Plasma Surface Modification of Biomedical Polymers and Metals

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May 07

Abstract

Biomedical materials are being extensively researched, and many different types such as metals, metal alloys, and polymers are being used. Currently used biomedical materials are not perfect in terms of corrosion resistance, biocompatibility, and surface properties. It is not easy to fabricate from scratch new materials that can fulfill all requirements and an alternative approach is to modify the surface properties of current materials to cater to the requirements.

Plasma immersion ion implantation (PIII) is an effective and economical surface treatment technique and that can be used to enhance the surface properties of biomaterials. The unique advantage of plasma modification is that the surface properties and functionalities can be enhanced selectively while the favorable bulk attributes of the materials such as strength remain unchanged. In addition, the non-line of sight feature of PIII is appropriate for biomedical devices with complex geometries such as orthopedic implants. However, care must be exercised during the plasma treatment because low-temperature treatment is necessary for heat-sensitive materials such as polymers which typically have a low melting point and glass transition temperature.

Two kinds of biomedical materials will be discussed in this thesis. One is nickel titanium (NiTi) alloy which is a promising orthopedic implant material due to its unique shape memory and superelastic properties. However, harmful ions may diffuse from the surface causing safety hazards.

In this study, we investigate the properties and performance of NiTi after nitrogen and oxygen PIII in terms of the chemical composition, corrosion resistance, and biocompatibility. The XPS results show that barrier layers mainly containing TiN and TiO_x are produced after nitrogen and oxygen PIII, respectively. Based on the simulated *in vitro* and electrochemical corrosion tests, greatly reduced ion leaching and improved corrosion resistance are accomplished by PIII. Porous NiTi is also studied because the porous structure possesses better bone ingrowth capability and compatible elastic modulus with human bones. These advantages promote better recovery in patients. However, higher risks of Ni leaching are expected due to the increased exposed surface area and rougher topography than dense and smooth finished NiTi. We successfully apply PIII to porous NiTi and *in vitro* tests confirm good cytocompatibility of the materials.

The other type of biomedical materials studied here is ultra-high molecular weight polyethylene (UHMWPE) which is a potential material for use in immunoassay plates and biosensors. In these applications, active antibodies or enzymes attached to a surface to detect molecules of interests by means of specific interactions are required. Moreover, the retention of enzyme activity is crucial in these applications. Therefore, the aim of this study is to investigate the use of PIII to prepare UHMWPE surfaces for binding of active proteins in terms of the binding density and 'shelf life' of the treated surfaces. Argon and nitrogen PIII treatments are attempted to modify the surface of UHMWPE. Horseradish peroxidase (HRP) is selected to conduct the protein binding test since it is a convenient protein to assay. Experimental results show that both PIII treated surfaces significantly improve the density of active HRP bound to the surface after incubation in buffer containing HRP. Furthermore, the PIII treated surfaces are found to perform better than a commercially available protein binding surface and the shelf life of the PIII treated surfaces under ambient conditions is at least six months.

In conclusion, a biocompatible barrier layer on NiTi and a protein binding surface on UHMWPE is synthesized by PIII. The surface properties such as corrosion resistance and functionality on these two different types of substrates are improved by PIII.

Acknowledgements

This research was conducted under the Joint PhD program between the Plasma Laboratory of the Department of Physics and Materials Science at City University of Hong Kong and School of Physics, the University of Sydney, Australia during 2004-2007. This research was supported by 2005 Endeavour Australia Cheung Kong Award, Sir Edward Youde Memorial Fellowship 2004/2005, Research Activities Fund and Research Tuition Scholarships of City University of Hong Kong.

First of all, I would like to express my gratitude to my supervisor Prof. Paul Chu who offered the opportunity for me to pursue my PhD degree. I am grateful for his support, patience, encouragement and his suggestion me to join this wonderful joint PhD program. Also I would like to thank my supervisor at University of Sydney, Prof. Marcela Bilek, and associated supervisor, Prof. David McKenzie, for their guidance, sharing of scientific knowledge and providing me with an excellent research environment. I also owe my thanks to my M. Phil supervisor, Prof. Peter Yu, for his advice to extend my research work and encourage me to continue my postgraduate study three year ago.

For the research team in Hong Kong, I am grateful to Dr. Sunny Kwok who kindly helped me settle down in Sydney and gave valuable advice. My sincere thanks go to Dr. Xuanyong Liu and Dr. Guojiang Wan for their guidance when my research began and taught me Putonghua and Ray Poon for sharing of knowledge and experience. I would like to thank Mr. Shuilin Wu, Ms. Xiangmei Liu, Dr. C. Y. Chung, and Dr. Kelvin Yeung for working with me in the NiTi work, Dr. Ricky Fu, Mr. S. W. Wong and everyone else in the Plasma Laboratory for making the lab such a nice place.

