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Wear of PEEK/Ti6Al4V systems under
micro-abrasion and linear sliding conditions

Universidade do Minho
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Dissertação de Mestrado
Ciclo de Estudos Integrados Conducentes ao
Grau de Mestre em Engenharia Biomédica

Trabalho efectuado sob a orientação do
Professor Doutor José Manuel Ramos Gomes
Professor Doutor Júlio César Matias de Souza

É AUTORIZADA A REPRODUÇÃO INTEGRAL DESTA DISSERTAÇÃO APENAS PARA EFEITOS DE INVESTIGAÇÃO, MEDIANTE DECLARAÇÃO ESCRITA DO INTERESSADO, QUE A TAL SE COMPROMETE.

Universidade do Minho, __/__/____

Assinatura: _____

I dedicate this work to my Family and friends for all the support they gave me
in the preparation of this work.

"The reason is the step, the increase of science the way, and the benefit of mankind is the end."

Thomas Hobbes

ACKNOWLEDGMENTS

First of all, I would like to thank my supervisor, Prof. José Manuel Ramos Gomes, for the support, dedication, flexibility, guidance, encouragement and scientific teachings throughout the project. It was a pleasure to work with you.

To my co-supervisor, Prof. Júlio Souza that despite to be far always offset this distance in the development of work. Thank you for all the transmitted knowledge and all the support.

To Prof. Filipe Samuel Silva, for the encouragement and support that you gave me throughout the project.

To Prof^a. Mihaela Buciumeanu, for all the patience, flexibility, guidance, support, encouragement, sympathy, friendship and full availability for the experimental tests throughout this project.

To Sergio Carvalho for the excellent technical assistance and the constant words of support and encouragement. It was a pleasure working with you.

To Doctors Bruno Henriques and Óscar Carvalho for all the support and help with the hot-pressing machine.

To all my friends for supporting me at this stage, for being patient and listening to my concerns and discouragements. Thanks for all the help.

To my relatives for all the support, patience, understanding and help. Thank you for always being with me.

Finally, I want to thank especially my parents. All this would not be possible without your help and sacrifice. Always dedicated to giving me the best possible education and encouragement to follow front head high, never letting me down when I failed. Thanks for everything.

This work was supported by the Portuguese *Foundation of Science and Technology* through the projects: EXCL/EMS-TEC/0460/2012 and UID/EEA/04436/2013.



ABSTRACT

In dentistry, prosthetic structures must be able to support masticatory loads combined with a high biocompatibility and wear resistance in the presence of a corrosive environment. Also, abrasive wear is inevitable at exposed tooth or restorative surfaces, during mastication and tooth brushing. Thus, this work is dedicated to the tribological characterization of PEEK/Ti6Al4V systems under reciprocating sliding conditions in presence of artificial saliva taking in consideration tribocorrosion aspects, being also considered the micro-abrasion wear behavior of the same systems in presence of slurry containing hydrated silica particles representative of the abrasive agent present on toothpastes.

In order to improve the simultaneous wear and corrosion response of highly biocompatible prosthetic structures, a veneering poly-ether-ether-ketone (PEEK) to Ti6Al4V substrate was assessed by tribocorrosion tests under conditions mimicking the oral environment. Samples were synthesized by hot-pressing the PEEK veneer onto Ti6Al4V cylinders (8 mm diameter and 4 mm thick). The tribocorrosion tests on Ti6Al4V or PEEK/Ti6Al4V samples were performed on a reciprocating ball-on-plate tribometer at 30 N normal load, 1 Hz and stroke length of 3 mm. The tests were carried out in artificial saliva at 37 °C. Open circuit potential (OCP) was measured before, during and after reciprocating sliding tests.

Regarding the abrasive wear resistance, PEEK and Ti6Al4V samples were compared by under three-body abrasion conditions considering different hydrated silica content and applied loads. Micro-scale abrasion tests were performed at 60 rpm and on different normal loads (0.4, 0.8 or 1.2 N) for 600 revolutions of the testing ball using suspensions with different weight contents of hydrated silica.

In order to identify the dominant wear mechanisms the worn surfaces obtained from tribocorrosion and micro-abrasion tests were characterized by scanning electron microscope (SEM).

The tribocorrosion results revealed a lower wear rate on PEEK combined with a lower coefficient of friction (COF), when compared to Ti6Al4V. In fact, PEEK protected Ti6Al4V substrate against the corrosive environment and wear avoiding the release of metallic ions to the surrounding environment. The micro-abrasion results showed a higher volume loss on PEEK than that recorded on Ti6Al4V, when subjected to three-body abrasion tests involving hydrated silica suspensions. An increase of the volume loss was noted on both tested materials when the abrasive content or load was increased.

Keywords: PEEK, Ti6Al4V, Tribocorrosion, Micro-Abrasion, Reciprocating Sliding.

RESUMO

Na dentária, as próteses devem ser capazes de suportar cargas mastigatórias, combinadas com uma alta biocompatibilidade e resistência ao desgaste na presença de um ambiente corrosivo. O desgaste abrasivo é também inevitável no dente ou em superfícies restauradoras, durante a mastigação e escovagem dos dentes. Assim, este trabalho é dedicado à caracterização tribológica de sistemas PEEK/Ti6Al4V em condições de deslizamento linear alternativo na presença de saliva artificial tendo em consideração os aspetos de tribocorrosão, sendo também considerado o comportamento de desgaste por micro-abrasão no mesmo sistema, na presença de uma solução contendo partículas de sílica hidratada representativas de um agente abrasivo presente em pastas dos dentes.

De forma a melhorar a resistência ao desgaste e à corrosão de estruturas de próteses altamente biocompatíveis, foi considerado um recobrimento de poli-éter-éter-cetona (PEEK) sobre um substrato de Ti6Al4V o qual foi testado por tribocorrosão, em condições que procuraram imitar o ambiente oral. As amostras foram sinterizadas a quente sendo que o recobrimento de PEEK foi processado sobre o substrato de Ti6Al4V (8 mm de diâmetro e 4 mm de altura). Os testes tribocorrosão em amostras de Ti6Al4V ou PEEK/Ti6Al4V foram realizados num tribómetro de esfera-placa, com movimento linear alternativa da placa, para uma carga normal de 30 N, 1 Hz de frequência de oscilação e 3 mm de comprimento de pista. Os testes foram realizados em saliva artificial a 37 °C. O potencial de circuito aberto (OCP) foi medido antes, durante e após testes de deslizamento.

Em relação à resistência ao desgaste abrasivo, foram comparadas amostras de PEEK e de Ti6Al4V, em testes de micro-abrasão, com diferentes concentrações de sílica hidratada e diferentes valores de carga aplicada. Os testes de micro-abrasão foram realizados a velocidade constante de rotação da esfera (60 rpm), para diferentes cargas (0.4, 0.8 ou 1.2 N) e durante 600 rotações, usando diferentes concentrações de sílica hidratada.

De forma a identificar os mecanismos de desgaste dominantes, as superfícies de desgaste obtidas nos testes de tribocorrosão e de micro-abrasão foram caracterizadas por microscopia eletrónica de varrimento (SEM).

Os resultados de tribocorrosão revelaram uma baixa taxa de desgaste do PEEK, combinada com um baixo coeficiente de atrito, comparado com o Ti6Al4V. De facto, o PEEK protege o Ti6Al4V contra o ambiente corrosivo, evitando a libertação de iões metálicos para os tecidos. Os resultados de micro-abrasão mostram uma maior perda de volume de desgaste do PEEK do que o registado no Ti6Al4V, quando sujeito a abrasão a três corpos promovida por partículas de sílica hidratada. O aumento do volume de desgaste é notado nos dois materiais quando a concentração do abrasivo ou a carga aplicada aumenta.

Palavras-Chave: PEEK, Ti6Al4V, Tribocorrosão, Micro-Abrasão, Deslizamento linear alternativo.

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LIST OF ABBREVIATIONS

PEEK – Poly-ether-ether-ketone

SEM – Scanning electron microscope

OM – Optical microscope

FEGSEM – Field Emission Guns Scanning Electron Microscopy

EDS – Energy Dispersive Spectrometry

AFM – Atomic Force Microscope

PDLLA – Poly (D, L-lactide)

PAEK – Poly-aryl-ether-ketone

CT – Computed tomography

MRI – Magnetic resonance imaging

CFR-PEEK – Carbon fibers reinforcement of poly-ether-ether-ketone

COF – Coefficient of friction

OPC – Open circuit potential

CF – Carbon fibers

GB – Glass fibers

HP – Hot-pressing

SCE – Saturated calomel electrode

SE – Secondary electron

HV – Hardness Vickers

ANOVA – Analysis of variance

LIST OF SYMBOLS

Ra – Arithmetic average of roughness

R_{máx} – Maximum roughness

Rq – Root mean square

F – Friction force

μ – Coefficient of friction

N – Normal load

μ_s – Static friction

μ_d – Dynamic friction

s – Shear strength

σ – Yield stress

θ – Semi-open angle of the asperity of harder material

K – Wear coefficient

V – Wear volume

K_{abr} – Wear coefficient by abrasion

x – Distance of sliding

h/σ – Specific film thickness

b – Crater diameter

R – Radius of the test ball

S – Total sliding distance

k – Specific wear rate

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CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1. Motivation of the study

The human dentition has an important role in the daily routine, not only for masticatory function, but it is also associated with speech and facial esthetics. Bad practices of oral hygiene and aging are traumatic and pathological factors leading to injuries, such as tooth decay and loss of all or partial tissue. The American Association of Oral and Maxillofacial Surgeons report that 69% of persons aged between 35 and 44 had lost at least one tooth due to an accident, gum disease, a failed root canal or tooth decay. In case of people over 74 years old, 26% have lost all of their permanent teeth [1]. In the last years, the market of dental implants in all the world is increasing, and this tendency is still estimated to continue over the coming years, with a global annual evolution rate of 10%, from US \$ 3.4 billion in 2011 to levels around US \$ 6.6 billion in 2018 [2].

Biomaterials, such as titanium and titanium alloys have been used in dental implantation process due to their good biocompatibility, high mechanical strength and corrosion resistance. It is well known that the main disadvantage of titanium alloy is their poor tribological properties [3-7].

In order to overcome the drawbacks of titanium and titanium alloys, poly-ether-ether-ketone (PEEK) biocompatible polymer seem to be a good alternative due its good mechanical (e.g. Young's modulus around 3.6 GPa, close to the bone), wear and fatigue properties [7-10].

Quantification of friction and wear are fundamental for understanding the tribological behavior of biomedical materials, as well as to ensure that their use becomes feasible in implant dentistry practices.

Through the tribological evaluation, it is possible to ensure that the frictional forces will not be excessive, causing damage in the materials involved in the contact. Moreover, the *in vivo* occurrence of wear of a biomaterial can not only damage its structure, but also may lead to the production of debris that can migrate into tissues, generating inflammatory responses over time [11-13]. To overcome these drawbacks, tribological studies to assess the friction and wear response of biomaterials are mandatory.

1.2. Scope and aim of the thesis

In this thesis, a theoretical and experimental investigation in the field of biomaterials of dental implants is described.

The main objective of this work was to study the tribocorrosion and micro-abrasion behavior of a hybrid structure based on veneering biomedical PEEK to Ti6Al4V structures for biomedical applications.

The main goals of this thesis are:

- i) Veneering PEEK to Ti6Al4V samples as hybrid structures synthesized by hot-pressing technique;
- ii) Evaluation of the tribocorrosion behavior of Ti6Al4V and PEEK/Ti6Al4V samples performed on a reciprocating ball-on-plate configuration, in artificial saliva at 37 °C;
- iii) Evaluate the wear by micro-abrasion tests (ball-cratering), in the presence of abrasive particles;
- iv) Characterization of worn surfaces after tribocorrosion and micro-abrasion tests by Optical Microscopy (OM), Field Emission Guns Scanning Electron Microscopy (FEGSEM) and Energy Dispersive Spectrometry (EDS).

It is expected that the thesis is of particular interest in the field of dentistry, as the knowledge on tribocorrosion and micro-abrasion of biomedical materials is essential for dental implantology practices.

1.3. Structure of the thesis

The flowchart presented in Figure 1.1 shows the general line (evolution) of the thesis and also the steps forward in order to better understand the tribological behavior of the materials in study.

