ADHESION OF ORGANICS TO THE SURFACES OF TITANIUM AND TI-6AL-4V

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INTRODUCTION: Enhancing adhesion of bone growth proteins and, ultimately, bone to the surface of titanium (alloy) implants is a well-recognized research challenge. Self-assembled monolayers have been used to surface bind appropriate peptide sequences, such as RGD, which stimulate osteoblast adhesion to silica or gold.[1] However, these SAMs utilize thiols[2] or silyl[1] compounds as the "head group", and neither functional group strongly adheres to the titanium native oxide surface; organophosphonates, a common class of surface derivatisation reagents for other metals, also adhere poorly to titanium.[3] We have now shown that alkanethiols and phosphonates can be adhered to the titanium surface through surface bound organo-metallic complex interfaces.[4] Synthesis and characterization of appropriate surface "linkers", and attachment of organics to the titanium surface will be described.

METHODS: Tetra-(*tert* butoxy) zirconium is vapor deposited onto clean titanium foils, with a native oxide layer present. The complex reacts with hydroxyl groups at the oxide surface. Alkanethiols and organo-phosphonates react with the zirconated surface by the aerosol spraying of a dilute solution under N_2 flow, followed by evacuation. Depositions and stability of the surface species were studied by diffuse reflectance infrared spectroscopy.

RESULTS: Control experiments, showing direct deposition of an organic monomer, *i.e*. alkanethiol, onto the native titanium surface, resulted in an 'ordered' monolayer, as evidenced by the IR spectra. However, this layer was easily removed by solvent rinse, and only the oxide remained. When the zirconium interface was deposited first onto the native surface, the adhesion of the organic compound was significantly enhanced. An IR of the samples after deposition of the organic showed characteristic 'disordered' long alkyl chain pattern, however, this surface was resistant to rinses and 'peel' testing. See Fig. 1.

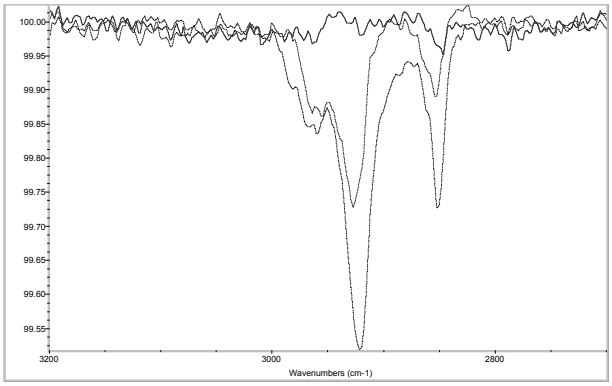

Fig. 1 IR analysis of ocatadecanephosphonate surface species on oxidized Ti: With Zr alkoxide pretreatment, bottom spectrum, as deposited; middle, after two rinses and tape 'peel'; top, without Zr alkoxide pretreatment, after one rinse.

DISCUSSION & CONCLUSIONS: The zirconium alkoxide interface allows the covalent attachment of thiols, phosphonic acids, carboxylic acids, phosphate esters and amines to the surface of titanium and its alloys. The most important group are the first two: it should be possible to utilize known thiol-based peptide coupling and cell attachment reagents directly to the titanium surface, the substrate of choice for biomedical implants.

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