

**Plasma Surface Modification of Biomedical
Polymers and Metals**

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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.

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List of Tables

<i>Table 2.1. Examples of different types of biomedical use materials.</i>	16
<i>Table 2.2. Typical physical and mechanical properties of HDPE and UHMWPE. (from [42])</i>	25
<i>Table 2.3. Examples of biomolecules immobilized on polymeric biomedical materials and their applications. (from [43])</i>	27
<i>Table 3.1. Ion concentration in SBF in comparison with human blood plasma.</i>	57
<i>Table 4.1. The number of sputtered atoms of NiTi per incident nitrogen or oxygen ion with energy from 20k-40keV.</i>	75
<i>Table 4.2. The number of sputtered atoms of UHMEPE per incident nitrogen or oxygen ion with 20keV.</i>	78
<i>Table 5.1. Nitrogen PIII treatment parameters for samples #1 -4.</i>	87
<i>Table 5.2. Oxygen PIII treatment parameters for samples #5 -7.</i>	88
<i>Table 5.3. Nitrogen and Oxygen PIII conditions with different annealing temperatures for samples #8 -11.</i>	89
<i>Table 5.4. Nitrogen PIII treatment conditions for different pulsing frequencies for samples #12-14.</i>	90
<i>Table 5.5. Roughness of 40kV N treated by different pulse frequency of implantation (#12-#14) and control sample.</i>	114
<i>Table 5.6. Oxygen plasma implantation parameters</i>	121
<i>Table 6.1. Plasma and PIII treatment parameters. For the PIII processes the high voltage bias applied was 20 kV for a pulse length of 20 and with a frequency of 50 Hz.</i>	145
<i>Table 6.2. A summary of the roughness and surface area of untreated and treated UHMWPE AFM scans of different side length size.</i>	155
<i>Table 6.3. Macroscopic surface roughness of untreated and treated surfaces measured by FTPGI.</i>	158
<i>Table 6.4. Surface chemical composition atomic percentage, oxygen to carbon ratio (obtained by fitting the survey scan data) and peak location of the Cls peak for untreated, argon and nitrogen-treated UHMWPE</i>	170

List of Figures

Fig. 2.1. Schematic diagram for explanation of transformation from martensitic to austenitic phase by shape memory effect of NiTi. (from [23])	18
Fig. 2.2. Transition of martensite and austenite by temperature change. M_s : martensite starting temperature; M_f : martensite finish temperature; A_s : austenite starting temperature; A_f : austenite finish temperature. (from [29])	19
Fig. 2.3. Chemical structures for ethylene and polyethylene. (from [42]).....	23
Fig. 2.4. Surface properties of biomedical materials which can modified by PIII.(from [50]).....	31
Fig. 3.1. Schematic diagram of PIII system for surface modification of NiTi in City University of Hong Kong.	43
Fig. 3.2. Schematic diagram showing the plasma treatment system used to modify the polymer surfaces.	45
Fig. 3.3. Schematic diagram of the emission process of photoelectrons excited by X-rays.....	46
Fig. 3.4. XPS survey spectrum of as-received UHMWPE.....	48
Fig. 3.5. FTIR-ATR spectrum of an as-received UHMWPE	50
Fig. 3.6. Schematic diagram of the working principle of AFM.....	52
Fig. 3.7. Three dimensions AFM image of untreated UHMWPE of size $1\mu\text{m} \times 1\mu\text{m}$	53
Fig. 3.8. Schematic stylus movement of FTPGI.	54
Fig. 3.9. Three dimensions FTPGI image of nitrogen plasma treated UHMWPE of size $1\text{mm} \times 1\text{mm}$	55
Fig. 3.10. Schematic side view diagram of water drop with contact angle (θ)	58
Fig. 4.1. Schematic diagram of ion-solid interaction.....	64
Fig. 4.2. Schematic diagram of the development of concentration profile of ions implanted.....	66
Fig. 4.3. Ion range distribution graph of 20keV nitrogen ion on UHMWPE.....	68
Fig. 4.4. Nuclear stopping power of nitrogen ion in UHMWPE with	