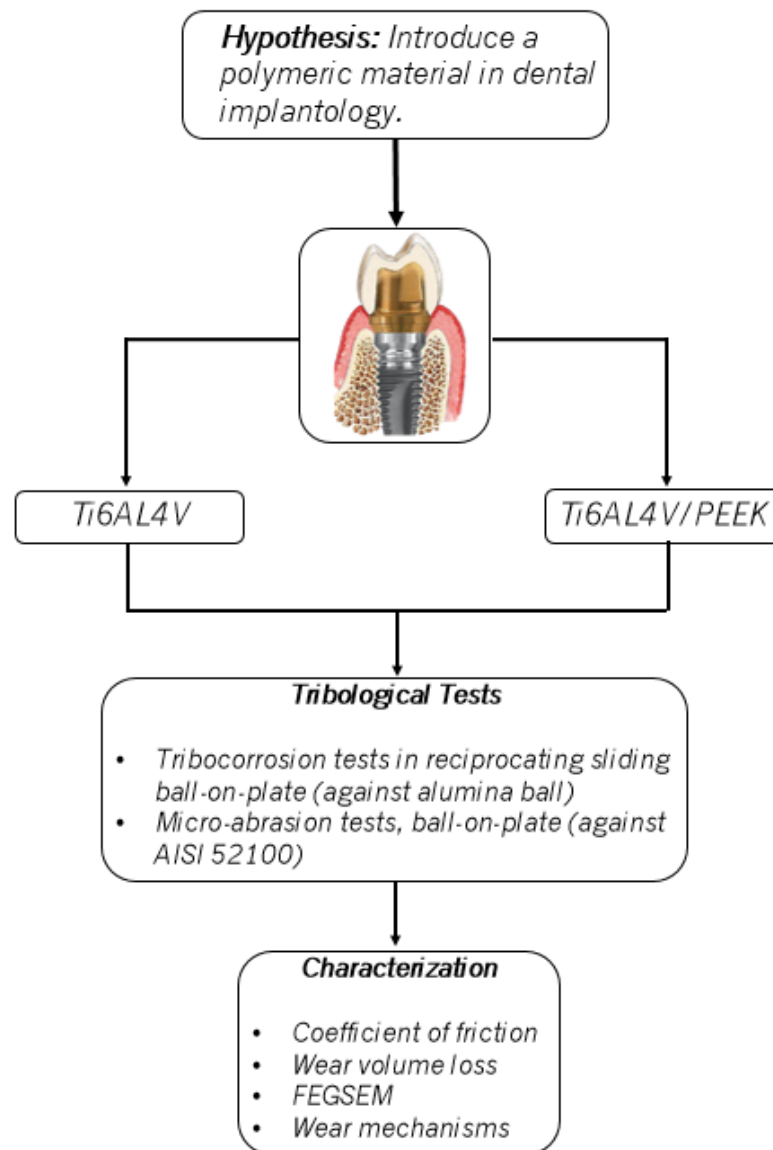


Figure 1.1 - Flowchart of the evolution of the thesis.

This thesis consists of six chapters.

Chapter 1 presents the motivation of this study. The objective and structure of the thesis are also presented in this chapter.

A state of the art in Biotribology is presented in Chapter 2, organized according to the different subjects studied. This chapter is divided into three sections. The first section concerns the concepts of Tribology. A detailed description of the most important fundamentals of tribology (contact between surfaces, friction, wear and lubrication) is provided. The second section of this chapter is dedicated to the Biotribology of teeth, where the common clinical problems relatively to the irreversible loss of tooth structure from the

external surface are presented such as abrasion, attrition, demastication, abfraction, resorption and erosion. From the third section can be depicted the theoretical background about prostheses and dental implants. A particular consideration is given to the materials used in dental implants. Titanium alloys and PEEK are presented in detail.

The outcomes of this work are compiled in the form of two scientific papers (one already published and another submitted for publication in international journals).

Chapter 3 (Tribocorrosion behavior of veneering biomedical PEEK to Ti6Al4V structures) presents the experimental results and discussion regarding tribocorrosion behavior of a hybrid structure based on veneering biomedical PEEK to Ti6Al4V for biomedical applications.

Chapter 4 (A comparative study between micro-scale abrasion wear of PEEK and Ti6Al4V concerning dental applications), is dedicated to the experimental results of the micro-abrasion tests. A comparison between abrasive wear behavior of PEEK and Ti6Al4V is presented, in order to evaluate the susceptibility of these materials to surface degradation by three-body abrasion under conditions mimicking dental applications.

Chapter 5 is devoted to a general discussion of the outcomes of the experimental work.

Chapter 6 presents the major concluding remarks and findings of this research program together with possible future lines of work related with the present research.

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CHAPTER 2

STATE OF THE ART

2. STATE OF THE ART

2.1. Concepts of Tribology

2.1.1. Definition and importance of Tribology

The concept of tribology was announced in 1966 in a report by Professor H. Peter Jost from the UK Department of Education and Science. This term was adopted to define the science and technology of interacting surfaces in relative motion. Tribology derives from the Greek word *tribos*, meaning rubbing. It is a multidisciplinary science that is based on mechanics, physics, chemistry and materials science [1].

The friction, wear and lubrication correspond to the major branches of Tribology, applied over the years to control friction and reduce wear.

Although the aspects concerning friction, wear and lubrication are object of study nowadays, our ancestors used intuitively those concepts to reduce the friction in translation motion. The rock painting shown in Figure 2.1 demonstrates that ancestors used Tribology concepts to reduce friction. They used water and animal-fat as lubricant to transport colossal monuments. Many years early, the fire was found by the frictional movement at two materials, proving that Tribology is present in man's life since the Pre-History [1,2].



Figure 2.1 - Ancestors moving a statue with water and animal-fat lubrication[3]

Since 1966, Tribology has focused primarily on solving industrial problems with wear and friction by applying best materials, new surface processing technologies, and development of better lubricants and lubrication methods [1,2]. The enormous cost of tribological deficiencies is mostly caused by the large number of energy and material losses occurring practically on every mechanical device in operation [4]. Therefore, Tribology assumed an important role in the industry, because the energetic resources, preservation of the environment, and highest costs of repairing of the industrial machines, that were prevent with these tribological studies [1,4]. On the other hand, Tribology assumes increasing importance in medicine due to the improvement of health and life quality, with the development of materials that enable the construction of prostheses and artificial articulations.

As said above, the practical objective of tribology is to minimize the main disadvantages of the contact between moving solids: friction and wear. Figure 2.2 illustrates some situations of the importance of the friction and wear in daily use.

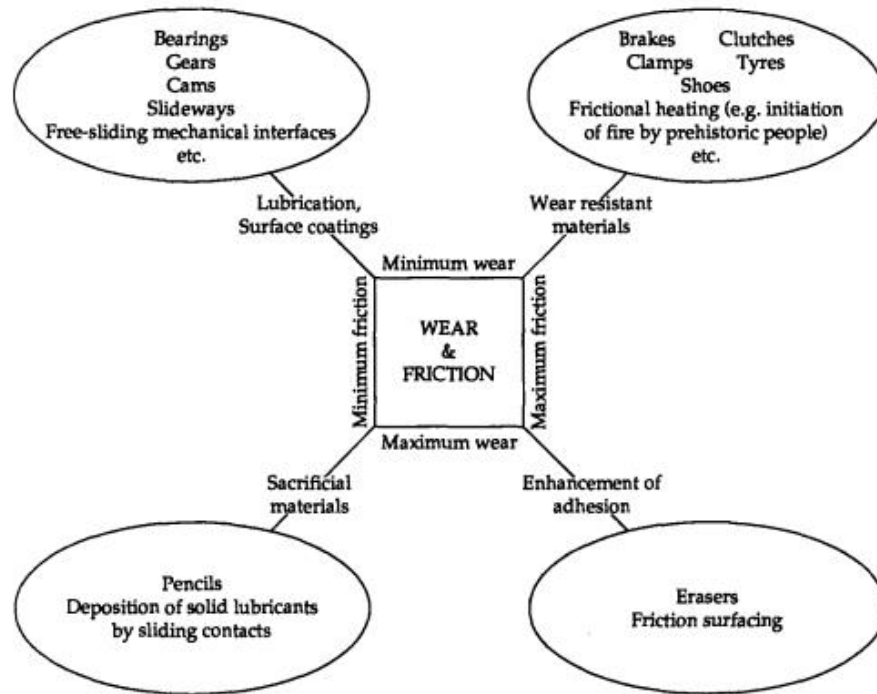


Figure 2.2 – Importance of Tribology in very distinct situations [4].

2.1.2. Contact between surfaces

Surfaces could seem to be perfectly smooth, but if they are observed through the microscope or with mechanical contact techniques of profilometry, they reveal a distribution of peaks and valleys, forming the surface roughness. Optical and mechanical methods can be used to measure the nano, micro or macroscopic geometrical characteristics of the surfaces. There are several statistical parameters for characterizing the topography of the surfaces, being the most common the *c.l.a.* (center line average). This value of *c.l.a* roughness (or roughness R_a) is the arithmetic average of roughness deviations from the mean line considering the dimensions of peaks and valleys. Others parameters currently used are the R_z or *RMS* (root mean square), that is as its name suggests, the mean square deviation of the profile from the mean line, and maximum roughness, R_{max} or R_t , that is defined as the higher distance between the highest peak and deeper valley in effective profile of roughness [1,2,4]. All of those parameters can be measured by a profilometer (mechanical or optical). An Atomic Force Microscope (AFM) can also be used to measure and characterize nano-roughness of surfaces.

As surfaces are not smooth, the contact between two surfaces occurs through the peaks of the highest asperities (Figure 2.3). The contact area between two surfaces without considering surface roughness concepts is named apparent contact area, whereas the real contacts between the tops of mating

asperities give rise to the called real area of contact. Typically, the real area of contact is 0.0001%-1% of the apparent contact area [1,2,4].

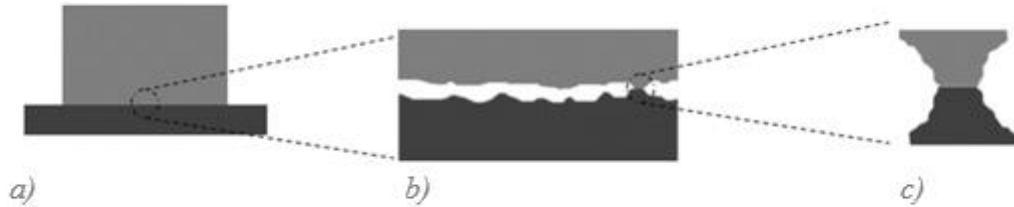


Figure 2.3 - Interface of contact between two surfaces: a) apparent contact area, b) and c) real contact area.

2.1.3. Friction

Friction is the resistance to movement during sliding or rolling that can be verified when one solid body moves tangentially over another one with which it is in contact. The tangential force, which acts in opposition to the direction of the movement, is named friction force. The friction can be the force which resists to movement (kinetic friction) or that avoid the movement (static friction). The kinetic friction is usually somewhat smaller than the static friction. The static friction is defined as the coefficient of friction corresponding to the maximum force that must be overcome to initiate macroscopic motion between two bodies [1,5].

For a pair of materials tested under certain sliding conditions, the coefficient of friction tends to assume a steady mean value. Two basic laws of friction are generally used in a wide range of applications. These laws were presented by Guillaume Amontons, in 1699, which reviewed and formulated the previous study of Da Vinci, who describe these rules 200 years early [1]. The first law establishes that the friction force, F , is directly proportional to the normal load, N , applied between two bodies, as follows in the Expression (2.1):

$$F = \mu \times N \quad (2.1)$$

Where the coefficient of friction is symbolized by μ [1,5]. The second law establishes that the friction force is independent of the apparent contact area, hence the coefficient of friction is the same between two bodies regardless their apparent contact size. A third law was introduced by Coulomb, in 1785, stating that the friction force is independent of velocity once movement starts. However, experimental observations show that this is not always true as the friction coefficient could vary significantly with the variation of sliding speed. On the other hand, it's observed that the frictional force necessary to initiate sliding is generally greater than that required to maintain it, and hence, the coefficient of static friction (μ_s) is greater than the coefficient of dynamic friction (μ_d). In many systems, μ_d is found to be almost independent of velocity when this parameter varies in a short range of values, but when the velocity significantly increases for contacts involving metals, the coefficient of friction usually decreases [1,6].

During the sliding contact between two surfaces in non-lubricated conditions, friction may occur from a single or a combination of pathways, such as the adhesion between the protruding asperities of the mating surfaces and/or plowing.

The adhesion theory of friction is based on the fact that the contact between surfaces is established only at the asperity peaks, being able to suffer elastic or plastic deformation, according to the intensity of normal applied load. In real contact zones, a strong adhesion between the mating surfaces occurs due to interatomic and intermolecular forces. Under those conditions, the sliding of a body over a counterbody starts when the tangential force (F) is high enough to cause the rupture of adhesive junctions. This theory predicts that the value of coefficient of friction is associated with the mechanical properties of the contacting materials, being given by the Expression (2.2):

$$\mu = \frac{s}{\sigma} \quad (2.2)$$

where, μ is the coefficient of friction, s is the shear strength of the softer material involved in the contact and σ is the yield stress of the softer material [7-9].

