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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Publications

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.

2. **J. P. Y. Ho**, S. L. Wu, R. W. Y. Poon, C. Y. Chung, S. C. Tjong, P. K. Chu, K. W. K. Yeung, W. W. Lu, K. M. C. Cheung, and K. D. K. Luk, "Oxygen Plasma Treatment to Restrain Nickel Out Diffusion from Porous Nickel Titanium Orthopedic Materials", *Surface and Coatings Technology*, 201 (2007), 4893-4896.

3. **J. P. Y. Ho**, N. J. Nosworthy, M. M. M. Bilek, B. K. Gan, D. R. McKenzie, P. K. Chu and C. G. dos Remedios, " Plasma Treated Polyethylene Surfaces for Improved Binding of Active Protein", *Plasma Processes and Polymers*, (accepted).

4. K. N. Yu, F. M. F. Ng, **J. P. Y. Ho,** C. W. Y. Yip and Nikezic, D., "Measurement of parameters of tracks in CR-39 detector from replicas", *Radiation Protection Dosimetry*, 111 (2004), 93-96.

5. K. W. K. Yeung, R. W. Y. Poon, X. Y. Liu, **J. P. Y. Ho**, C. Y. Chung, P. K. Chu, W. W. Lu, D. Chan, and K. M. C. Cheung, "Investigation of Nickel Suppression and Cyto-Compatibility of Surface Treated NiTi Shape Memory Alloy by Using Plasma Immersion Ion Implantation", *Journal of Biomedical Materials Research A*, 72 A (2005), 238-245.

6. X. Y. Liu, X. B. Zhao, R. K. Y. Fu, **J. P. Y. Ho**, C. X. Ding, and P. K. Chu, "Plasma-Treated Nanostructured TiO_2 Surface Supporting Biomimetic Growth of Apatite", *Biomaterials*, 26 (31) (2005), 6143-6150.

7. R. W. Y. Poon, **J. P. Y. Ho**, X. Y. Liu, C. Y. Chung, P. K. Chu, K. W. K. Yeung, W. W. Lu, and K. M. C. Cheung, "Formation of Titanium Nitride Barrier Layer in Nickel-Titanium Shape Memory Alloys by Nitrogen Plasma Immersion Ion Implantation for Better Corrosion Resistance", *Thin Solid Films*, 488 (1 – 2) (2005), 20 – 25.

8. R. W. Y. Poon, **J. P. Y. Ho**, X. Y. Liu, C. Y. Chung, P. K. Chu, K. W. K. Yeung, W. W. Lu, and K. M. C. Cheung, "Improvements of Anti-Corrosion and Mechanical Properties of NiTi Orthopedic Materials by Acetylene, Nitrogen, and Oxygen Plasma Immersion Ion Implantation", *Nuclear Instruments and Methods in Physics Research B*, 237 (1 – 2) (2005), 411 – 416.

9. R. W. Y. Poon, **J. P. Y. Ho**, X. Y. Liu, C. Y. Chung, P. K. Chu, K. W. K. Yeung, W. W. Lu, and K. M. C. Cheung, "Anti-Corrosion Performance of Oxidized and Oxygen Plasma-Implanted NiTi Alloys", *Materials Science and Engineering A*, vol. 390, no. 1 - 2, pp. 444 - 451 (2005).

10. K. W. K. Yeung, R. W. Y. Poon, X. Y. Liu, **J. P. Y. Ho**, C. Y. Chung, P. K. Chu, W. W. Lu, D. Chan, and K. M. C. Cheung, "Corrosion Resistance, Surface Mechanical Properties, and Cytocompatibility of Plasma Immersion Ion Implantation - Treated Nickel-Titanium Shape Memory Alloys", *Journal of Biomedical Materials Research A*, 75 (2) (2005), 256 – 267.

11. R. W. Y. Poon, **J. P. Y. Ho**, C. M. Y. Luk, X. Y. Liu, J. C. Y. Chung, P. K. Chu, K. W. K. Yeung, W. W. Lu, and K. M. C. Cheung, "Improvement on Corrosion Resistance of NiTi Orthopedic Materials by Carbon Plasma Immersion Ion Implantation", *Nuclear Instruments and Methods in Physics Research B*, 242 (1 – 2) (2006), 270 – 274.

12. G. J. Wan, R. K. Y. Fu, P. Yang, **J. P. Y. Ho**, X. Xie, N. Huang, and P. K. Chu, "Surface Wettability of Nitrogen Plasma-Implanted Silicon", *Nuclear Instruments and Methods in Physics Research B*, 242 (1 – 2) (2006), 296 – 299.

13. C.W.Y. Yip, D. Nikezic, **J. P.Y. Ho,** K.N. Yu, "Chemical Etching Characteristics for Cellulose Nitrate", *Materials Chemistry and Physics*, 95 (2006), 307-312.

