.125” × 0.5” coupons that were treated with 1 to give 3a and then glued with Cytec Fiberite FM 1000

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<th>deposition time</th>
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<tr>
<td>1 h</td>
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<td>1966 ± 33 Hz</td>
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Figure 2. Osteoblast cell attachment on derivatized PEEK. (a) Cells on RGD-modified PEEK (5), (b) 1,12-dodecylbisphosphonate-modified PEEK (4c), or (c) PEEK control surfaces, all after 3 h, fixed and stained with antivinculin antibodies and fluorescein-conjugated secondary antibodies. Scale bars are 50 µm. (d) Number of cells per 10× microscope field counted for untreated PEEK, RGD-derivatized, and 1,12-dodecylbisphosphonate-derivatized PEEK. Average values from at least three fields are shown with error bars representing ±1 standard deviation.

Scheme 1. Deposition of Titanium or Zirconium Tetra(tert-butoxide) onto PEEK, PET, or Si Followed by Heating Gives the Adhesion Layer 3, Which May Be Converted to a Phosphonate (4) or a Carboxylate (5) Derivative by Reaction with the Corresponding Acid

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Supporting Information Available: Full experimental details for formation of the metal alkoxide/oxide adhesion layer; XPS spectra; adhesion layer stability measurements; and cell counting and spreading protocols. This material is available free of charge via the Internet at http://pubs.acs.org.

References


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