The plowing theory of friction considers that a hard asperity is embedded in the soft mating material and that it pushes the plastic flow of the soft material away to form a groove during sliding. The resistance to sliding motion due to the penetration of the asperity in the opposing softer material defines the component of friction, gives in the Expression (2.3):

$$\mu = \frac{2}{\pi} \cot \theta \quad (2.3)$$

where, θ is the semi-open angle of the asperity of harder material, assuming that the asperities present a conical geometry. This theory explains the friction phenomenon based only on the surface roughness of the harder surface of the sliding pair [6-9].

The junction growth concept is an extension of the adhesion theory of friction. This theory admits that the area of contact at the junctions grows due to the plastic deformation when the tangential force (F) promote the sliding of one body over another. The rupture of the junction occurs when the combination of the applied tangential stress (due to tangential force F), with the contact pressure reaches a value corresponding to the shear strength (s) of the junction. Accordingly to this theory, the coefficient of friction is given by the Expression (2.4):

$$\mu = \frac{K}{[\alpha (1 - K^2)]^{1/2}} \quad (2.4)$$

where, K is a factor that takes into account the existence of less resistance films at the interface and α is a constant of the materials, with a constant value for metals. This theory is more realistic than the previous ones, since it shows that the friction is determined by the shear resistance of the film existing at the interface [7,9].

The mentioned theories of friction constitute the basis for the understanding of the friction phenomenon. However, a mathematical formulation to estimate the friction coefficient for a given real sliding contact situation does not exist as friction depends on many parameters whose effects are difficult to determine without experimental evaluation.

2.1.4. Wear

Wear is commonly defined as the progressive loss of surface material caused by mechanical and chemical action due to the contact and relative movement against a solid body. This process can be controlled, but not completely eliminated.

The usual mechanisms of wear are: adhesion, abrasion, surface fatigue and tribochemical reactions. These mechanisms classify the process by which material is removed from the contact surface, promoting changes on the surface morphology and the generation of wear particles [1,2,4,5,7-9].

Adhesive wear is a surface degradation mechanism explained by the interatomic and intermolecular forces established between the asperities of two contacting surfaces at the real contact zones. Thus, adhesion between mating asperities occurs, giving rise to a cold welding phenomenon. Therefore, to slide one mating surface against the other, the junctions established by adhesion will broke up. The volume loss of material, according to the formulation of this mechanism is given by the Expression (2.5) [9]:

$$V = K \frac{Wx}{3\sigma} \quad (2.5)$$

where, V is the wear volume, K is the wear coefficient, W is the normal load applied, x is the sliding distance and σ is the yield stress of the softer material of the contact. Considering such equation, it is possible to define the three laws of wear: (i) the wear volume is proportional to the distance of sliding; (ii) the wear volume is proportional to the normal load; and (iii) the wear volume is inversely proportional to the yield stress of the softer material.

When transfer of material from the softer surface to the hardest one occurs, this adhesion phenomenon gives rise to an adherent third body (Figure 2.4). This transfer of material can occur by the agglomeration and adhesion of loose wear debris, tribochemical adherent films, or material directly transferred between the mating surfaces [2].

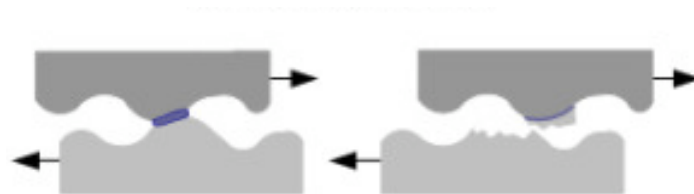


Figure 2.4 - Adhesion wear phenomenon with transfer of material ¹

Abrasive wear occurs when asperities of a rough, hard surface or hard particles are embedded in one or both of the mating surfaces in relative motion. These hard particles may be the product of processing, wear debris or dirt from outside of the tribo-system. There are two general situations for abrasive wear.

¹ <http://brianesser.com/2013/03/the-simplicity-and-sophistication-of-engine-bearings-part-2/>

In the first case, the abrasion mechanism is due to the penetration of the asperities of the hard material in the soft material (two-body abrasion) (Figure 2.5). In the other case, small hard particles present at contact interface, are able to abrade either one or both of the surfaces in contact (three-body abrasion) (Figure 2.5). The volume of wear described by the abrasion mechanism is given by the Expression (2.6) [1]:

$$V = K_{abr} \frac{Wx}{3\sigma} \quad (2.6)$$

where, V is the wear volume, K_{abr} is the wear coefficient by abrasion, W is the normal load; x is the distance of sliding and σ is the yield stress of the softer material. K_{abr} depends only on the roughness of the hard surface, which means that this type of wear can be reduced improving the surface quality of the harder surface. The three-body abrasion mode reveals typical values for K_{abr} one order of magnitude lower than two-body abrasion mode. In fact, many particles tend to roll rather than slide, as the abrasive particles spend about 90% of the time rolling, and the remaining time in sliding and abrading the surfaces [1,2,5].

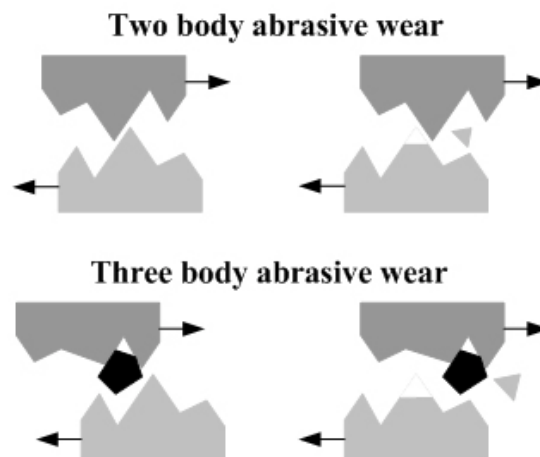


Figure 2.5 – Schematic representation of the two and three body abrasive wear²

Fatigue wear is related to the repeated loading and unloading cycles to which the materials are exposed. This may induce the formation of subsurface or surface cracks, which eventually, can result in the breakup

² <https://natinere.wordpress.com/surface-engineering/wear/>

of the surface with the formation of large fragments, leaving large pits on the surface. Localized fatigue may occur on a microscopic scale due to continuous sliding contact of asperities on the surface of solids in relative movement. The fatigue of materials may be manifested by the occurrence of elastic and plastic deformation, hardening, or softening the material and appearance of cracks and their propagation. Since shear stresses below the surface tends to be larger, there is a higher probability of occurrence of subsurface cracks. However, cracks can still be initiated from the surface by mechanical and chemical interaction between contacting surfaces and surrounding environment or the interfacial element (Figure 2.6). The surface fatigue, in the case of sliding contact, may be associated with mechanisms of adhesion or abrasion, since the repetitive sliding of hard asperities on a solid surface can lead to the formation and propagation of cracks on the surface or subsurface [2,7,8].

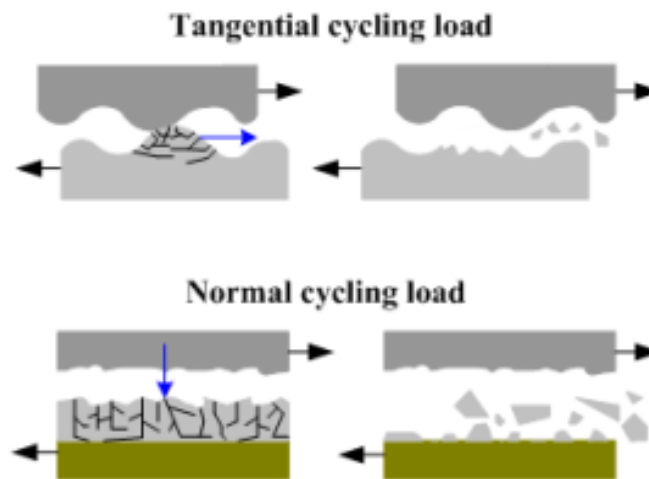


Figure 2.6 - Different types of fatigue wear due cyclic applied loads ³

The tribochemical wear, also known as wear by corrosion or oxidation, results from continuous removal of material and formation of new layers at the contact surfaces involving chemical reactions. In presence of atmospheric oxygen, the tribochemical wear is usually named oxidative wear, with the formation of oxide films on the surface of materials. This wear mechanism occurs during chemical instability of the materials. The thin oxide layer which protects the material is removed and allows corrosion of the material,

³ <https://natinere.wordpress.com/surface-engineering/wear/>

resulting in dissolution and/or diffusion of chemical elements from one material to another (Figure 2.7) [1,2].

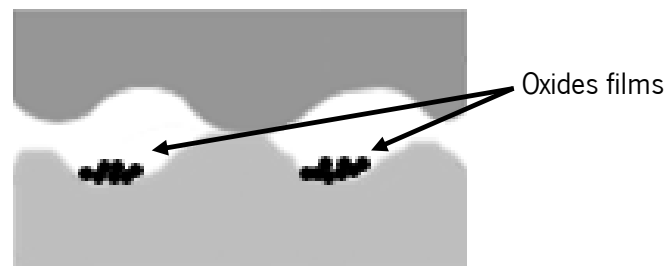


Figure 2.7 - Tribochemical wear effects with oxide films

In many systems, materials that are in tribological contact, beyond the mechanical wear are also exposed to a corrosive environment involving chemical and electrochemical processes [10–14]. Therefore, the term tribocorrosion refers to the surface degradation mechanisms when mechanical wear and chemical/electrochemical processes interact with each other [10–14]. As referred above, the tribological processes involve many different material loss phenomena. Thus, depending on the situation, this process includes the interaction of corrosion, abrasion, adhesion, or surface fatigue wear processes, being many times linked to the synergy resulting from the coupling of mechanical and environmental effects [12,13,15]. Tribocorrosion is present in many places, such as transportation, mining, metallurgy, chemical and oil industries, food industry or medical prostheses. In this last case, the field of knowledge is called biotribocorrosion due to its relation with biologic environments [14,16–19].

The wear of a mechanical component can be measured by its weight loss, due to an irreversible deformation or by the variation of surface roughness. Tribological tests allow to characterize the friction and wear behavior of materials in sliding contact in the absence or presence of a lubricant.

In the technical literature, wear equipments (tribometers) are machines used to measure the friction and wear behavior of materials. Figure 2.8 shows a commercial tribometer (Bruker, USA) for reciprocating sliding friction and wear tests. This machine allows a versatility of tests with a wide range of loads and may allow to perform micro or macro scale tribological tests. It can operate under a variety of test configurations including pin/ball-on-disc and pin/ball-on-plate, both in dry or lubricated sliding environment. Figure 2.9 shows a micro-abrasion machine (Plint TE66, UK). This equipment allows a maximum load of 5 N between a rotating ball (\varnothing 25 mm) and the plate sample where a three-body abrasive action is promoted by the presence of slurry containing micro-sized hard particles.



Figure 2.8 - Tribometer for friction and wear tests (Bruker, USA), courtesy of the Tribology Laboratory, UMinho

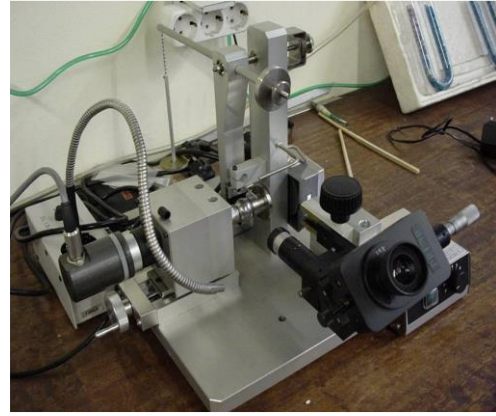


Figure 2.9 - Micro-abrasion machine (Plint TE66, UK), courtesy of the Tribology Laboratory, UMinho

2.1.5. Lubrication

In order to minimize or control wear and friction at the contact surfaces, a protective film or a fluid between surfaces in sliding or rolling contact is required as it proved to be an efficient method for this purpose. Thus, the reduction of friction between the bodies in contact also promotes a decrease on the wear of surfaces and reduces the heat generated between the surfaces. Those are the main beneficial effects of the use of liquid lubricants [1,7,8]. Depending on the thickness of the lubricant film, various regimes of lubrication may be defined (Figure 2.10).