14. G. J. Wan, P. Yang, R. K. Y. Fu, Y. F. Mei, T. Qiu, **J. P. Y. Ho**, N. Huang, X. L. Wu, and P. K. Chu, “Characteristics and Surface Energy of Silicon-Doped Diamond-like Carbon Films Fabricated by Plasma Immersion Ion Implantation and Deposition”, *Diamond and Related Materials*, 15 (9) (2006), 1276-1281.

15. X. Y. Liu, R. K. Y. Fu, **J. P. Y. Ho**, P. K. Chu, and C. X. Ding, “Bone-like Apatite Formation on Amorphous Silicon Containing Hydrogen”, *Materials Science and Engineering C* (*in press*).

16. S. L. Wu, P. K. Chu, X. M. Liu, C. Y. Chung, **J. P. Y. Ho**, C. L. Chu, S. C. Tjong, K. W. K. Yeung, W. W. Lu, K. M. C. Cheung, and K. D. K. Luk, “Surface Characteristics, Mechanical Properties, and Cytocompatibility of Oxygen Plasma-Implanted Porous Nickel Titanium Shape Memory Alloy”, *Journal of Biomedical Materials Research A*, 79A (1) (2006), 139 – 146.

17. S. C .H. Kwok, G. J. Wan, **J. P. Y. Ho**, P. K. Chu, D. R. McKenzie, and M. M. M. Bilek, “Anticoagulation Behavior of Phosphorus-Doped Carbon (P_xC) Films Synthesized by Plasma Immersion Ion Implantation and Deposition”, *New Diamond and Frontier Carbon Technology*, 16 (1) (2006), 39 – 48.

18. S. C. H. Kwok, G. J. Wan, **J. P. Y. Ho**, P. K. Chu, M. M. M. Bilek, and D. R. McKenzie, “Characteristics of Phosphorus-Doped Diamond-Like Carbon Films Synthesized by Plasma Immersion Ion Implantation and Deposition”, *Surface and Coatings Technology* (*in press*).

19. K. F. Chan, **J. P. Y. Ho**, W. Y. Li, B .M .F. Lau, A. K. W. Tse, W. F. Fong, M. M. M. Bilek, D. R. McKenzie, P. K. Chu, and K. N. Yu, “Investigation of Cytocompatibility of Surface-Treated Cellulose Nitrate Films by Using Plasma Immersion Ion Implantation”, *Surface and Coatings Technology* (*in press*).

20. S. L. Wu, X. M. Liu, Y. L. Chan, **J. P. Y. Ho**, C. Y. Chung, P. K. Chu, C. L. Chu, K. W. K. Yeung, W. W. Lu, K. M. C. Cheung, and K. D. K. Luk, “Nickel Release Behavior, Cyto-Compatibility and Superelasticity of Oxidized Porous Single-Phase NiTi”, *Journal of Biomedical Materials A* (*in press*).

21. G. J. Wan, N. Huang, P. Yang, R. K. Y. Fu, **J. P. Y. Ho**, X. Xie, H. F. Zhou, and P. K. Chu, "Platelet Activation Behavior on Nitrogen Plasma-Implanted Silicon", *Materials Science and Engineering C* (*in press*).

22. S. L. Wu, C. Y. Chung, X. M. Liu, P. K. Chu, **J. P. Y. Ho**, C. L. Chu, Y. L. Chan, K. W. K. Yeung, W. W. Lu, K. M. C. Cheung, and K. D. K. Luk, "Pore Formation Mechanism and Characterization of Porous NiTi Shape Memory Alloys Synthesized by Capsule-Free Hot Isostatic Pressing", *Acta Materialia* (*in press*).

23. N. J. Nosworthy, **J. P. Y. Ho**, A. Kondyurin, D. R. McKenzie and M. M. M. Bilek, "The Attachment of Catalase and Poly-L-lysine to Plasma Immersion Ion Implantation-Treated polyethylene", *Acta Biomaterialia* (in press).

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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 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.

1.5 Reference

[1] H. S. Tran, M. M. Puc, C. W. Hewitt, D. B. Soll, S. W. Marra, V. A. Simonetti, J. H. Cilley and A. J. DelRossi, Diamond-like carbon coating and plasma or glow discharge treatment of mechanical heart valves. *J. Investigative Surgery* 12 (1999), 133-140.

[2] D. Ikeda, M. Ogawa, Y. Hara, Y. Nishimura, O. Odusanya, K. Azuma, S. Matsuda, M. Yatsuzuka and A. Murakami, Effect of nitrogen plasma-based ion implantation on joint prosthetic material, *Surface & Coating Technology* 156 (2002), 301-305.

[3] X. Y. Liu, P. K. Chu and C. X. Ding, Surface modification of titanium, titanium alloys, and related materials for biomedical applications, *Materials Science and Engineering R* 47 (2004), 49-121.