<i>energy range from 0 to 100keV</i>	70
<i>Fig. 4.5. Collision events distribution graph of 20keV of nitrogen ion on UHMWPE</i>	70
<i>Fig. 4.6. Depth profile of nitrogen ion with incident energy of (a) 40keV, (b) 30keV and (c) 20keV. Oxygen ion with incident energy of (d) 40keV, (e) 30keV and (f) 20keV.</i>	72
<i>Fig. 4.7. Ion range of nitrogen and oxygen ion on NiTi substrate with energy from 0 to 100keV.</i>	73
<i>Fig. 4.8. Stopping power of nitrogen and oxygen ion with different energies. Elec N, Elec O, Nucl N and Nucl O are electronic or nuclear stopping power of nitrogen and oxygen ion respectively. Total N and Total O are sum of nuclear and electronic stopping power.</i>	74
<i>Fig. 4.9. Ion range of nitrogen and oxygen ion on NiTi substrate with energy from 0 to 100keV.</i>	76
<i>Fig. 4.10. Stopping power of nitrogen and oxygen ion with different energies. Elec N, Elec Ar, Nucl N and Nucl Ar are electronic or nuclear stopping power of nitrogen and argon ion respectively. Total N and Total Ar are sum of nuclear and electronic stopping power.</i>	76
<i>Fig. 4.11. Depth profiles with 20keV incident ion energy of (a) nitrogen and (b) argon in UHMWPE are depicted. The damages caused by these ions are also shown in (c) nitrogen and (d) argon</i>	77
<i>Fig. 5.1. (a) XPS depth profile of control sample (sample #1), (b) XPS depth profile of N treated NiTi by 40 kV bias voltage and 450 °C (sample #2), (c) XPS depth profile of O treated NiTi by 40 kV bias voltage and 450 °C (sample #5), (d) XPS depth profile of O treated NiTi by 40 kV bias voltage without annealing (sample #10).</i>	96
<i>Fig. 5.2. (a) XPS depth profiles of Ni in samples #2 – 40kV N, #3 – 30kV N and #4- 20kV N (b) XPS depth profiles of Ni in samples #5 – 40kV O, #6 – 30kV O and #4- 20kV O (c) XPS depth profiles of N in samples #2 –40kV N, #3 – 30kV N and #4- 20kV N (d) XPS depth profiles of O in samples #5 – 40kV O, #6 – 30kV O and #4- 20kV O.</i>	99
<i>Fig. 5.3. (a) XPS depth profile of Ni at different annealing temperature or without anneal NiTi treated by N or O (b) XPS</i>	

<i>depth profile of O at different annealing temperature or without anneal NiTi treated by O.</i>	103
<i>Fig. 5.4. Ni ion concentration in SBF leached from samples (#1- #11) after 5 week immersion in SBF as detected by ICPMS.</i>	105
<i>Fig. 5.5. Summary of the results from electrochemical corrosion test.</i>	107
<i>Fig. 5.6. (a) Hardness depth profile of treated and untreated NiTi from surface to 100nm acquired by nano-indenter (b) Elastic modulus depth profile of treated and untreated NiTi from surface to 100nm acquired by nano-indenter.</i>	109
<i>Fig. 5.7. Viable cell number versus days. (D2 - Day 2, D4 – Day 4, D6 – Day 6 and D8 – Day 8).</i>	111
<i>Fig. 5.8. (a) Osteoblasts microscopic views ($\times 200$) of (N treated) sample #2 after 2 days cell culturing. (b) after 8 days cell culturing.</i>	112
<i>Fig. 5.9. AFM 3D topographies acquired ($5\mu\text{m}\times 5\mu\text{m}$): (a) #1 – control; (b) #12 – 50Hz; (c) #13 – 100Hz; (d) #14 – 200Hz; (e) #13 – 100Hz; (d) #14 – 200Hz.</i>	115
<i>Fig. 5.10. Surface morphology of typical porous NiTi before implantation.</i>	124
<i>Fig. 5.11. XPS depth profiles acquired from the different porous NiTi samples: (a) oxygen plasma implanted and immersed in SBF for 28 days, (b) without plasma treatment and immersed in SBF for 28 day, (c) oxygen plasma implanted and not immersed in SBF and (d) without plasma treatment and not immersed in SBF.</i> 127	
<i>Fig. 5.12. Ni ion concentration in SBFs for dense and porous NiTi samples after immersion for 7 to 28 days determined by ICPMS.</i>	130
<i>Fig. 5.13. Compression stress against strain of untreated and O PIII treated porous NiTi.</i>	132
<i>Fig. 5.14. Images of proliferation clusters ($4\times$magnification) of osteoblasts on porous NiTi after culturing for 8 days. (a) Untreated and (b) O PIII treated.</i>	133
<i>Fig. 5.15. Cell morphology image captured by using SEM (after culturing for 8 days).</i>	134
<i>Fig. 6.1. Surface morphology of UHMWPE scans in side length size $10\mu\text{m}$ (column A) and $1\mu\text{m}$ (column B). (a) and (b) Untreated; (c) and (d) Ar PIII 1200s; (e) and (f) Ar Plasma 1200s; (g) and (h)</i>	