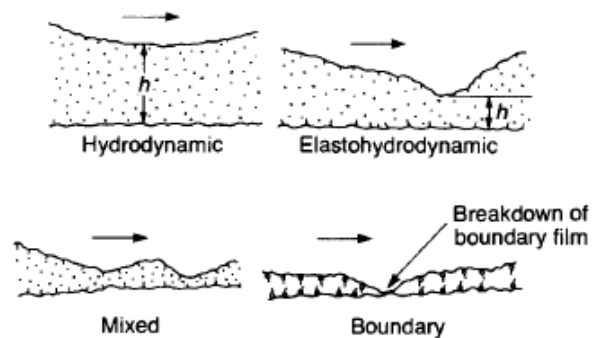


Figure 2.10 - Different regimes of lubrication, adapted of [1]

In boundary lubrication solid surfaces are so close to each other, with significant asperity interaction (Figure 2.10). Such regime of lubrication is comparable to the non-lubrication conditions at the contact area, once the presence of lubricant film between the surfaces is very small, in the range $0.005\text{-}0.1\ \mu\text{m}$ (Figure 2.11). A good lubricant for this mechanism is one that strongly adheres to the solid surface via

molecular forces, preventing the adhesion between the two solids, and thus the occurrence of damage to their surfaces. In fact, friction and wear can be controlled by chemical properties (additives) of the lubricant [1,5,7,8].

In the case of hydrodynamic lubrication regime, the two surfaces in relative motion are completely separated by a lubricant film (Figure 2.10), with a considerable thickness between 1 and 100 μm or more, having a specific film thickness ranging from 10 up to 100 (Figure 2.11). The empty space between the surfaces is filled with a lubricant, generating up by a hydrodynamic effect associated with the relative motion between the bodies. The lubricating film ensures the reduction of the coefficient of friction and wear. The hydrodynamic pressure is low compared to the strength properties of the solids and will not cause appreciable plastic deformation. The condition of hydrodynamic lubrication is governed by the bulk physical properties of the lubricant, mainly by the viscosity [1,5,7,8]. In elastohydrodynamic lubrication, the local elastic deformation of the solids provides a coherent hydrodynamic film, which prevents asperity interaction (Figure 2.10). The combination of the sliding speed, the elastic deformation and the increase in lubricant viscosity allow the formation of a film with sufficient thickness to separate the two contact surfaces. An elastic hydrodynamic film has a thickness ranging from 0.01 up to 10 μm and corresponding specific film thickness in a range of 3-10 (Figure 2.11)[1,5,7,8]. The mixed lubrication regime corresponds to the transition between the boundary lubrication and hydrodynamic lubrication. The surfaces are mostly separated by a thin lubricant film although asperity contact still takes place (Figure 2.10). The total applied load is thought to be partly supported by asperity contacts and hydrodynamic action. Mixed lubrication has been defined with a lubricant film thickness ranging from 0.01 up to 1 μm while a specific film thickness in a range of 1-4 (Figure 2.11) [1,5,7,8].

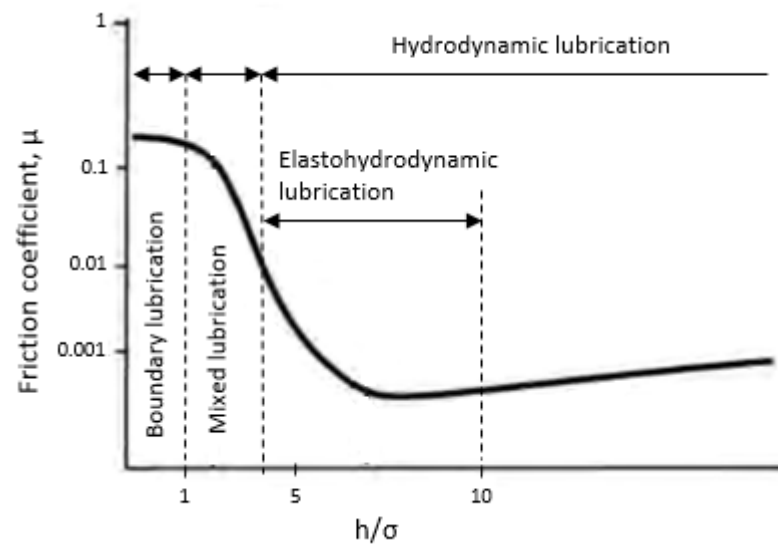


Figure 2.11 - Variation of coefficient of friction with the specific film thickness (h/σ), adapted of [7]

2.2. Biotribology in the oral cavity

The oral environment has a very important role in the tribological behavior of human and artificial teeth and restorative materials [20].

Dental erosion is the combination of several factors such as chemical, biological and behavioral factors. These factors are crucial and helps to explain why certain people present more erosion on the teeth than others [21]. For example, acidic drinks increase the acidity in the mouth (pH) and can decrease the hardness and the elastic modulus of enamel, resulting in the loss of dental hard tissue (tooth wear) [22,23].

Saliva has been considered a very important biological factor in the case of dental erosion. Several salivary defensive mechanisms act during the erosive process, such as the dilution and clearance of erosive agent from the mouth, neutralization and buffering of acids. These mechanism are slowing down the rate of enamel dissolution through the ion effect by salivary calcium and phosphate. Erosion can be related with the low salivary flow and low protecting capacity. The enamel pellicle that cover the tooth enamel, protects the oral surfaces against wear originated from masticatory contacts and determines the adherence of microorganisms pellicle that can protect the teeth of an acid environment [24]. So, the protective

properties of saliva are extremely significant for minimizing the corrosive effects of acids on teeth and restorations. Saliva can supply calcium and phosphate ions for the enamel remineralization [20,21,23].

Even if the contact is tooth-to-tooth or restorative material-to-natural tooth, it has been mentioned that the wear is a result of four mechanisms such as: abrasion (wear at non-contacting sites together with a number of other situations which cannot be ascribed to erosion or attrition), attrition (describe the physiological wearing away of dental hard tissue as a result of tooth-to-tooth contact with no foreign substance intervening) (Figure 2.12), erosion (describe surface loss attributed to chemical effects. These are usually acidic and may be the result of extrinsic causes such as dietary acids or intrinsic as a result of gastric regurgitation – in tribology this is known as corrosive wear) and abfraction (that includes fatigue) [20,25,26]. Demastication and resorption are other two mechanisms mentioned in technical literature that affect the teeth and lead to an irreversible loss of tooth structure from the external surface. Demastication is the mechanical interaction between food and teeth. Resorption defines the process of biological degradation of substances produced by the body [25].



Figure 2.12 - Erosion caused by refrigerant and attrition caused by bruxism [27]

The tooth wear has significant clinical consequences both aesthetic and functional. The loss of the tooth surface caused by abrasion is the most common clinical problem. Some epidemiological studies estimated that 97% of the teeth loss is caused by wear, with 7% of the population requiring treatment. If the wear is not controlled, the enamel will eventually crack causing exposure of dentin which in turn will accelerate the wear rates, resulting in disastrous effects such as unacceptable damage to occlusion surfaces, alteration of masticatory movements, hypersensitivity of dentin and disorders of the dental pulp [20].

All of these effects will lead to replacement of the tooth/teeth by a dental restoration/implant.

2.3. Prostheses and dental implants

2.3.1. Dental implants

The replacement of a missing tooth is a very old process. The ancient cultures used sometimes stone, shells, bones and gold or even other human or animal teeth. However, this practice did not become popular, once that was identified to be the reason for infectious diseases and even deaths [28].

In 1809, Maggiolo developed a gold post anchor into fresh extraction sockets. After the healing process, he attached a tooth to the gold post. This has extraordinary similarity with the modern dental implant procedures. Concerning teeth losses during World War II, there was an interest growing in the design of biocompatible substitutes as well as the possible shape of implants. Dr. Norman Goldberg in association with Dr. Aaron Gershkoff were pioneers in teaching techniques on sub-periosteal implants in dental schools around the world [28,29].

Nowadays, dental implants are increasingly used for the replacement of missing teeth and to support dentures, providing health to patients. Furthermore, this technique have the purpose of providing additional masticatory units [30]. Dental implants correspond to artificial substitutes for natural roots of teeth and have the function of the fixed support of the ceramic crown, which replaces the natural tooth (Figure 2.13).

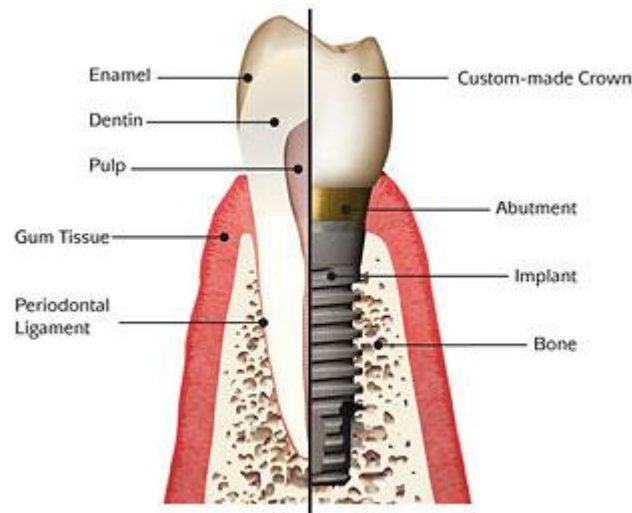


Figure 2.13 - Difference of the constitution of natural and artificial tooth⁴

Dental implants are fixed to the inside of the gums and in contact with the jawbone. It is essential to ensure that the body does not reject the implant. Due to this problem, the material must be used respecting certain conditions, in particular the appropriate mechanical properties for the function to be performed by the implant and biocompatibility, as well [31].

The osseointegration must occur after the introduction of the implant, i.e. the implant needs to interact with the bone cells (osteoblasts) to form a stable structure [30,32–34]. This process can be improved using certain treatments (e.g. sandblasting, anodic treatment, etc.) or coating on the surface of the material [12,13,30,32,35,36]. The osseointegration concept emerged in 1952, through a fortuitous discovery, made by Per Ingvar Brånemark, when the application of a titanium chamber in vivo research of the tibia of a rabbit, being present a strong integration of the chamber applied with the surrounding bone. Brånemark in 1983 [as cited in 29] defined this concept as a direct structural and functional connection of the bone tissue and the implant surface subjected to functional loads. With the use of titanium in dental implants, there has been a significant evolution in terms of osseointegration [36].

⁴ <http://midwestdentalimplantology.com/implant-dentistry/>

2.3.2. Biomedical requirements

In order for dental implants to have success at a long-term and short-term, it is essential to comply with some conditions, such as: biocompatibility, osseointegration, tribocorrosion resistance, resistance to fatigue and corrosion and proper mechanical properties (which provide to the implant stability). These conditions will be affected by parameters such as the surface properties (roughness, topography, formation of oxides, hydrophilicity), geometry and chemistry composition [36-38].

The fixation is a requirement for the implant to have proper support, thus producing a successful implantation. Some properties of the surface, as well as the composition, hydrophilicity and the roughness correspond to characteristics that have an important role in the interaction between the implant and the tissue contributing directly to the quality and rate of osseointegration. The response to the environment, structural integrity and the interaction of cells with the implant are influenced by the characteristics of the surface. The hydrophilicity is also influenced by the constitution of the surface, being that the surfaces which have a greater hydrophilicity are more desirable in terms of the interaction of the implant with the biological fluids, cells and tissues. It's possible to divide the roughness in three categories taking into account the scale of the topological dimensions (macro, micro e nano). This roughness influences the osseointegration and biomechanical fixation to the implant. The composition and the loads to which the implant is subject are critical parameters for protein adsorption and cell attachment [37,38].

2.3.3. Materials used in dental implants

There are many types of materials used in dental implants, for example: metals, ceramics and polymers. The three most used metals for implants are stainless steel, CoCr alloys and Ti alloys [10,12,39,40]. Regarding ceramics, the most studied are Alumina (Al_2O_3), Zirconia (ZrO_2) and ceramic based-composites. For example, zirconia have some characteristics that makes it a promising material for dental implants, because of its esthetics benefits and less bacterial adhesion on the material [41–44]. Concerning polymers, they are used as veneer on metals in order to decrease the transfer of ions to surrounding tissues. There are studies of poly(D,L-lactide) (PDLLA) and poli-ether-ether-ketone PEEK related with dental implants [12,13,45].

Titanium corresponds to a material frequently used by the dental industry because it presents a high biocompatibility, excellent mechanical properties and corrosion resistance. The bone also presents these properties and for this reason titanium became an important material to be applied in dental implants [15,39,46–48]. As titanium is a biocompatible material, it allows the natural functions of the tissue to be

restored, not causing rejection by the organism. However, due to the high Young's modulus (110-120 GPa) of titanium as compared with the cortical bone (8-18 GPa), loading occlusion can cause stress shielding to the peri-implant area, making them incompatible [10,12,13,47].