In Sydney, my appreciation goes to Dr. Bee Kwan Gan for giving me the knowledge to initiate the UHMWPE work, Chanokporn Chaiwong for sharing academic and social life, Keisuke Mizuno for solving experimental or technical problems alongside, and Dr. Dixon Kwok for brain storming and criticism. All of the friendship is deeply cherished.

Heartfelt thanks go to Mary Cain for taking care of me all the time and her caring warms my heart. I am grateful for her help, sharing and making a comfortable home. Let me also extend my warmest thanks to Mitsue Kimpara for cheering me up and providing helpful suggestions making me feel pleasant due to the warm and truehearted regards.

During these years, the support of my friends has been extremely valuable. I give my wholehearted special thanks to Fish for being with me. My appreciation goes to Linda, Yee Ki, Raelee, and Dan for advices, comforting and support since the very beginning of our friendship. I also thank my old friends Sylvia, Alice, Chai and skychatter from SS. Peter and Paul Church.

I would like to express my deep gratitude to my father. He is always there, believes in me, and supports me throughout my life, especially during my graduate study. At the same time, I lost my beloved grandfather. I must say that completion of this thesis in such circumstance is not easy. My grandfather left me before I finish this thesis, but this thesis is dedicated to him because he is always in my heart and inspires me in my life.

Thanks to God.

List of Tables

List of Figures

Table of Contents

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Awards and Scholarships

- 2005 Endeavour Australia Cheung Kong Award
- Sir Edward Youde Memorial Fellowship 2004/2005
- Research Tuition Scholarships of City University of Hong Kong (April 2005 - March 2007)

Chapter 1

Introduction

1.1 Introduction

Plasma surface modification techniques are applied to biomaterials is the theme of my thesis work. Two kinds of biomaterials were examined. One was nickel titanium (NiTi) and another one was ultra high molecular weight polyethylene (UHMWPE). In this thesis, the procedures, experimental setup and design together with results and discussions are described.

First of all, in this Chapter, an overview of past research is presented followed by the motivation of the research. The objectives of the research are stated at the end of this Chapter.

The background knowledge of plasma immersion ion implantation (PIII) system and biomaterials related applications is presented in Chapter 2. In Chapter 3, the equipment including the PIII systems used in the research and basic concept of the biomedical tests are introduced. The theoretic study of ion-matter interactions is discussed in Chapter 4. Experimental details and results and discussion of surface modification of nickel titanium (NiTi) and ultra high molecular weight polyethylene (UHMWPE) are presented in Chapter 5 and 6 respectively. Lastly, conclusion and future work are covered in Chapter 7.

1.2 Overview of surface modification of biomaterials

Biomedical materials are being extensively researched, and many different types such as metals, metal alloys, and polymers are being used or have high potentials as implants in humans. Examples of such implants are artificial heart valves[1], joints[2], bones[3], spine[4] and stents[5]. Besides those implanted inside humans, biomedical materials have many external applications such as single use articles e.g. syringes, blood pouches, catheters[6] and enzyme-linked immunosobent assay (ELISA) plates[7]. Unfortunately, current biomaterials are not perfect in terms of mechanical properties, bioactivity, biocompatibility, as well as functionality. Therefore, there is an urgent need to find more suitable biomaterials. It is not easy to discover new biomaterials that can fulfill all requirements, and so an alternative approach to modify the surface properties of current materials to improve their mechanical characteristics and biocompatibility is adopted.

In biomedical perspective, "good biocompatibility[8]" is referred to the biomaterial being non-toxic, exhibiting no induced deleterious reactions such as chronic inflammatory response and unusual tissue formation, and performing the designed functions properly for a reasonable lifetime. Furthermore, biointegration[9] is the ultimate goal in for example, orthopedic implants that bones establish a mechanically solid interface with complete fusion between the artificial implanted materials and bone tissues under good biocompatibility conditions. The properties of the uppermost few molecular layers are of critical importance in biomaterials surface science[10]. Since the surface layers are in physicochemical contact with the biological environment, the uppermost layer properties including surface chemistry and morphology determine the biocompatibility of the biomaterials. Moreover, some of the biomaterials have good biocompatibility but poor mechanical or physical properties such as wear resistance, anti-corrosion, wettability or lubricity. In this case, surface modification is utilized to deposit a layer of coating or mixing with substrate to form a composite layer. As a result the rationale for surface modification is straightforward.

There are a number of surface modification techniques such as plasma spraying, ion implantation, ion beam, laser treatment, radiation including X-ray, γ-ray and UV irradiation and grafting including chemical, radiation and photografting. Some of them are particularly used for certain functions or kinds of materials. One of the advantages of plasma immersion ion implantation (PIII) is that most materials can be treated. A more detailed discussion of the different method of surface modification is presented in Chapter 2.

