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Enhanced Bonding of Poly(ethylene-*co*-acrylic acid) to Oxides through Surface-Bound Alkoxyzirconium Complex Interfaces

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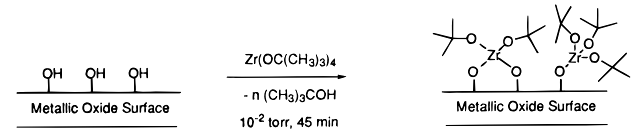
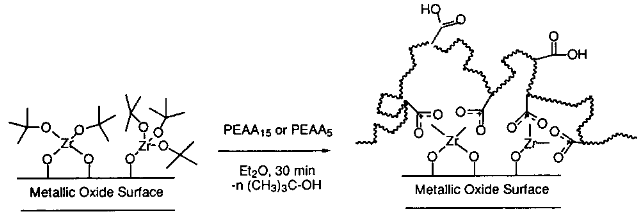
Copolymers of polyethylene and poly(acrylic acid) have been used for more than 30 years to enhance adhesion of polyethylene to a variety of inorganic and organic surfaces,[1,2] ranging from aluminum,[1−4] copper,[1,2] lead,[5] and iron[6,7] to silicon[8] and even paper.[9] In these classical procedures, interaction between the substrate surface and the copolymer is effected by processing involving heat and pressure. While this type of technology might be appropriate for adhesion enhancement to large-dimension bulk materials with high mechanical strength, it might not be applicable in nanoscale device processing or in cases where the substrate is characterized by mechanical fragility. A second drawback of classical processing is that adhesion increases with increasing amounts of copolymer carboxylic acid and increasing basicity of the substrate surface;[1] for higher strength applications a high acid content must be used. Since many metallic surfaces, for example copper, can react with carboxylic acid residues over time,[2] the polymer layer tends to peel. In addition, adhesion depends on the basicity of the oxide or oxided overlayer, so adhesion can be poor for nonbasic surfaces, even when high acid content copolymers are used. Clearly, application of copolymer technology to nanoscale processing or to use with low-basicity surfaces, would benefit from more controllable interface synthesis than is currently available. We recently reported the use of tetra(*tert*-butoxy)zirconium to prepare a stable interface between the hydroxylated oxide surface of aluminum and an alkanecarboxylic acid.[10] In this process a surface-bound alkoxyzirconium species is first formed, and subsequent ligand metathesis with the carboxylic acid generates a new, covalently bound alkanecarboxyzirconium surface complex species. We now report that poly(ethylene-*co*-acrylic acid)−15%$_{wt}$ acrylic acid (PEAA$_{15}$) and poly(ethylene-*co*-acrylic acid)−5%$_{wt}$ acrylic acid (PEAA$_5$) can be used to form stable, covalently bound adducts with a variety of surfaces, including surface-oxidized aluminum, iron, porous silicon (PS), and indium tin oxide (ITO), via an alkoxyzirconium complex interface.

Scheme 1. Deposition from the Vapor Phase of Tetra-*tert*-butoxyzironium onto a Hydroxylated Surface



Scheme 2. Deposition from Solution of Poly(ethylene-*co*-acrylic acid) onto a Zirconium Alkoxide Complex-Treated Substrate



In a typical procedure, a clean substrate[11] was treated with tetra(*tert*-butoxy)zirconium vapor at ca. 10^{-2} Torr for 45 min, followed by evacuation for 60 min at ca. 10^{-2} Torr to remove any physisorbed intact zirconium tetraalkoxide.[10] Depending on substrate surface hydroxyl group content, either one or two alkoxide ligands can be lost by protonolysis to give a surface $[M]-[O]_{4-n}-Zr(OBu^t)_n$ species ($n = 2$ or 3;[12] Scheme 1). The treated substrate was analyzed by FTIR spectroscopy to confirm the presence of the surface-bound Zr complex. Substrates were then dipped in a saturated, ethereal solution of either PEAA$_5$ or PEAA$_{15}$ for 30 min, removed, rinsed with copious amounts of diethyl ether, and dried in vacuo to give the surface-bound zirconium carboxy copolymer (Scheme 2); monitoring was done by FTIR. Control procedures were effected on similarly prepared substrates, however without first forming the surface zirconium alkoxide. Comparison of the infrared reflectance or transmittance in the 2800−3000 cm^{-1} region gave a qualitative assessment of relative loadings for the copolymers adhering to either clean or Zr complex treated surfaces.