Initially, pure titanium was used for biomedical applications, but due to its low abrasion resistance, the creation of titanium based alloys was required. Ti6Al4V alloy was used originally for aeronautical purposes, since it presents high mechanical strength and better corrosion resistance when compared with pure titanium. The main problem of this alloy in biomedical terms is that the modulus of elasticity exceeds the value of the bone [10,15,47,48]. This, porous titanium was created by powder metallurgy, which has a lower modulus of elasticity and allows the bone to grow normally, making it an important material to use in implants [11,49].

Within the different titanium alloys, the most used is Ti6Al4V alloy, due to the fact that it presents good mechanical characteristics and capacity to resist to corrosion in dental implants. The creation of a layer of titanium oxide (TiO₂), stable and dense on the surface of titanium is responsible for its chemical stability in the organism [11,15,29]. This oxide layer is spontaneously formed when the surface is exposed to oxygen or environments containing oxygen, having normally a thickness in a range of 2-5 nm. This characteristic, along with good mechanical properties makes titanium and their alloys attractive for use in orthopedic and dental applications [50].

Although all the mentioned advantages of titanium, it has poor wear resistance. On the other hand its degradation by wear increases in contact with body fluids, leading to the release of metal ions into surrounding tissues [15,24]. In dental implants, the contact between abutment and implant is exposed to sliding wear in the presence of saliva and abrasive wear due to hard particles from food intake or tooth brushing [11,15]. In the case of orthopedic articular implants, sliding contact occurs between the articular joints which are exposed to body fluids [51–53]. A major concern of the used of titanium and titanium alloys is on the toxicity of the wear particles released to the body and ions released. The titanium-based surfaces have been linked to inflammatory tissue reactions [51–53]. In particular, a study revealed that Al and V have a cytotoxic effect on human cells [54].

The action of cyclic loading in implantology, produced for example by mastication movements, leads to the development of micro-cracks, which over time tends to increase, and may lead to its breakage. On the other hand, the aggressive chemical environment to which implants are exposed (e.g. oral cavity, body fluids etc.) is favorable to the degradation of metallic parts. Hence, the need of understanding the

response of implant materials from the wear and corrosion point of view, i.e., tribocorrosion behavior, is an important issue. It is well known that the tribocorrosion is an irreversible process that occurs at the surface of a material causing degradation due to the combination of wear and corrosion actions that occur simultaneously [24,39,48].

Biocompatible polymers and composites have revealed mechanical and biological properties to replace many parts of the human body, mainly in direct skeletal contact [55,56]. For instance, such materials possess low Young's modulus values, close to that of human bone, although characterized by low mechanical strength which imposes them some limitations [55,57,58]. Poly-ether-ether-ketone (PEEK), is commercialized for the industry since 1980. It belongs to the Poly-aryl-ether-ketone (PAEK) family that is a group of high-performance thermoplastic polymers, presenting an aromatic backbone molecular chain composed of ketone and ether functional groups [57]. PEEK presents two ether and a ketone groups, as shown in Figure 2.14.



Figure 2.14 - Structural formula of PEEK [56]

PEEK and their composites are increasingly used in different industrial fields due to their attractive mechanical properties and relatively low manufacturing cost [58]. Those materials have higher wear and chemical resistance associated with a high biocompatibility when compared to titanium, titanium alloys or stainless steel [59,60]. Poulsson et al. [61] evaluated the osseointegration of PEEK implants with or without surface treatment by oxygen plasma after 4, 12 and 26 weeks. Results from histomorphometry and mechanical push-out tests revealed a limited inflammatory response associated with a good osseointegration. Additionally, the oxygen plasma surface modification improved osseointegration and implant stability.

Conventional biomedical metals are radiopaque and create artifacts in X-ray radiography, computed tomography (CT), or magnetic resonance imaging (MRI). This is an issue in the use of metallic materials in implantology. Considering PEEK is radiolucent, it is possible to monitor the status of the healing bone around PEEK by using those imaging techniques [57,60].

For some implant devices, PEEK reinforced with carbon fibers (CFR-PEEK) can be an alternative depending on the loading. The microstructure of CFR-PEEK concerning the concentration and geometry of the carbon fibers is very important to provide the maximum mechanical strength for biomedical applications [55,57]. PEEK presents a Young's modulus of approximately 3.6 GPa while CFR-PEEK can have a Young's modulus around of 24 GPa (closer to the values of the cortical bone) [55,57,58,62]. The tensile strength of PEEK is approximately 95 MPa while for CFR-PEEK is 214 MPa [55,57,58]. Also, the mechanical and tribological properties of PEEK make this polymer an attractive material for biomedical applications [12,44,63–68]. Some authors believe that by using PEEK as a veneer it is possible to overcome the problems that arise in titanium implants due to the ions release to surrounding tissues [69,70]. A recent work on a polymeric veneering material to Ti6Al4V alloy revealed a way to avoid the release of metal ions to the human tissues [13]. The test conditions carried out on PDLLA/Ti6Al4V were similar to the ones used in the present work. PDLLA protected the titanium substrate against wear due to the low coefficient of friction during sliding. That could be a good strategy to reduce the degradation of the titanium surface when placed in bone tissue [13].

Furthermore, PEEK and their composites revealed an excellent thermal and chemical stability, being resistant to a variety of organic and inorganic fluids. Concerning the aggressive environment in the oral cavity, PEEK can be used as a protective layer of metal surfaces against corrosion, being a potential strategy for prostheses and implants applied in dentistry [67,71]. In dentistry, PEEK can be used to synthesize transitional abutments [72], healing caps [73] and orthodontic bite sticks.

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Wear of PEEK/Ti6Al4V systems under micro-abrasion and linear sliding conditions

CHAPTER 3

TRIBOCORROSION BEHAVIOR OF VENEERING BIOMEDICAL PEEK TO Ti6Al4V STRUCTURES

3. TRIBOCORROSION BEHAVIOR OF VENEERING BIOMEDICAL PEEK TO Ti6Al4V STRUCTURES

Published in Journal of the Mechanical Behavior of Biomedical Materials, 54 (2016) 123–130

Tribocorrosion behavior of veneering biomedical PEEK to Ti6Al4V structures

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Abstract

In dentistry, prosthetic structures must be able to support masticatory loads combined with a high biocompatibility and wear resistance in the presence of a corrosive environment. In order to improve the simultaneous wear and corrosion response of highly biocompatible prosthetic structures, a veneering poly-ether-ether-ketone (PEEK) to Ti6Al4V substrate was assessed by tribocorrosion analyses under conditions mimicking the oral environment. Samples were synthesized by hot-pressing the PEEK veneer onto Ti6Al4V cylinders. The tribocorrosion tests on Ti6Al4V or PEEK/Ti6Al4V samples were performed on a reciprocating ball-on-plate tribometer at 30 N normal load, 1 Hz and stroke length of 3 mm. The tests were carried out in artificial saliva at 37 °C. Open circuit potential (OCP) was measured before, during and after reciprocating sliding tests. The worn surfaces were characterized by scanning electron microscope (SEM). The results revealed a lower wear rate on PEEK combined with a lower coefficient of

friction (COF), when compared to Ti6Al4V. In fact, PEEK protected Ti6Al4V substrate against the corrosive environment and wear avoided the release of metallic ions to the surrounding environment.

Keywords: Biotribology, Tribocorrosion, Ti6Al4V, PEEK, Sliding wear

3.1. Introduction

Titanium and its alloys are widely used in various fields of engineering (e.g. aerospace, shipbuilding) and medicine (e.g. orthopedics, implantology) due to their physico-chemical properties including high tensile strength (915-976 MPa), Young's modulus (110-120 GPa), biocompatibility and corrosion resistance [1-4]. Nevertheless, the mismatch in Young's Modulus between the titanium-based implant and bone tissue on occlusal loading can cause stress shielding at the peri-implant area. Thus, the Young's modulus of titanium-based implants should be closer to that of cortical bone tissue (8-18 GPa) to decrease the bone loss rate per year. In spite of efforts accomplished up to date on titanium alloys, there is still a mismatch in the mechanical properties of implants and bone tissue [4,9].

Titanium forms an oxide film, mainly composed of TiO_2 , which spontaneously covers the titanium surface. TiO_2 -based film play an important role in the corrosion resistance and biocompatibility of titanium implants [2,5]. However, titanium can corrode in the oral environment releasing metallic ions to surrounding tissues [2,6]. For instance, Souza et al. [41] reported a progressive corrosion process of titanium in artificial saliva containing fluorides. Localized corrosion was detected after immersion in 12,300 ppm F solutions. In addition, titanium has poor wear resistance which increases its degradation in contact with body fluids. In the case of dental implants, contacting surfaces at abutment-implant joints are exposed to sliding wear in presence of saliva and hard particles from food intake or tooth brushing [2,5]. In orthopedic implants, the sliding contact takes place between articular joints which are exposed to body fluids. A major concern regarding the toxicity of the wear particles released into the human body during the performance of the orthopedic implants has been reported in literature [6, 27-35]. Wear debris and ions release produced due to the loss of material by bio-tribocorrosion of titanium-based prosthetic surfaces have been related to tissue inflammatory reactions [6, 27-35]. The presence of metallic ions and particles in human tissues induces the activation of macrophages, neutrophils, and T-lymphocytes with elevation of cytokines and metallic proteinases that can promote bone resorption [29,30]. Coalescence of particles of all classes (including titanium particles) originating from prostheses was often seen in the vesicles of

macrophage cytoplasm in the liver (0.1–10 μm in diameter), spleen, and para-aortic lymph nodes [30-33]. In the lymph nodes, titanium particles ranged from 0.1 μm up to 50 μm , while in the liver and spleen the particles ranged from 10 μm [32]. Hallab et al. [34] investigated the binding of metals such as Ti, Co, Cr, Al (originating from implant wear and corrosion) to serum proteins that can mediate immune reactions [34]. Even though the long-term biologic effect of circulating metals is not completely known, it could be determined by the detection and characterization of these metal–protein complexes [34]. After wear tests of titanium alloys in vitro, Okazaki et al. [35] verified a low cellular growth in mediums containing Al and V compared to that in free-Al and free-V mediums. This indicates a potential cytotoxic effect of Al and V for human cells.

The degradation of titanium by simultaneous corrosion and wear in artificial saliva containing or not fluorides was also reported by Licausi et al. [64] and Souza et al. [46]. In fact, the degradation phenomena of titanium increased in presence of artificial saliva containing high fluoride contents [41]. Tribocorrosion is an irreversible process of degradation of materials due to the combined effect of corrosion and wear [5,7]. When such phenomena takes place in presence of biological tissues and fluids a bio-tribocorrosion system is established [6,8]. It is well known that the oral cavity is a complex environment where corrosive substances from dietary, human saliva and oral biofilms can substantially increase surface degradation processes, namely wear [46]. A passive film can be partially damaged or totally removed when the titanium surface is rubbed, depending on the severity of the wear conditions [14]. As reported by Souza et al. [41], the corrosion potential shifts to lower values due to the exposure of the bare metal to the solution. Thus, the corrosion potential measured during sliding is a result of the galvanic coupling between the passive metal on the unworn area and the bare metal on the worn track. When the sliding stops, repassivation occurs [2,7].

Biocompatible polymers and polymer-based composite materials have been considered as potential alternative to overcome the tribocorrosion processes occurring on titanium-based materials. Poly-ether-ether-ketone (PEEK) is a biocompatible polymer which has been recently studied due to its good mechanical properties such as Young's modulus around 3.6 GPa and tensile strength around 90-100 MPa [9,10]. The Young's modulus of PEEK can be increased up to 18 GPa by reinforcement with inorganic filler (e.g. carbon fibers (CF)). Such values are close to the cortical bone (10-18 GPa) [9–17]. Also, a CF/PEEK composite can reach a tensile strength at 180-200 MPa. Additionally, PEEK has good resistance to wear and fatigue, resulting in low coefficient of friction (0.10-0.17) for a large range of sliding conditions and low creep rate at about 250°C, especially when reinforced by carbon fibers [10,11]. Those

mechanical and tribological properties are attractive for biomedical applications [10,11–17]. Also it was reported that PEEK have an excellent thermal and chemical stability. PEEK is resistant to an extensive variety of organic and inorganic fluids. As a layer of material, this polymer can protect metal surfaces from corrosion [61]. Therefore, PEEK-based composites are gaining increasing interest as a possible alternative to titanium prostheses and implants applied in orthopedics and dentistry [58].