PIII is an effective and economical surface treatment technique and can be used to enhance the surface properties of biomaterials[6,8,11,12,13,14]. The unique advantage of plasma modification is that the surface properties and biocompatibility can be enhanced selectively while the favorable bulk attributes of the materials such as strength remain unchanged. PIII is an effective method to modify medical implants with complex shape. By altering the surface functionalities using plasma modification, the optimal surface, chemical and physical properties can be obtained.

PIII is a low-temperature processing make the techniques suitable for low melting point materials such as polymers. PIII is widely accepted to improve adhesion between pinhole free layers and substrates. Also, due to the non-line-of-sight advantage, it is relatively easy to process an object with a complex shape and is therefore a very attractive technique in the industry.

Enhancement of properties of biomaterials such as biocompatibility, corrosion resistance and functionality by PIII is the subject of extensively research, such as the fabrication of different types of biomedical thin films and implanted them with various different biologically important elements such as nitrogen[15], phosphorus[16], calcium[17,18]and sodium[19]. Different kinds of thin films such as titanium oxide[20], titanium nitride[21] and diamond-like carbon[22,23] have been treated and the preliminary results indicate that the processed materials exhibit better biocompatibility compared to some current ones used in biomedical implants. In order to evaluate the biocompatibility of the fabricated thin films, various *in vitro* biological experiments have been conducted.

1.3 Motivation of the research

Materials for medical applications are in huge demand especially those with better functionality, durability and biocompatibility. As mentioned in the previous section, surface modification is a promising way in order to satisfy the needs. The focus of this research is to demonstrate the possibility of utilizing PIII technique to modify the surface of biomaterials for different medical application.

Plasma modification is used to improve orthopedic implant materials[3,24,25] and has attracted much interest from the biomedical industry. In particular, we have been working on the use of NiTi shape memory alloys in spinal implants. NiTi is a promising orthopedic implant material due to its unique shape memory and super-elastic properties. However, harmful ions may diffuse from the surface causing safety hazards. In this study, PIII is utilized to create a barrier layer in order to reduce harmful Ni ions leaking from the metal. Furthermore, we investigate the properties and performance of NiTi after nitrogen and oxygen PIII in terms of the chemical composition, corrosion resistance, and biocompatibility. Further application of PIII to porous structured NiTi is studied. The porous structure possesses better bone ingrowth capability and compatible elastic modulus with human bones. It is believed that the closer properties of porous NiTi with human bone better enhances patients' recovery.

The other type of biomedical materials studied here is ultra-high molecular weight polyethylene (UHMWPE) which is a well known biomaterial in artificial prostheses components such as hip and knee joint replacements. PIII has been widely investigated to enhance the mechanical properties such as hardness, elastic modulus, wear resistance and reduce wear debris together with good biocompatibility[26]. Besides implant applications, it is a potential material in immunoassay plate and biosensors. In these applications, active antibodies or enzymes attached to a surface to detect molecules of interests by means of specific interactions are required. Advantages of polmer for these applications include their low cost, ease of forming and etching for patterning structure such as microfluidic channels. Moreover, the retention of enzyme activity is crucial in these applications. However, the surface functionality in immobilization of proteins on PIII treated UHMWPE surface has been unexplored. There are some commercial products (e.g. NUNC) of protein attachment plate in the market. However, the costs are relatively high. In other words, PIII treated UHMWPE may benefit the public. Therefore, the improvement of protein attachment by PIII on polymer is a useful and worthwhile functionality to develop.

1.4 Objectives of the research

This research focuses on the feasibility of utilizing PIII to enhance surface properties of two kinds of biomaterials, namely NiTi and UHMWPE, in terms of mechanical, cyto-compatibility and functionality. The studies on NiTi and UHMWPE were conducted in both the City University of Hong Kong and the University of Sydney. The objectives are

NiTi

(1) To create barrier layers to impede the out-diffusion of Ni ions by implanting nitrogen or oxygen ion by PIII.

(2) To enhance the anti-corrosion ability of the PIII treated NiTi in human body environment.

(3) To investigate the performance of modified layer formed by using different PIII parameters in order to obtain optimal surface properties.

(4) To assess the cyto-compatibility by using *in vitro* cell culture tests on the newly formed layer.

(5) To examine the further application of the PIII technique on porous structure NiTi to reduce outdiffusion of Ni ions from enlarged surface.

UHMWPE

(6) To investigate the use of plasma surface modification (PSM) to prepare UHMWPE surfaces for binding active proteins such as Horseradish peroxidase (HRP).

(7) To assess the shelf life and aging effect of the treated surfaces in terms of the retention of HRP binding performance and the activity of the bound

HRP over time while subjected to repeated washing steps.

(8) To determine the optimal PIII treatment parameters to yield the best possible HRP attachment.

(9) To correlate the improvements in active protein binding characteristics with physicochemical change occurring on the polymer surface.

(10) To benchmark the PIII treated surfaces with a popular commercial protein binding polymer.

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