Aluminum substrates were analyzed using specular reflectance (SR) FTIR, with a grazing angle of 85°. SR

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[11] Aluminum substrates were prepared by evaporating approximately 100 nm of the metal onto glass slides. ITO substrates were obtained from Delta Technologies and were cleaned prior to use in an ultrasonic bath, followed by rinsing in hot trichloroethylene, acetone, and hot methanol. PS substrates were prepared according to the literature. (Kelly, M. T.; et al. *J. Phys. Chem. B* **1997**, *101*, 2702−2708.) Iron substrates were cleaned by vigorous abrading with sandpaper, rinsed with deionized water, and dried at 250 °C. Poly(ethylene-*co*-acrylic acid), 5%$_{wt}$ acrylic acid (PEAA$_5$) and poly(ethylene-*co*-acrylic acid), 15%$_{wt}$ acrylic acid (PEAA$_{15}$) were both obtained from Aldrich and were used as received.

[12] The stoichiometry of deposition was not determined for iron, PS, or ITO. For a well-defined study of surface deposition on Al, see: Lu, G.; Purvis, K. L.; Schwartz, J.; Bernasek, S. L. *Langmuir* **1997**, *13*, 5791−5793.

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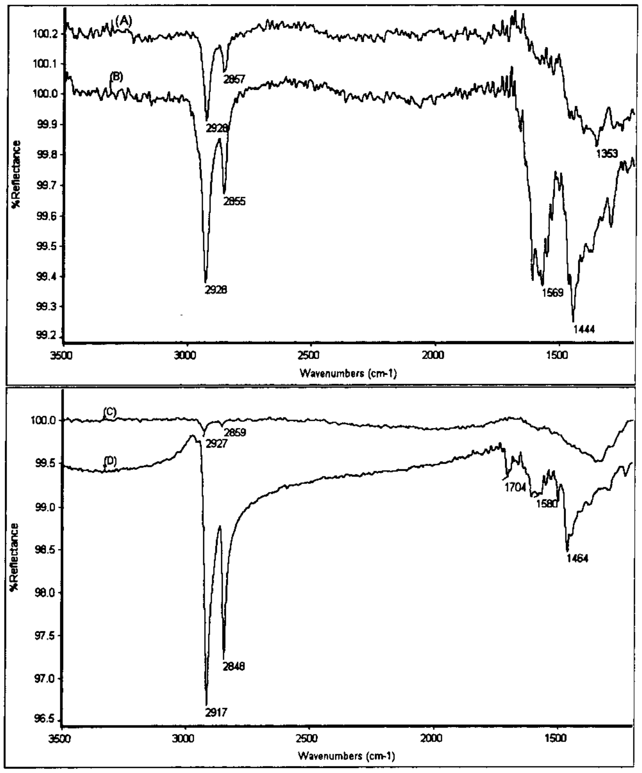

Figure 1. SR FTIR spectra of poly(ethylene-*co*-acrylic acid) on aluminum. (A) $PEAA_{15}$ on bare aluminum; (B) $PEAA_{15}$ on $[Al]-[O]_2-Zr(OBu^t)_2$; (C) $PEAA_5$ on bare aluminum; (D) $PEAA_5$ on $[Al]-[O]_2-Zr(OBu^t)_2$.