<i>N PIII 800s</i>	154
<i>Fig. 6.2. Surface morphology of UHMWPE captured by Form Talysurf PGI with a scan side length of 1mm, (a) is a 3D profile of the untreated surface and (b) is the cross section taken along the dotted line in (a); (c) is a 3D profile of the Ar PIII 1200s treated UHMWPE surface and (d) shows the cross section along the dotted line in (c).</i>	157
<i>Fig. 6.3. Water contact angles of plasma treated UHMWPE surfaces as a function of time since removal from the treatment chamber. Measurements are from surfaces treated using the Ar plasma (8), the Ar PIII process (7), the N plasma (∇) and the N PIII process (!).</i>	159
<i>Fig. 6.4. Correction of water contact angle of (a) N PIII-treated and (b) Ar PIII-treated samples by the Wenzel equation.</i>	161
<i>Fig. 6.5. FTIR spectra of nitrogen-treated and untreated UHMWPE. (a) N PIII 2mTorr 800s; (b) N PIII 2mTorr 100s; (c) N Plasma 2mTorr 800s; (d) N PIII 2mTorr 20s; (e) N PIII 0.3mTorr 20s; (f) Untreated UHMWPE.</i>	163
<i>Fig. 6.6. FTIR spectra of argon-treated and untreated UHMWPE. (a) Ar Plasma 2mTorr 1200s; (b) Ar PIII 2mTorr 800s; (c) Ar Plasma 2mTorr 800s; (d) Ar PIII 2mTorr 20s (e) Ar PIII 0.3mTorr 20s; (f) Untreated UHMWPE.</i>	166
<i>Fig. 6.7. XPS survey scan of the nitrogen treated UHMWPE (N PIII 2mTorr 800s).</i>	167
<i>Fig. 6.8. XPS C1s spectra of untreated, argon or nitrogen treated UHMWPE. (a) Untreated; (b) Ar PIII 2mTorr 800s; (c) Ar Plasma 2mTorr 1200s; (d) Ar PIII 2mTorr 1200s; (e) N Plasma 2mTorr 800s; (f) N PIII 2mTorr 800s; (g) N Plasma 2mTorr 20s; (h) N PIII 2mTorr 20s.</i>	168
<i>Fig. 6.9. Optical density measurements from the HRP activity assay on UHMWPE surfaces treated using Ar Plasma 2mTorr 800s (●) and Ar PIII 2mTorr 800s (▲) as well as on untreated control surfaces (■). The day 0 data points correspond to activity measured on samples which were incubated in HRP solution overnight and then washed in fresh buffer before testing by a colorimetric activity assay. For data taken on subsequent days, the buffer solution was changed each day and further activity assays were conducted from day 1 to 5. This data was</i>	

- measured using HRP from bottle 1*..... 173
- Fig. 6.10. Optical density measurements from the HRP activity assays on surfaces treated for 20 seconds, Ar Plasma 2mTorr 20s (●) and Ar PIII 2mTorr 20s (▲). The activities on untreated (■) surfaces are also shown. This data was measured using HRP from bottle 1. 174
- Fig. 6.11. Optical density measurements from the HRP activity assays on surfaces treated for 1200 seconds Ar Plasma 2mTorr 1200s (▲) and Ar PIII 2mTorr 1200s (△). Since bottle 2 of HRP was used for these measurements, an 800 seconds PIII treatment (Ar PIII 2mTorr 800s, ●) was repeated and is shown for comparison. The results from untreated samples (■) are also shown. 175
- Fig. 6.12. Optical density measurements from the HRP activity assays on surfaces treated in Argon at two different working pressures over the same treatment time (20s). Circles show the results for the 2mTorr treatments and triangles represent those done using 0.3mTorr. This data was measured using HRP from bottle 1. 176
- Fig. 6.13. Optical density measurements from the HRP activity assay on surfaces treated in N PIII 2mTorr 800s (800PIII), N PIII 2mTorr 100s (100PIII) and N PIII 2mTorr 20s (20PIII) and in N Plasma 2mTorr 800s, N Plasma 2mTorr 100s and N Plasma 2mTorr 20s (800P, 100P and 20P). Results from three sets of untreated samples used as controls (800U, 100U and 20U) are shown for comparison. This data was obtained using protein sourced from bottle 1. 177
- Fig. 6.14. Optical density measurements from the HRP activity assays on surfaces treated in Nitrogen at two different working pressures over the same treatment time (20s). Circles show the results for the 2mTorr treatments and triangles represent those done using 0.3mTorr. This data was measured using HRP from bottle 1. 178
- Fig. 6.15. Optical density measurements from the HRP activity assay on surfaces incubated within 5 hours of the treatment process (■), 2 weeks after treatment (●), and 4 weeks after treatment (▲). (a) shows results by the Ar Plasma 2mTorr 800s treatment and (b) shows results by the Ar PIII 2mTorr 800s treatment.