The main restriction of PEEK concerning, biomedical applications such as prostheses and implants, is its relatively low integration to bone [66]. Walsh et al. [66], reported the advantages of mechanical and physical properties of PEEK for implant devices, although the hydrophobic nature and the lack of direct bone contact remains a limitation. In order to overcome this issue, plasma-sprayed titanium coating onto PEEK was evaluated by mechanical and histologic analyses at the bone-implant interface. Thus, it was concluded that the plasma-sprayed titanium coating improved mechanical properties at the cortical bone sites while bone integration occurred at cortical and cancellous bone sites. Also, Han et al. [67] reported *in vitro* and *in vivo* behavior of PEEK coated with a thin Ti layer by using e-beam deposition method.

Veneering PEEK on Ti-based substrate can be useful for biomedical joints considering that titanium provides a high mechanical strength while PEEK enables enhanced biocompatibility and wear resistance to the assembly. In the case of abutment-implant or crown-abutment joints, such hybrid structure is able to support the masticatory forces combined with a high wear resistance avoiding the release of metallic ions from the substrate.

The main aim of this study was to investigate the tribocorrosion behavior of a hybrid structure based on veneering biomedical PEEK to Ti6Al4V structures for biomedical applications.

3.2. Materials and methods

3.2.1. Preparation of Ti6Al4V substrates

Cylindrical samples (8 mm diameter and 4 mm thick) were cut from Ti6Al4V (VSMPO TIRUS, US, ASTM B 348, Grade V) bars and wet ground on SiC abrasive papers down to 4000, followed by polishing with diamond paste down to 1 μm . After grinding, the samples were ultrasonically cleaned in isopropyl alcohol for 15 min and distilled water, and placed in a desiccator for 24 h before performing tribocorrosion tests. The chemical composition of Ti6Al4V alloy is given in Table 3.1.

Table 3.1 - Chemical composition (weight %) of the Ti6Al4V substrate following manufacturer's information.

Elements	Al	V	Fe	H	C	O	N
Ti6Al4V	6	4.05	0.02	0.003	0.01	0.1	0.008

The metallic substrate surface was abraded with alumina particles (~ 250 μm) with an impact angle of 90° under a pressure of 5 bars at a distance of 80 mm from the surface to obtain a rough surface, accordingly to the procedures reported by Ourahmoune et al. [21]. All blasting parameters were kept constant in order to guaranty similarity of surface roughness between all samples before PEEK deposition. After gritblasting, samples were ultrasonically cleaned in isopropyl alcohol during 15 min and then in distilled water for 15 min.

3.2.2. Veneering procedure

A poly-ether-ether-ketone (PEEK OPTIMA 450, Victrex, England) was selected as a biocompatible polymer veneer. The polymeric veneers were processed by the traditional hot-pressing (HP) technique (Figure 3.1). The veneering of PEEK onto the Ti6Al4V substrates was performed in a graphite cylindrical die with an internal diameter of 8 mm and 30 mm height. The Ti6Al4V cylinders were placed in the mold with its upper surface corresponding to the grit blasting treatment, as seen in Figure 3.1(A). Then, an appropriate volume of PEEK particles were placed in the mold (Figure 3.1(B)). In order to avoid the adhesion of PEEK material to the graphite punch, a mirror face polished Ti6Al4V sample was placed on top of the PEEK particles.

The following procedure was used: (1) the mold was placed inside the chamber where the veneering PEEK was compressed at 2 bars; (2) PEEK was heated up to the stage temperature at 380 °C (slightly above PEEK melting point at 345 °C) with a heating rate of 80 °C/min; (3) the temperature was decreased down to 300 °C; (4) at that stage, a pressure of 4 bars was applied and maintained for 4 seconds (Figure 3.1(C)); (5) then the power was turned off and the system cooled down to room temperature under vacuum (Figure 3.1(D)). Finally, a PEEK layer with 2 mm thickness was deposited on the grit blasted Ti6Al4V substrate. After cooling, PEEK was polished by using the same procedure of Ti6Al4V. The samples were cleaned in ultrasonic bath immersed in isopropyl alcohol for 15 min and then in distilled water for 15 min.

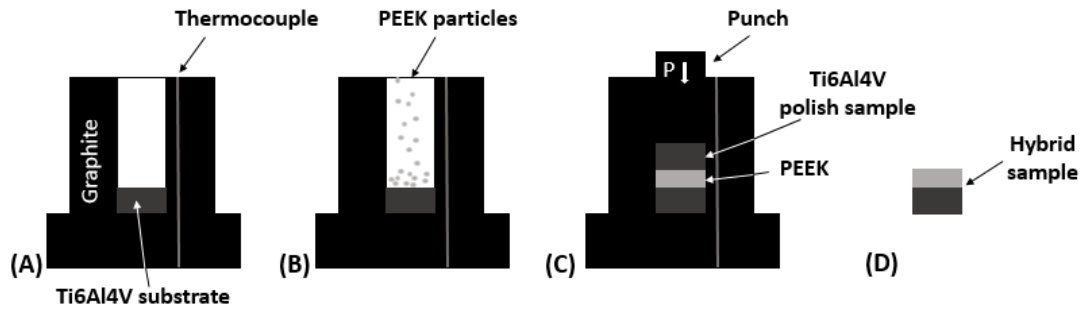


Figure 3.1 - Schematic representation of the hot-pressing process: (A) graphite mold containing the Ti6Al4V substrate, (B) introducing the veneering PEEK particles into the mold, (C) overall arrangement by applying pressure, and (D) veneering PEEK to Ti6Al4V sample.

3.2.3. Tribocorrosion tests

A modified Fusayama's artificial saliva (Table 3.2) was formulated for the tribocorrosion tests.

Table 3.2 - Composition of the stock Fusayama's artificial saliva [22]

Compounds	g/L
NaCl	0.4
KCl	0.4
CaCl ₂ · 2H ₂ O	0.795
Na ₂ S · 9H ₂ O	0.005
NaH ₂ PO ₄ · 2H ₂ O	0.69
Urea	1

To perform the tribocorrosion tests a reciprocating ball-on-plate tribometer (Bruker-UMT-2, USA) was used. The counterbody consisted of an alumina ball with 10 mm diameter (Al₂O₃, Goodfellow, USA). The samples were mounted in an acrylic electrochemical cell attached to the tribometer. The tribocorrosion tests were carried out into 30 ml of *Fusayama's* artificial saliva at 37 °C, mimicking the temperature and electrochemical behavior of the oral cavity [22].

Before starting up reciprocating sliding tests, the open circuit potential (OCP) was recorded on Ti6Al4V for 60 min using a potentiostat/galvanostat (Gamry 600, USA). A standard two-electrode electrochemical

cell was used for the electrochemical measurements, whereas saturated calomel electrode (SCE) was used as the reference electrode and samples having an exposed area of 0.5 cm² were used as the working electrode. The reciprocating sliding tests were performed at 30 N normal load, at a sliding frequency of 1 Hz, and a linear displacement amplitude of 3 mm under OCP measurement for 30 min. One set of each test condition was repeated five times ($n = 5$).

After the end of the sliding tests, the OCP was measured for another 60 min. After reciprocating sliding testing, wear volume was estimated by measuring the lateral width of the wear scars and using empirical mathematical equations assuming that the wear scars are formed by perfect ball geometry.

The volume loss values of the samples were determined by following the wear track model represented in Figure 3.2. The calculation of the mid zone area of the wear track was performed accordingly the schematic representation in Figure 3.3. The total volume loss of the wear track corresponding to the wear of the samples was calculated using the following Expression (3.1):

$$\Delta V = L \times \left[\frac{1}{2} \times R^2 \times 2 \sin^{-1} \left(\frac{s}{R} \right) - \frac{b \times h'}{2} \right] + \frac{\pi \times b^4}{64R} \quad (3.1)$$

where ΔV is the total volume loss of the wear track, in mm³, L is the stroke length in mm, R is the radius of the alumina ball in mm, s is the half of the width of the wear track ($s=b/2$) in mm and h' is the height of the triangle in mm (see Figure 3.3(B)).

The volume loss values were converted into specific wear rate using the following Expression (3.2):

$$k = \frac{\Delta V}{F \times S} \quad (3.2)$$

where k is the specific wear rate in mm³/N.m, F is the normal applied load in N and S is the total sliding distance in m.

The results were statistically analyzed following ANOVA at a significance level of $p < 0.05$.

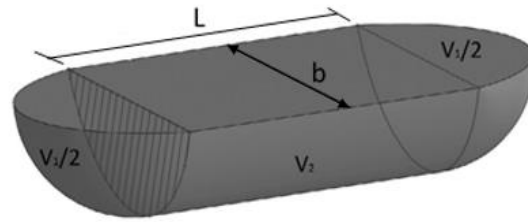


Figure 3.2 - Wear track model [23].

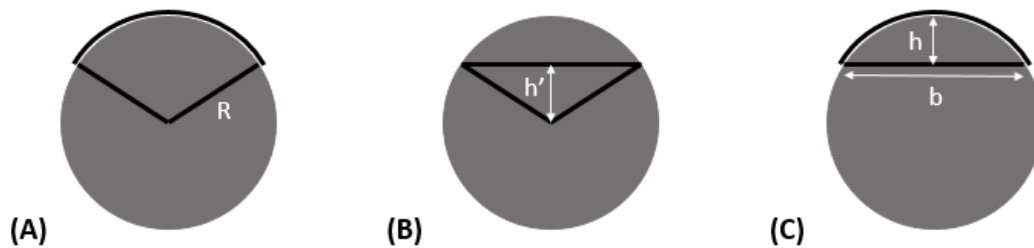


Figure 3.3 - Calculation of the area of the mid zone of the wear track: (A) Area of section, (B) Area of triangle, and (C) Real area of wear track.

3.2.4. Microstructural characterization

After the tribocorrosion tests, samples were ultrasonically cleaned using the same procedure previously presented. All the worn surfaces were inspected by Optical Microscopy (Leica DM 2500M, Leica Microsystems, Germany) and Field Emission Guns Scanning electron microscopy (FEGSEM, FEI Nova 200, USA). PEEK surfaces were sputter-coated with Gold-Palladium.

3.3. Results and discussion

3.3.1. Tribocorrosion measurements

The evolution of the OCP recorded for PEEK/Ti6Al4V or Ti6Al4V before, during and after the reciprocating sliding tests against Al_2O_3 is shown in Figure 3.4.

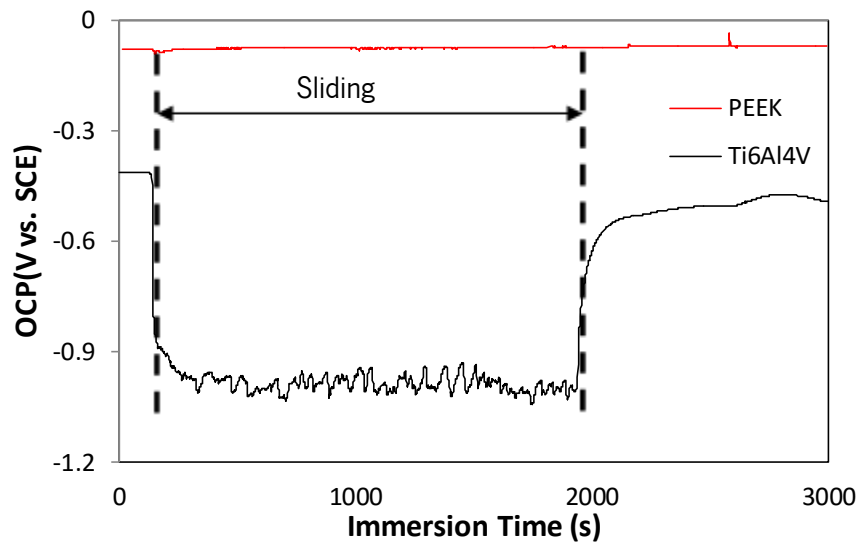


Figure 3.4 - Evolution of the open circuit potential (OCP) of PEEK/Ti6Al4V or Ti6Al4V immersed in artificial saliva solution at 37 °C in contact with Al_2O_3 ($F_N = 30$ N, displacement amplitude 3 mm, 1 Hz, 30 min of sliding).