[4] J. M. Toth, M. Wang, B. T. Estes, J. L. Scifert, H. B. Seim III and A. S. Turner, Polyetheretherketone as a biomaterial for spinal applications, *Biomaterials* 27 (2006), 478-482.

[5] K. Gutensohn, C. Beythien, J. Bau, T. Fenner, et al. In vitro analyses of diamond-like carbon carbon coated stents: Reduction of Metal ion release, platelet activation, and thrombogenicity, *Thrombosis research* 99 (2000), 577-585.

[6] C. Oehr, Plasma surface modification of polymers for biomedical use, *Nuclear Instruments and Methods in Physics Research B* 208 (2003), 40-47.

[7] R. K. Y. Fu and P. K. Chu, Plasma modification of materials, Encyclopedia of Biomaterials and Biomedical Engineering (2005), 1-12.

[8] P. K. Chu, J. Y. Chen, L. P. Wang and N. Huang, Plasma-surface modification of biomaterials, *Materials Science and Engineering R* 36 (2002), 143-206.

[9] L. Hao and J. Lawrence, Laser Surface Treatment of Bio-implant Materials, John Wiley & Sons, (2005) p.5.

[10] L. Hao and J. Lawrence, Laser Surface Treatment of Bio-implant Materials, John Wiley & Sons, (2005) p.xvi.

[11] W. Moller and S. Mukherjee, Plasma-based ion implantation, *Current Science* 83 (3) (2002), 237-253.

[12] S. Mandl and B. Rauschenbach, Improving the biocompatibility of medical implants with plasma immersion ion implantation, *Surface & Coating Technology* 156 (2002), 276-283.

[13] J. Pelletier and A. Anders, Plasma-based ion implantation and deposition: A

review of physics, technology and applications, *IEEE Transactions on Plasma Science* 33 (2005), 1944-1959.

[14] J. Meichsner, M. Nitschke, R. Rochotzki and M. Zeuner, Fundamental investigations in plasma modification of polymers, *Surface Coating & Technology* 74-75 (1995), 227-231.

[15] I. Bertoti, M. Mohai, A. Toth and T. Ujvari, Nitrogen-PBII modification of ultra-high molecular weight polyethylene: composition, structure and nanomechanical properties, *Surface Coating & Technology* (2006), in press.

[16] S. C. H. Kwok, J. Wang and P. K. Chu, Surface Energy, Wettability, and Blood Compatibility Phosphorus Doped Diamond-like Carbon Films, *Diamond and Related Materials* 14 (1) (2004), 78-85.

[17] X. Y. Liu, R. W. K. Poon, C. H. Kwok, P. K. Chu and C. X. Ding, Structure and properties of Ca-plasma-implanted titanium, *Surface Coating & Technology* 191 (2005), 43-48.

[18] A. Dorner-Reisel, C. Schürer, C. Nischan, O. Seidel and E. Müller, Diamond-like carbon: alteration of the biological acceptance due to Ca–O incorporation, *Thin Solid Films* 420–421 (2002) 263–268.

[19] M. F. Maitz, R. W. Y. Poon, X. Y. Liu, M. T. Pham and P. K. Chu, Bioactivity of titanium following sodium plasma immersion ion implantation and deposition, *Biomaterials* 26 (2005), 5465-5473.

[20] X. L. Zhu, J. Chen, L. Scheideler, R. Reichl and J. Geis-Gerstorfer, Effects of topography and composition of titanium surface oxides on osteoblast responses, *Biomaterials* 25 (2004), 4087-4103.

[21] Y. Fu, H. Du and S. Zhang, Deposition of TiN layer on TiNi thin films to improve surface properties, *Surface Coating & Technology* 167 (2003), 129-136.

[22] J. Lankford, C. R. Blanchard, C. M. Agrawal, D. M. Micallef, G. Dearnaley and A. R. McCabe, Adherence of diamondlike carbon coatings on total joint substrate materials. *Nuclear Instruments and Methods in Physics Research B* 80-81 **(**1993), 1441-1445.

[23] S. Affatato, M. Frigo and A. Toni, An *in vitro* investigation of diamond-like carbon as a femoral head coating, *Journal of Biomedical Materials Research* 53 (3) (2000), 221-226.

[24] L. Tan and W. C. Crone, Surface characterization of NiTi modified by plasma source ion implantation, *Acta Materialia* 50 (2002), 4449-4460.

---

[25] V. Saikko, T. Altroos, O. Calonius and J. Keranen, Wear simulation of total hip prostheses with polyethylene against CoCr, alumina and diamond-like carbon, *Biomaterials* 22 (2001), 1507-1514.

[26] A. R. Marcondes, M. Ueda, K. G. Kostov, A. F. Beloto, N. F. Leite, G. F. Gomes and C. M. Lepienski, Improvement of ultra-high molecular weight polyethylene mechanical properties by nitrogen plasma immersion ion implantation, *Brazilian Journal of Physics* 34 (4B) (2004), 1667-1672.