- HRP was taken from bottle 1. 180*
- Fig. 6.16. Optical density measurements from the HRP activity assays on surfaces aged in desiccators for 1 year after undergoing plasma (●) and PIII (▲) treatments are compared with untreated controls (U, ■). and a freshly treated (Ar PIII 2mTorr 800s) which was incubated in protein solution within 5 hours (▼) of the treatment. All treatments were conducted in 2 mTorr of Argon for 800s. HRP was taken from bottle 2. 181*
- Fig. 6.17. Optical density measurements from HRP activity assays on surfaces incubated in HRP solution within 5 hours of the treatment process (■), 4 weeks (▲) and 6 months after treatment (●). Since the assays were done at different times, one set of control samples was analysed together with each, hence three sets of data for untreated surfaces are shown in the figure. The controls are shown on the left; the surfaces treated with the nitrogen PIII process on the right and the nitrogen plasma treated surfaces in the centre. HRP was taken from bottle 1. 183*
- Fig. 6.18. Optical density measurements from the HRP activity assay on argon PIII treated and untreated NUNC and UHMWPE surfaces. Activity assays were conducted on the day after incubation in protein solution day 0 and on day 3. The buffer was replaced each day, even on days when the assay was not carried out. HRP was taken from bottle 1. 185*
- Fig. 6.19. Optical density measurements from the HRP activity assays on untreated and PIII treated NUNC and PIII treated UHMWPE surfaces stored in ambient for 6 months (6m NUNC, 6m NUNC+PIII and 6m UHMWPE+PIII) and for easy comparison the NUNC and NUNC+PIII from Fig. 6.18 are also shown. The HRP used came from bottle 1. 187*

Table of Contents

ABSTRACT	I
ACKNOWLEDGEMENTS	IV
LIST OF TABLES	VII
LIST OF FIGURES	VIII
TABLE OF CONTENTS	XIV
PUBLICATIONS	XIX
AWARDS AND SCHOLARSHIPS	XXIII
CHAPTER 1	1
INTRODUCTION	1
1.1 Introduction.....	1
1.2 Overview of surface modification of biomaterials	2
1.3 Motivation of the research	5
1.4 Objectives of the research	7
1.5 References.....	9
CHAPTER 2	12
LITERATURE REVIEW	12
2.1 Introduction	12
2.2 Plasma immersion ion implantation (PIII).....	12
2.3 Biomedical materials.....	15

2.3.1 Metal – Nickel Titanium.....	17
2.3.1.1 Shape memory and Super elasticity effects	18
2.3.1.2 Medical applications of NiTi.....	20
2.3.1.3 Biocompatibility of NiTi	21
2.3.2 Polymer – Ultra high molecular weight polyethylene.....	23
2.3.2.1 Composition and structure.....	23
2.3.2.2 Medical applications of UHMWPE	25
2.4 Surface modification of biomedical materials.....	27
2.5 Applications of PIII to biomedical materials.....	31
2.6 References.....	35
CHAPTER 3	40
EQUIPMENT AND CHARACTERIZATION METHODS	40
3.1 Introduction	40
3.2 Plasma immersion ion implantation system.....	41
3.3 Characterization techniques	46
3.3.1 X-ray Photoelectron spectroscopy (XPS)	46
3.3.2 Fourier Transform Infrared – Attenuated Total Reflectance Spectroscopy (FTIR-ATR)	48
3.3.3 Inductively Coupled Plasma Mass Spectroscopy (ICPMS)	50
3.3.4 Atomic Force Microscopy (AFM)	51
3.3.5 Form Talysurf PGI (FTPGI).....	54
3.3.6 Scanning electron microscopy (SEM)	55
3.3.7 Nanoindentation.....	56
3.3.8 Electrochemical test.....	57
3.3.9 Contact angle measurement	57
3.4 Biomedical tests	58
3.4.1 Simulated body fluid (SBF) immersion test	58
3.4.2 In vitro cyto-compatibility test.....	59
3.4.3 Horseradish peroxidase (HRP) attachment and functionality assay	60
3.5 References.....	61

