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Functionalization of New Biocompatible Titanium Alloys with Harmonic Structure Design by Using UV Irradiation

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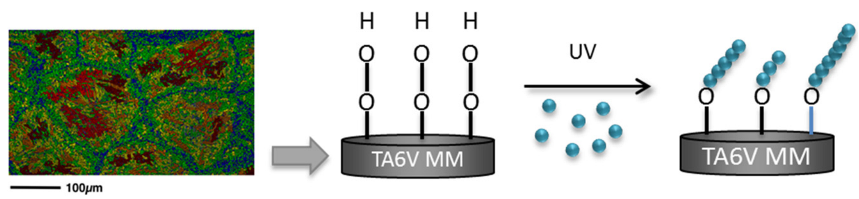
Graphical abstract



Abstract

Background: Titanium based materials slowly induce the formation of a fibrous layer after several years of implantation, compromising the quality of bone/implant interface and leading progressively to an aseptic loosening of the implants. The functionalization of Titanium based materials by bioactive polymers bearing ionic groups has been shown to be an excellent solution to improve the osseous integration of the implant.
Objective: Our laboratory has demonstrated that the grafting of bioactive polymers onto biomaterials can improve cell and antibacterial response. The objective of this work is to develop the grafting of a bioactive polymer onto new Titanium alloys of particular structure as named “harmonic structure”.
Methods: The grafting of a bioactive polymer on new Titanium alloys of particular structure named “harmonic structure” was realized in a two-steps reaction process using chemical oxidation and UV irradiation. Titanium alloys samples were (1) oxidized in a mixture of sulfuric acid and hydrogen peroxide allowing the formation of titanium hydroxides and peroxides, (2) then incubated with an aqueous solution of sodium styrene sulfonate and placed under UV irradiation to induce the decomposition of titanium peroxides and the formation of radicals initiating the polymerization of the monomer. Different parameters such as polymerization time and lamp power were studied in order to optimize the yield of poly(sodium styrene sulfonate) grafting. Colorimetric assay, Fourier-transformed infrared spectra recorded in an attenuated total reflection (ATR-FTIR), scanning electron microscopy with Oxford energy dispersive spectroscopy (SEM-EDS) and contact angle measurements were applied to characterize the surfaces.
Results: Various techniques showed that the grafting of ionic polymers bearing sulfonate groups was successful by using radicals from titanium peroxides able to initiate the radical polymerization of ionic monomers onto new Titanium alloys of particular structure named “harmonic structure”.
Conclusion: We have applied the methods used previously in the laboratory in terms of bioactive polymers grafting in particular by UV irradiation onto the surface of new developed titanium alloys with or without harmonic structure. In parallel, a preliminary biological response study to assess toxicity, cell viability, adhesion and morphology on the different titanium alloys functionalized or not by bioactive polymers giving encouraging results.

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1. Introduction

For several years, the joint implant biomaterials are becoming increasingly important in the treatment of the musculoskeletal system diseases. Several facts contribute to an amplification of this phenomenon. The lifestyle of industrialized countries increases the prevalence of diseases such as osteoporosis, osteoarthritis, and sports injuries. In parallel, the life expectancy increases and the population of these countries refuses disability and the restriction of physical possibilities and turn to the implantology like the orthopedic implants such as hip prosthesis or dental implants. A disease like osteoporosis becomes one of the main public health problems.

From the perspective of research, the biomaterial field intended for implantation requires very accurate knowledge in many varied fields from materials, biology, physics to chemistry. Indeed, during the implantation of a synthetic material into the human body, we are faced to two major problems (i) In the short term, the risk of infection: Despite increasingly strict and controlled hygiene standards, about 1 to 2% of implants are infected leading to complications, which may extend until the implant removal [1]. (ii) In the long term, the lack of biocompatibility of the materials used: many materials used in implantology are chosen according to their mechanical properties. However, being considered as foreign body from the organism, these materials do not allow controlled host response and in some cases leads to "foreign body response". This phenomenon leads to an aseptic loosening of the implants, which can require their removal [2]. In order to solve these two major problems, many methods have been developed to reduce the risk of infection and improve the biocompatibility of materials. These approaches vary from mechanical to thermal and electrochemical methods [3–6]. An alternative method that is gaining popularity is the grafting of biomolecules and/or bioactive polymers [3].

Among these methods, the one developed at the Laboratory of Biomaterials for Health (LBPS) consists in the grafting of bioactive polymers onto the implant [7–10]. Indeed, previous results showed that polymers such as poly(sodium styrene sulfonate) (PNaSS) can favor osteoblast cell adhesion and differentiation [8–14] and exhibit an antibacterial activity against the two bacteria mainly responsible for nosocomial infections (*Staphylococcus aureus* and *Staphylococcus epidermedis*), while promoting the biocompatibility [12–22].

Materials for developing bone implants, such as hip prostheses or dental implants, must present a number of characteristics: low elasticity modulus, high mechanical strength, wear and corrosion resistance, and good biocompatibility [10]. Titanium and its alloys are largely used for various biomedical applications such as dental and orthopedics implants. They largely replaced the steel, which presented in particular a Young modulus too distant from that of the human bone, and the chrome–cobalt alloys which posing serious problems of biocompatibility and public health.

Exceptional properties of titanium (Ti) and its alloys in such a context stem from two aspects that are linked to their surface and mechanical properties.

Indeed, due to their inherent excellent corrosion resistance, Ti and Ti alloys resist particularly and completely to the body fluids, which makes it one of the most biocompatible metals.

However, in spite of their performances these metallic materials are not always free from toxicity for the living system.

Furthermore, the conditions of use; permanent and constant efforts, physiological medium, can generate damages because of corrosion and other mechanical defects [23].

Therefore, the development of alloys with optimized microstructures and enhanced mechanical properties are needed. Indeed, in a framework of a collaborative project, based on methodologies for microstructures' design by both HP-HT-LSPM group (High pressure Processes–High Temperature – Laboratory of Sciences of the Processes and Materials) and Ameyama group at Ritsumeikan alloys having a good balance between the mechanical properties and ductility have been fabricated [24–34]. Materials having bimodal grain structures are known for the good balance of strength and ductility. However, methods for their fabrication often lack the control of such structure characteristics. The concept of "harmonic" structure fabrication allowing to controlling both topology and scale of the bimodal structure heterogeneity proposed by Ameyama et al. have been concisely formulated [25].

In short, the "harmonic" structure is a heterogeneous microstructure with bimodal grain size distribution and unique spatial distribution of coarse and fine-grained areas. It has been demonstrated that the harmonic structure materials enable strengthening without any significant decrease in the ductility. The outstanding mechanical properties of the "harmonic" structure materials are found to be strongly influenced by the microstructural characteristics such as grain size, volume fraction, and size of the fine-grained areas [24,26]. Such a concept has been successfully applied to process Ti and Ti alloys such as Ti–6Al–4V (TA6V).

In order to improve the biological response onto titanium and titanium alloy surfaces, we have decided to associate the chemical modification by the grafting of bioactive polymers and the microstructure modification. In this paper, we will describe, the grafting of bioactive polymers on conventional titanium alloy surfaces and show the different results obtained on these new alloys in order to confirm or invalidate the possibility of applying this method to the these news titanium alloys.