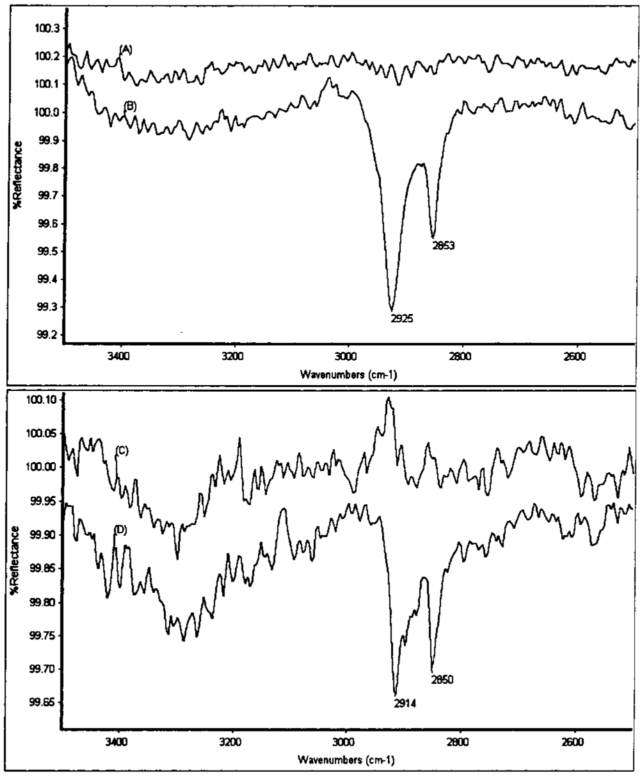

Figure 2. DRIFT spectra of poly(ethylene-*co*-acylic acid) on iron. (A) $PEAA_{15}$ on bare iron; (B) $PEAA_{15}$ on $[Fe]-[O]_{4-n}-Zr(OBu^t)_n$; (C) $PEAA_5$ on bare iron; (D) $PEAA_5$ on $[Fe]-[O]_{4-n}-Zr(OBu^t)_n$.

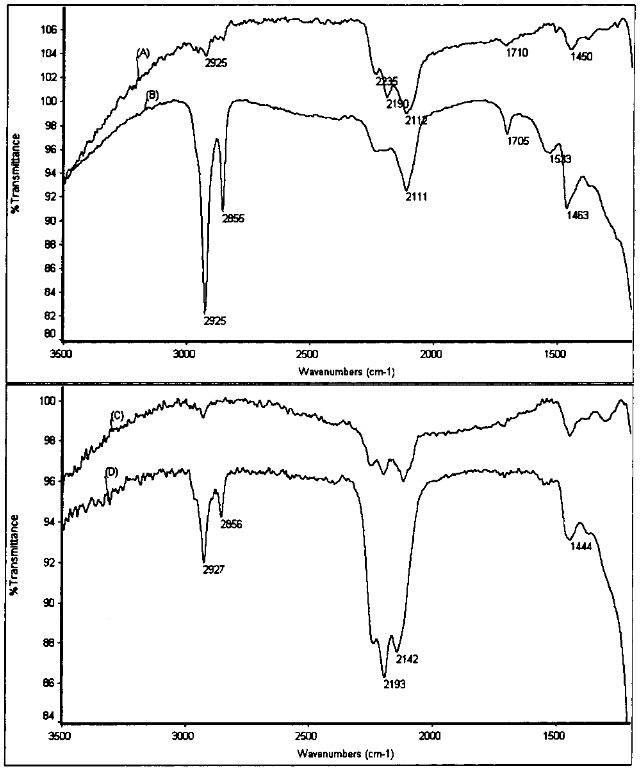

Figure 3. FTIR spectra of poly(ethylene-*co*-acylic acid) on porous silicon. (A) $PEAA_{15}$ on bare PS; (B) $PEAA_{15}$ on $[PS]-[O]_{4-n}-Zr(OBu^t)_n$; (C) $PEAA_5$ on bare PS; (D) $PEAA_5$ on $[PS]-[O]_{4-n}-Zr(OBu^t)_n$.