CHAPTER 4	63
THEORY - INTERACTIONS BETWEEN ENERGETIC IONS AND MATERIALS IN SURFACE MODIFICATION PROCESSES.....	63
4.1 Introduction	63
4.2 Theory – PIII ion and matter interaction	63
4.2.1 Sputtering and implanted ion distribution.....	65
4.2.2 Ion stopping and Ion range.....	66
4.2.3 Damage by implantation	68
4.3 Computational calculation by TRIM.....	71
4.3.1 Nickel Titanium (NiTi).....	71
4.3.2 Ultra high molecular weight polyethylene (UHMWPE).....	75
4.4 Structural change in NiTi and UHMWPE	78
4.4.1 Nickel titanium (NiTi).....	79
4.4.2 UHMWPE.....	80
4.5 References.....	81
CHAPTER 5	83
SURFACE MODIFICATION OF NICKEL TITANIUM SHAPE MEMORY ALLOY APPLICATION IN ORTHOPEDICS	83
5.1 Introduction	83
5.2 Dense Nickel Titanium.....	85
5.2.1 Sample preparation.....	86
5.2.2 Depth profile and chemical state analysis.....	91
5.2.3 Dissolution Test	91
5.2.4 Electrochemical Corrosion Test	92
5.2.5 Hardness Measurement	93
5.2.6 Biomedical test	93
5.2.7 Surface roughness.....	94
5.2.8 Results and Discussion.....	95
5.2.8.1 Depth profiles and chemical states analysis.....	95
5.2.8.2 Dissolution test	104
5.2.8.3 Electrochemical corrosion analysis.....	106

5.2.8.4 Nano-indentation	108
5.2.8.5 Cell culture.....	110
5.2.8.6 AFM	113
5.2.9 Summary – Dense NiTi.....	117
5.3 Porous Nickel Titanium	119
5.3.1 Sample preparation.....	121
5.3.2 Surface Characterisation.....	122
5.3.3 Dissolution Test	122
5.3.4 Mechanical properties test.....	123
5.3.5 Biomedical test	123
5.3.6 Results and Discussion	124
5.3.6.1 SEM	124
5.3.6.2 XPS	125
5.3.6.3 Dissolution test	129
5.3.6.4 Compression test.....	131
5.3.6.5 Cytocompatibility	133
5.3.7 Summary – Porous NiTi.....	135
5.4 References.....	136
CHAPTER 6	141
SURFACE MODIFICATION OF ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE FOR PROTEIN BINDING.....	141
6.1 Introduction	141
6.2 Materials and sample preparation	143
6.2.1 Materials	143
6.2.2 Sample preparation – Plasma surface modification (PSM) methods.....	143
6.3 Experimental methods	146
6.3.1 Surface characterizations.....	146
6.3.2 Protein attachment process and functionality assay for HRP.....	148
6.3.3 Stability of attached protein activity	149
6.3.4 Shelf life of treated UHMWPE	149
6.3.5 Plasma treatment on commercial protein binding surface.....	150
6.4 Results.....	151

6.4.1 Surface characterizations.....	151
6.4.1.1 Surface morphology	151
6.4.1.2 Wettability.....	159
6.4.1.3 ATR-FTIR.....	162
6.4.1.4 XPS	167
6.4.2 Protein attachment.....	172
6.4.3 Aging of Plasma treated surfaces	179
6.4.4 Commercial protein binding surface.....	184
6.5 Discussion	188
6.6 Conclusion	193
6.7 References.....	195
CHAPTER 7 CONCLUSION AND FUTURE WORK.....	201
7.1 Conclusion	201
7.1.1 NiTi.....	201
7.1.2 UHMWPE.....	204
7.2 Future work.....	207

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1. **J. P. Y. Ho**, R. W. Y. Poon, X. T. Xie, P. C. T. Ha, and P. K. Chu, "Anti-Corrosion Properties of Nitrogen and Oxygen Plasma-Implanted Nickel-Titanium Shape Memory Alloy", *Solid State Phenomena*, 107 (2005), 111 – 114.
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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 valves¹, joints², bones³, spine⁴ and stents⁵. Besides those implanted inside humans, biomedical materials have many external applications such as single use articles e.g. syringes, blood pouches, catheters⁶ and enzyme-linked immunosorbent assay (ELISA) plates⁷. 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 biocompatibility⁸” 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, biointegration⁹ 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 science¹⁰. 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 nitrogen¹⁵, phosphorus¹⁶, calcium^{17,18} and sodium¹⁹. Different kinds of thin films such as titanium oxide²⁰, titanium nitride²¹ 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 biocompatibility²⁶. 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 polymer 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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