Before the sliding tests, the OCP of Ti6Al4V immersed in artificial saliva stabilized at quite constant values. That indicates the presence of a passive film on the Ti6Al4V surface. Once stabilization was achieved, sliding tests were started. When the alumina ball was loaded onto that passive film and sliding is started, an abrupt drop in the OCP curve was noticed. That indicated the destruction of the passive titanium film named depassivation exposing the fresh active titanium in the wear track. Thus, a galvanic couple was established between worn and unworn areas in contact with the test solutions as reported by previous studies [2,24,25]. At the start of sliding, the OCP measured is a mixed potential which value depends on the state of undamaged and damaged materials. Then, the OCP decreased to a value that was maintained during the entire test indicating that active titanium reacts with the surrounding solution. During the sliding period, the material is not able to recover its protective passive film while the mechanical action of the reciprocating sliding alumina ball is in course. After unloading, the OCP immediately increased to initial value following from re-growth of a passive film on Ti6Al4V in the wear track. That phenomenon is named repassivation. Those observations are in accordance with the results presented by Souza et al. [2]. Chen et al. [1], also reported a similar trend of the OCP curve on the tribocorrosion behavior of Ti6Al4V and AISI 316 stainless steel in water or seawater. The drop in OCP was lower for AISI 316 stainless steel than for Ti6Al4V alloy.

On veneering PEEK to Ti6Al4V, the evolution of OCP curve revealed a different behavior. The OCP recorded on PEEK/Ti6Al4V was not altered due to the sliding. The thick layer of PEEK was preserved during sliding and, consequently, the alumina ball never established any direct contact with the titanium substrate. Therefore, it is expected that the OCP values remain constant during all course of the tribocorrosion tests, as confirmed by the obtained OCP measurement. Thus, comparing the OCP curves of PEEK and Ti6Al4V (Figure 3.4) it is proved that, as long as the PEEK layer does not break, the hybrid material has no tribocorrosion which makes this polymeric material very attractive for biomedical applications, particularly for dentistry and orthopedic implants or parts of biotribological devices.

The evolution of the coefficient of friction (COF) during sliding for both PEEK/Ti6Al4V or Ti6Al4V against Al_2O_3 immersed in artificial saliva at 37 °C is shown in Figure 3.5.

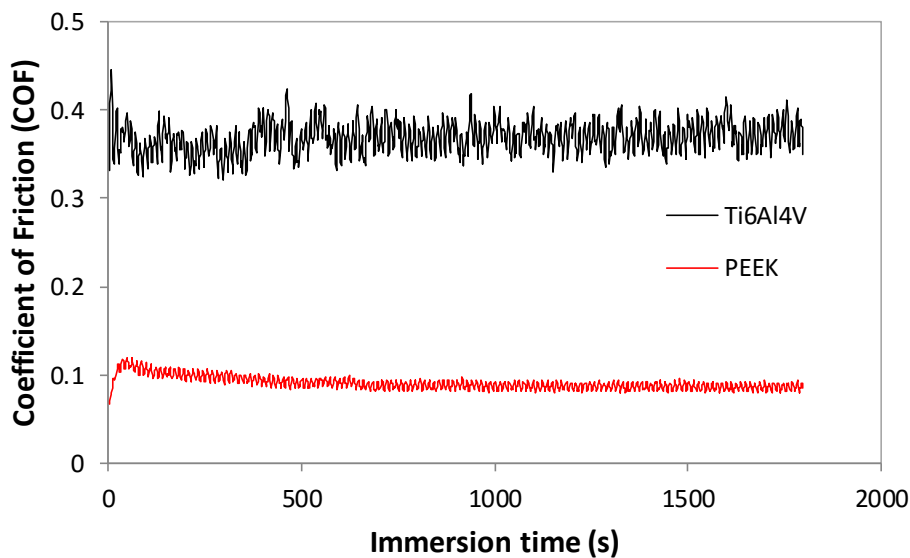


Figure 3.5 - Evolution of the coefficient of friction with time for Ti6Al4V and PEEK against Al_2O_3 in presence of modified Fusayama's artificial saliva at 37 °C ($F_N = 30$ N, displacement amplitude 3 mm, 1 Hz, 30 min of sliding).

In both cases, the COF attains the steady-state regime after a short running-in period, although the COF values recorded were more stable on PEEK than those on Ti6Al4V. The higher variation of COF for the contact involving Ti6Al4V surfaces can be attributed to the adhesive mechanism of friction, with the consequent transfer of metallic material to the ceramic counterface. The instabilities of friction values during sliding are typical of metal-on-metal sliding contacts and are related with the rupture of adhesion junctions established at the level of the real area of contact. Also, previous studies reported similar COF

oscillations during sliding caused by entrapment of wear particles in the contact region [6,9,25]. Concerning the COF mean values, a significant difference was found between the two contacts situations considered in this work. The COF measured on blank titanium sliding against alumina in artificial saliva was about 0.36, as reported by other studies [6,25]. However, the COF recorded when PEEK is involved in the contact was significantly lower, down to 0.07. Such value is close to one recorded on lubricated surface sliding contacts. Corroborating the COF results, the specific wear rate was significantly higher for Ti6Al4V ($k= 4.6 \times 10^{-4} \pm 5 \times 10^{-5} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}$) than that for PEEK ($k= 4.2 \times 10^{-5} \pm 3 \times 10^{-6} \text{ mm}^3\text{N}^{-1}\text{m}^{-1}$).

The COF mean values of titanium against alumina ball, at 3 N loading in artificial saliva solution obtained by Souza et al. [6] were between 0.45 and 0.50. Chen et al. [1] reported mean COF values on Ti6Al4V against alumina ball, in pure water or seawater at about 0.30 and 0.28. Also, a significant anti friction effect of seawater was noted in the tests although corrosion decreased the wear resistance of Ti6Al4V. Regarding the COF mean values recorded on PEEK, the results obtained in this study are in accordance with the results reported in literature. Sumer et al. [12] studied the tribological behavior of PEEK and PEEK reinforced by glass fibers (GF-PEEK) against AISI D2 steel discs immersed in water or under dry conditions. It was reported that the COF mean values on pure PEEK under dry conditions was slightly higher (0.37) when compared to those on GF-PEEK (0.27). On the other hand, the COF values recorded on PEEK immersed in water decreased down to 0.13. Also, COF values recorded on GF-PEEK in immersed water was about 0.11. In fact, the sliding under dry conditions can increase the temperature at the contacting surfaces that lead to the relaxation of polymer molecule chains, while the water prevents the increase of temperature under lubricated conditions.

In fact, there are limitations on *in vitro* studies concerning loading and environmental conditions. Mastication forces occurring during the chewing cycle have been reported ranging from 10 up to 120 N [6, 36, 37]. However, the magnitude of mastication forces generated on dental surfaces and prosthetic structures are influenced by the following factors: properties of the food bolus and prosthetic materials (thickness, elastic modulus, hardness); and human body features (muscle activity, gender, age, weight, presence of other dental prostheses) [27-31]. Also, the stress orientation is very important once axial loads promote the transfer of stress through prosthetic and implant structural materials to the bone tissue [6]. However, oblique loads can originate overloads on structural materials and on bone tissue that can promote failures by fatigue and wear of the implant-based system [6]. Regarding the environmental conditions, several artificial saliva solutions have been used to study the corrosion and tribocorrosion behavior of dental materials [2,5-8,22-25]. The formulation of artificial saliva solutions that react with the

test material in a way similar to that of natural saliva is not easy to achieve *in vitro*, concerning the unstable properties of human saliva [6,38]. Most of the reported artificial saliva solutions are a simplified version of what may actually occur in the oral cavity in terms of solubility of components and electrochemical behavior of dental materials [6,38].

3.3.2. Morphologic aspects of test sample surfaces after sliding

The representative morphology of the obtained wear tracks after the tribocorrosion tests are shown in Figure 3.6. The metallic worn surface (Figure 3.6(A),(B)) reveals a rougher appearance than that on the polymeric worn areas (Figure 3.6(C),(D)). Thus, Ti6Al4V denotes a higher level of surface degradation, which is in accordance with the results of OCP (Figure 3.4), COF (Figure 3.5) and specific wear rate. Concerning the wear mechanisms, Ti6Al4V worn surface is characterized by plastic deformation as a consequence of adhesive wear and also by the presence of grooves aligned along the sliding direction (Figure 3.6(A),(B)). Adhesion of material to the alumina contact surface as dispersed adherent tribolayers can be seen in Figure 3.6(E) (white areas) whose metallic nature was confirmed by EDS analysis (Figure 3.6(F)), thus confirming the transfer of material from Ti6Al4V alloy. Those mechanisms of surface degradation were responsible for the higher COF and specific wear rate (Figure 3.5).

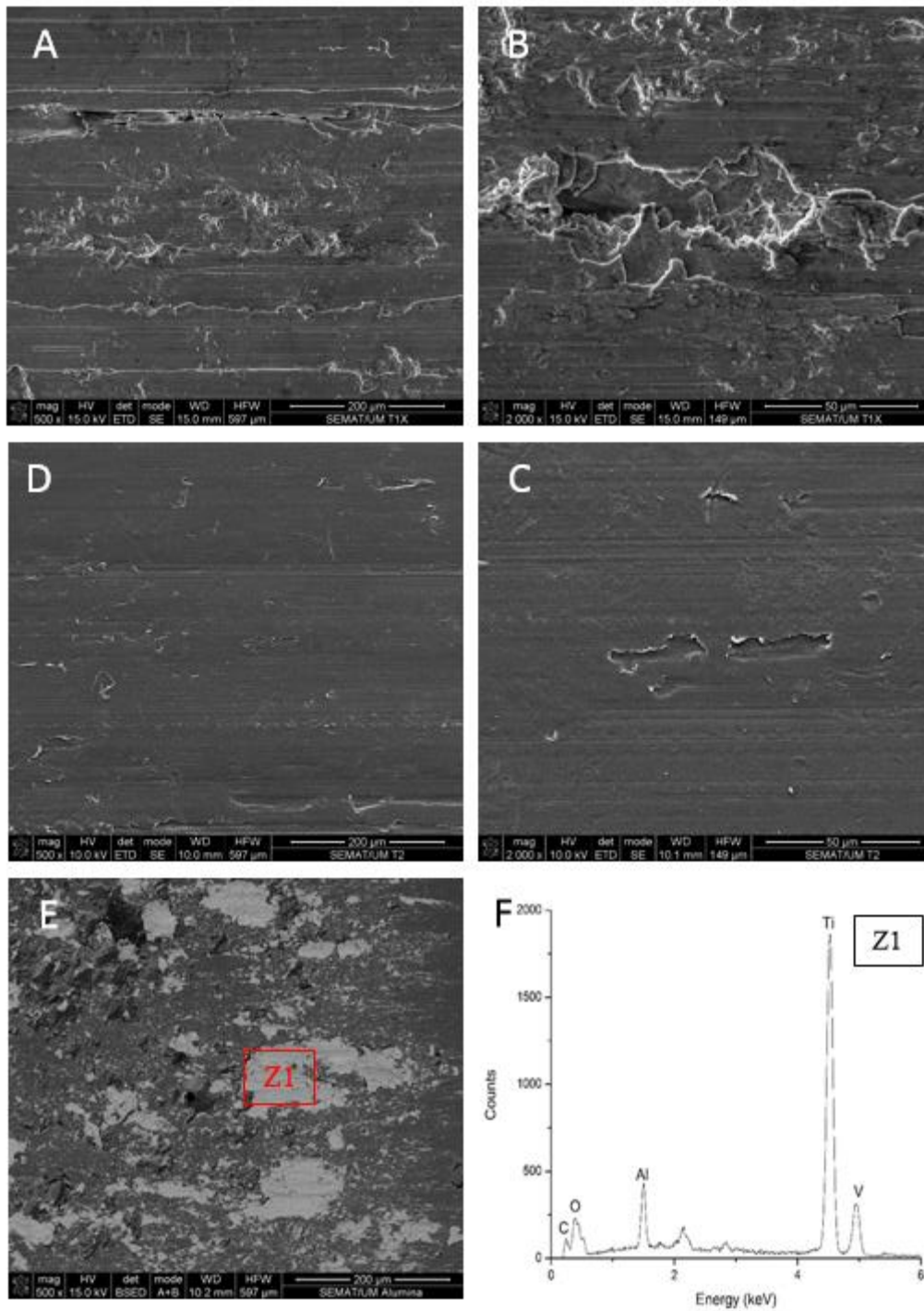


Figure 3.6 - FEG-SEM images of the worn surfaces after reciprocating sliding tests against Al_2O_3 immersed in artificial saliva at 37 °C: (A) and (B) Ti6Al4V; (C) and (D) PEEK; (E) Al_2O_3 ball after sliding against Ti6Al4V alloy and (F) EDS spectrum of Z1 of (E).

In the case of PEEK, the worn surface morphology denotes a relatively smooth appearance, with slight grooves aligned parallel to the sliding direction due to abrasion promoted by the ceramic counterface (Figure 3.6(D)). Concerning the Al_2O_3 contact surface, it revealed a clean appearance without signs of transfer of polymeric material. Therefore the tribocorrosion behavior of PEEK against alumina in presence of artificial saliva was mainly determined by smooth abrasion of the polymeric surface, resulting in low OCP combined with low friction and wear.