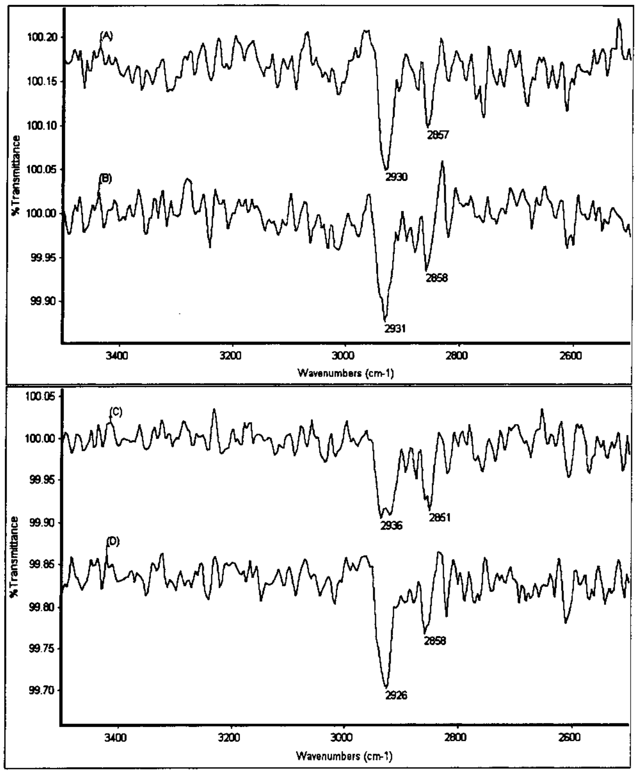

Figure 4. FTIR spectra of poly(ethylene-*co*-acylic acid) on indium tin oxide. (A) $PEAA_{15}$ on bare ITO; (B) $PEAA_{15}$ on $[ITO]-[O]_{4-n}-Zr(OBu^t)_n$; (C) $PEAA_5$ on bare ITO; (D) $PEAA_5$ on $[ITO]-[O]_{4-n}-Zr(OBu^t)_n$.

FTIR analysis of a clean aluminum substrate treated with $PEAA_{15}$ showed that some polymer had indeed adhered to the surface (Figure 1A);[13] the bands at 2928 and 2857 cm^{-1} are characteristic of CH_2 group asymmetric and symmetric stretching modes, respectively, of the polyethylene fraction of the polymer. No evidence was obtained for the formation of aluminum carboxylates.[4] Similar analysis was performed (Figure 1B) on the aluminum substrate first treated with the zirconium complex and then $PEAA_{15}$ solution and finally rinsed. In addition to strong signals in the methylene group region, two broad bands due to carboxylate ion stretches[10] were also prominent at 1569 and 1444 cm^{-1}.

A similar comparison was made using clean (Figure 1C) and Zr complex treated Al (Figure 1D) and $PEAA_5$. From these spectra, it is evident that little polymer has adhered to the clean Al surface compared to the substantial amount found for the Zr complex pretreated substrate. For the latter case, absorption due to the methylene groups is very strong; Zr carboxylate peaks are also in evidence (1580 and 1464 cm^{-1}), as was some unreacted carboxylic acid ($\nu_{CO} = 1704$ cm^{-1}).

Diffuse reflectance FTIR was used to analyze adhesion to the rough iron substrates, and transmission FTIR spectroscopy was done for both the PS and the ITO (on glass) substrates. Comparative copolymer loadings were determined as described for aluminum. Differences in copolymer adhesion for Zr complex treated versus untreated substrates varied according to the basicity of the substrate. For iron (Figure 2) and PS (Figure 3), virtually no polymer ($PEAA_{15}$ or $PEAA_5$) adhered to the untreated surface, but adhesion to the Zr complex pretreated substrate was substantial;[14] here, the preprocessing greatly improves copolymer loading, and as for Al, peaks for Zr carboxylate groups were in evidence. However, for ITO, on which self-assembly of carboxylic acids has been reported,[15] lesser, but significant, improvements were noted for the Zr complex-pretreated surfaces over the control "clean" substrate (Figure 4).

Surface bonding characteristics differentiate the simple use of an acrylic acid copolymer from a sequence in which a zirconium complex interface is first synthesized. These differences may be understood in terms of the molecular interactions present in the two cases which enable contact between the generally hydrophobic polymer and the hydrophilic oxide substrate surface. In classical cases, this interaction likely involves either hydrogen bonding or proton transfer between the carboxylic acid group and a basic oxygen site of the surface;[10] the degree of proton transfer depends on substrate basicity.[16] These types of interactions are likely reversible,[10] since the critical proton is not removed from the ensemble interface. In contrast, for the zirconium alkoxide interface, reaction with copolymer carboxylate groups generates a strong covalent bond[10] between the substrate and the organic material. Since alcohol is readily lost from the ensemble (Scheme 2), this carboxylate is formed irreversibly. We are now investigating the use of the zirconium alkoxide complex interface to prepare robust ensembles of oxide surfaces and copolymers of very low net acidity.

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(14) Peaks in Figure 3 between 2110 and 2240 cm^{-1} are due to Si–H stretches and are not related to the infrared bands of the poly(ethylene-*co*-acrylic acid).

(15) See: Gardner, T. J.; Frisbie, C. D.; Wrighton, M. S. *J. Am. Chem. Soc.* **1995**, *117*, 6927–6933. In this study, deposition occurred from isooctane, followed by washing with hexane.

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