Grafting sodium styrene sulfonate onto titanium surfaces for improved biocompatibility

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Introduction: Titanium and its alloys are commonly used as biomaterials due to their unique mechanical properties and good corrosion resistance. Still, titanium implants induce the formation of a fibrous layer due to weak bonding at the interface with the living tissue. These biomaterial–tissue weak interactions eventually cause failure when under stress. Since the biological response to implanted biomaterials is initiated at their surfaces, the usefulness of titanium and titanium alloys can be dramatically enhanced by modifying their surfaces. A promising approach for surface bio-modification is grafting a bioactive polymer onto titanium implant surfaces[1]. For optimal grafting, it is extremely important to fully understand the nature of the bio-modified surfaces as it has a pivotal role in the biomaterial performance.

The main thrust of this work is to graft bioactive sodium styrene sulfonate (NaSS) onto the surface of commercially pure titanium (cp-Ti) with the aim of controlling and improving its response in biological environment[1]. In particular, the goal of the current research is to fully characterize and study in details the structure and composition of the grafted NaSS layer.

Methods: Two types of substrates were investigated: polished cp-Ti plates (0.25 mm thickness) and smooth Ti films that were evaporated onto silicon wafers (Ti/Si).

Methacryloxypropyltrimethoxysilane (MPS) was used as a cross linker between the Ti and the NaSS; both types of substrates were soaked in a solution of MPS in chloroform (5%v/v) for 1 hr at room temperature and then removed from the solution and heated at 140°C for 4 hrs. The grafting procedure was carried out in a 0.7M solution of NaSS monomer in Dimethyl sulfoxide (DMSO) at 90°C in an oxygen free environment for 15hrs. The samples were characterized at each stage by X-ray photoelectron spectroscopy (XPS), time-of-flight secondary mass ion spectrometry (ToF-SIMS) and atomic force microscopy (AFM). The amount of the grafted NaSS was estimated by using the toluidin blue colorimetric assay (TBCA).

Results/Discussion: XPS analysis showed both polished cp-Ti and Ti/Si had similar surface compositions, covered with a layer of TiO_2[2]. The surface roughness values measured by AFM were 79.1nm and 0.7nm for polished cp-Ti and Ti/Si, respectively. These analyses indicate the Ti/Si is a convenient smooth model for detailed studies.

After attaching the MPS molecules to the titanium surfaces, XPS surface composition and high resolution XPS data suggested that the solid substrates were covered with a uniform thin film[3]. Additional evidence for the MPS attachment to the Ti surfaces was the appearance of the $C_xH_yO_z$ fragments (originated from the methacrylate group) along with the decease of the Ti, TiO_x and TiO_xH in ToF-SIMS (Fig 1a).

After NaSS grafting the XPS composition showed an increase of the carbon to titanium ratio and an appearance of sulfur and sodium. Moreover, XPS analysis at various takeoff angles showed an increase of the carbon, sulfur and sodium signals as the sampling depth decreased, indicating these elements were present in the grafted overlayer. The titanium signal showed the opposite trend as it originated from below the grafted overlayer (Fig 2a). ToF-SIMS successfully detected the sulfonate group, $C_8H_7SO_3$, and a decrease of the Ti containing fragments (Fig 1). The surface density of the grafted NaSS was estimated as 240ngr/cm^2 from the TBCA. AFM analysis showed a uniform coverage on the Ti/Si substrate with a roughness of 1.11nm (Fig 2b).

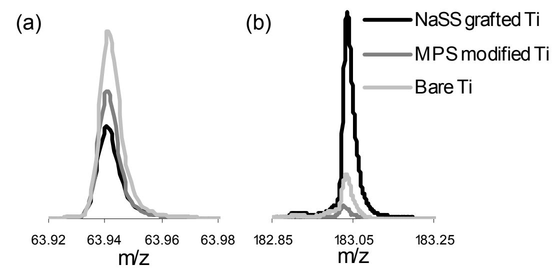

Figure 1. ToF-SIMS (a) TiO^+ and (b) $C_8H_7SO_3^-$ fragments' intensities.

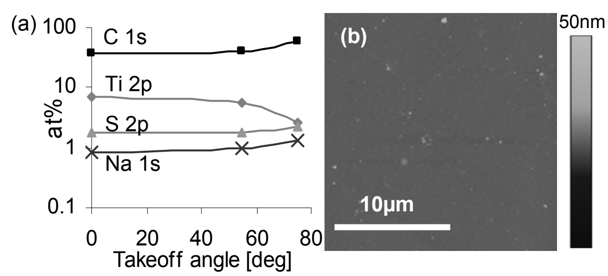

Figure 2. (a) XPS at various takeoff angles and (b) AFM micrograph of NaSS grafted Ti/Si.

Conclusions: A simple two-step procedure was developed to graft bioactive NaSS onto titanium surfaces. Smooth Ti/Si that has similar surface chemistry to cp-Ti allowed detailed surface studies of the grafted NaSS film. XPS, ToF-SIMS and AFM provided a complementary analysis at each stage of the grafting and showed that a robust and uniform NaSS layer was formed on the titanium surfaces.

Future Studies: Currently the mechanism of competitive protein adsorption on titanium surfaces before and after NaSS grafting is being studied.

References:

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