3.4. Conclusions

Within the limitations of this study, the main outcome of this work can be drawn as follows:

- Veneering PEEK to Ti6Al4V samples as hybrid structures were successfully synthesized by hot-pressing technique;
- Under tribocorrosion conditions against Al_2O_3 , the PEEK veneer protected the Ti6Al4V substrate from corrosion and wear, once the alumina ball did not contact the substrate;
- PEEK revealed lower coefficient of friction under tribocorrosion conditions against Al_2O_3 (0.07) than that recorded on Ti6Al4V (0.36);
- The specific wear rate of PEEK was one order of magnitude lower than that obtained for Ti6Al4V alloy;
- PEEK revealed high potential to be used as a veneering biomaterial to Ti6Al4V structures due to its biocompatibility combined with a low degradation by tribocorrosion mechanisms when immersed in artificial saliva. However, further tribocorrosion studies on PEEK and PEEK-based composites under different conditions (e.g. loading, electrolyte and temperature) are still required to the development of hybrid PEEK/titanium structures for biomedical applications.

Acknowledgements

This work has been supported by FCT (Fundação para a Ciência e Tecnologia -Portugal) in the scope of the project UID/EEA/04436/2013 and EXCL/EMS-TEC/0460/2012.

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Wear of PEEK/Ti6Al4V systems under micro-abrasion and linear sliding conditions

CHAPTER 4

A COMPARATIVE STUDY BETWEEN MICRO-SCALE ABRASION WEAR OF PEEK AND Ti6Al4V CONCERNING DENTAL APPLICATIONS

4. A COMPARATIVE STUDY BETWEEN MICRO-SCALE ABRASION WEAR OF PEEK AND Ti6Al4V CONCERNING DENTAL APPLICATIONS

Submitted for publication in Journal of the Mechanical Behavior of Biomedical Materials

A comparative study between micro-scale abrasion wear of PEEK and Ti6Al4V concerning dental applications

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Abstract

In the oral cavity, abrasive wear is inevitable at exposed tooth or restorative surfaces, during mastication and tooth brushing. Also, wear can occur at contacting surfaces between the Ti-based prosthetic structures and implants in presence of abrasive compounds from food or toothpaste. Thus, the aim of this work was to compare the abrasive wear resistance of PEEK and Ti6Al4V on three-body abrasion related to different hydrated silica content and loads. Surfaces of Ti6Al4V or PEEK cylinders (8 mm diameter and 4 mm height) were wet ground on SiC papers and then polished with 1 μm diamond paste. After that, surfaces were ultrasonically cleaned in propyl alcohol for 15 min and then in distilled water for 10 min. Micro-scale abrasion tests were performed at 60 rpm and on different normal loads (0.4, 0.8 or

1.2 N) after 600 ball revolutions using suspensions with different weight contents of hydrated silica. After the abrasive tests, wear scars on flat samples were measured to quantify the wear volume and characterized by scanning electron microscope (SEM) to identify the dominant wear mechanisms. The results showed a higher volume loss rate on PEEK than that recorded on Ti6Al4V, when subjected to three-body abrasion tests involving hydrated silica suspensions. An increase of the volume loss was noted on both tested materials when the abrasive content or load was increased. PEEK was characterized by less wear resistance than that of Ti6Al4V after micro-scale abrasion wear in contact with hydrated silica particles, as commonly found in toothpastes.

Keywords: Micro-scale abrasion, Bio-tribology, PEEK, Ti6Al4V, Hydrated silica

4.1. Introduction

Titanium and its alloys are widely used in several fields of engineering (e.g. aerospace, shipbuilding) and medicine (e.g. orthopedics, implantology), exhibiting excellent mechanical and physical properties, biocompatibility and corrosion resistance [1–5]. However, titanium has poor wear resistance which increases its degradation in body environments. Titanium forms an oxide film, mainly composed of TiO_2 , which spontaneously covers the titanium surface that play an important role in the biocompatibility of titanium implants [2,]. In orthopedic articular implants, the sliding contact exists between components which are exposed to body fluids. In the case of dental implants, their contacting surfaces are subjected to sliding wear in presence of saliva at acidic pH and hard particles from food intake or tooth brushing [2,6]. Degradation of titanium-based structures can take place by simultaneous wear and corrosion of physiologic environment. This phenomenon has been the target of study, in order to prevent failures of dental restorations, implant, and prostheses. Also, the wear debris originated from degradation of structural materials can become toxic for human tissues [7].

Biocompatible polymers and polymer-based composite materials have been considered as potential alternative to titanium-based structures in orthopedics, implant and prostheses. Poly-ether-ether-ketone (PEEK) is a biocompatible polymer which has been recently studied due to its good mechanical properties such as low elastic modulus around 3.6 GPa [8,9]. Therefore, PEEK-based materials gather increasing interest as a possible alternative to titanium-based prostheses and implants in orthopedics and dentistry,

once the elastic modulus is increased up to 18 GPa by the reinforcement with carbon fibers. Such elastic modulus can be close to the bone tissue (10-18 GPa) leading to a match in mechanical behavior [8,10].

The oral cavity is a complex environment in which corrosive substances from dietary, human saliva and oral biofilms can substantially amplify surface degradation processes by simultaneous wear and corrosion [7]. Wear by two-body abrasion in the oral environment takes place when surfaces are in sliding contact in the absence of hard particles. For instance, such condition occurs mainly in non-masticatory tooth movement or due to bruxism [11–13]. Wear can also be a consequence of masticatory and teeth brushing process as abrasive, considering particles from food intake or toothpaste increase the abrasive wear damage of tooth or restorative surfaces. Hard abrasive particles originated from food intake or toothpaste promote three-body abrasion mechanisms in the degradation process of tooth surfaces during mastication or tooth brushing [11–14]. The compounds often present in a tooth paste are surfactants, humectants, gelling, flavors, preservatives, colors, sweeteners and abrasives [15]. Among those compounds, abrasives ensure the removal of residues from dietary and oral biofilms. The most commonly used abrasives in tooth paste are hydrated silica, calcium carbonate and sodium bicarbonate at contents ranging from 10 up to 40 (wt. %) and mean diameter between 4 and 12 μm [15].

Micro-scale abrasion or ball cratering test, is a technique for assessing the wear resistance of coated and surface engineered components [16]. Such test consists in a mechanical system with a rotating ball on a flat test surface in the presence of a suspension containing abrasive particles, generating a wear scar on the surface of the material [11,14,16]. Trezona et al. [17], used this technique to investigate the three-body abrasion resistance of soft materials such as polymers and soft metals on low load. The authors concluded that the wear volume of soft materials is proportional to the normal load. Also, a high abrasive content suspension is essential to guarantee the rolling wear and proper entrainment of the abrasive particles. Another previous study reported the high wear rate of materials related to the increase of size and hardness of the abrasive particles [18].

The main aim of this study was to compare the abrasive wear behavior of PEEK and Ti6Al4V by ball-cratering tests in order to evaluate the susceptibility of these materials to surface degradation by three-body abrasion under conditions mimicking dental applications.

4.2. Materials and methods

4.2.1. Preparation of test samples

Ti6Al4V cylinders (8 mm diameter and 4 mm thick) were cut from bars (Ti6Al4V, VSMPO TIRUS, US, ASTM B 348, Grade V) and wet ground on SiC abrasive papers down to 4000, followed by polishing with 1 μm diamond paste. After grinding, the samples were ultrasonically cleaned in isopropyl alcohol for 15 min and distilled water, and placed in a desiccator for 24 h before performing micro-scale abrasion tests.

PEEK samples (PEEK OPTIMA 450, Victrex, England) were processed by the traditional hot-pressing (HP) technique on a graphite cylindrical die with an internal diameter of 8 mm and 30 mm height, as seen in Figure 4.1. A mirror face polished Ti6Al4V cylinder was placed on the bottom of the graphite die to avoid the adhesion of the PEEK to the graphite and obtain a homogenous sample (Figure 4.1(A)). Then, a proper volume of PEEK particles was placed in the mold (Figure 4.1(B)). Another mirror face polished Ti6Al4V cylinder was placed on the top of the PEEK particles (Figure 4.1(C)). The following procedure was used: (1) the mold was placed inside the chamber where the sample was compressed at 2 bars; (2) PEEK was heated up to 380 °C (slightly above PEEK melting point at 345 °C) with a heating rate of 80 °C/min; (3) after, the temperature was decreased to 300 °C; (4) at the stage, a pressure of 4 bars was applied and maintained for 4 s (Figure 4.1(C)); (5) then the power was turned off and the system cooled down to room temperature under vacuum (Figure 4.1(D)).

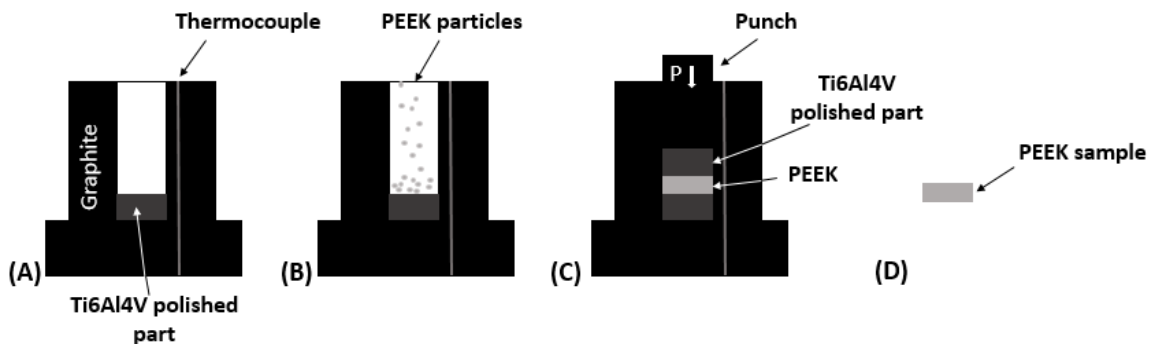


Figure 4.1 - Schematic representation of the hot-pressing process to obtain PEEK samples: (A) graphite mold with the Ti6Al4V polished part inside, (B) introducing the PEEK particles in the mold, (C) overall arrangement with applying pressure, and (D) final PEEK sample.

4.2.2. Details on micro-scale abrasion tests

Micro-scale abrasion tests were performed using a TE-66 micro-scale abrasion equipment (Phoenix Tribology Ltd, UK) schematically shown in Figure 4.2. The samples were mounted on an aluminum plate which was attached to the micro-scale abrasion machine. Different weight contents of 8-10 μm hydrated silica (Tixosil 73, Solvay) were prepared by dilution in distilled water, as follow: 1/32, 1/16, 1/8, 1/4. The abrasive suspension was maintained homogenized during the tests with the placement of the suspension container on a magnetic stirrer. Samples tested in distilled water were used as control group.

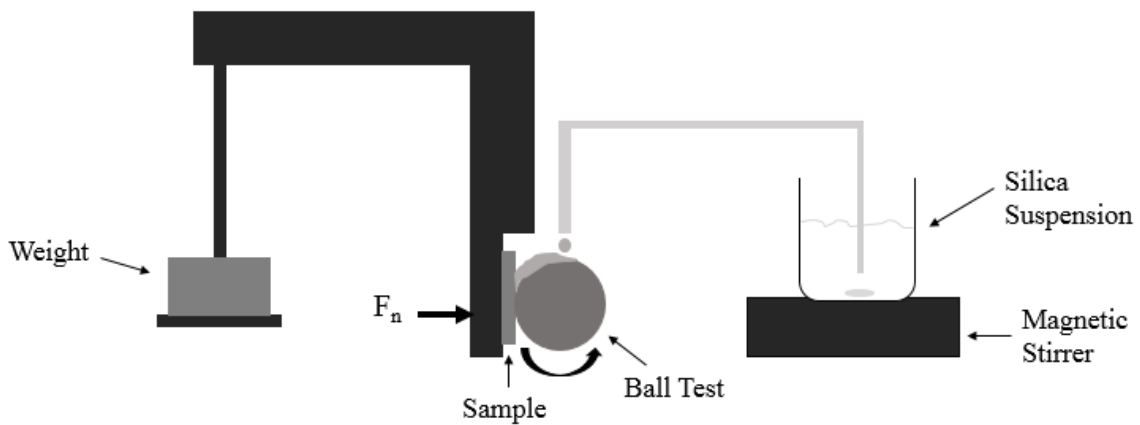


Figure 4.2 - Schematic representation of the micro abrasion test.

The micro-scale abrasion tests were performed against a stainless steel ball (ASTM 52 100) with 25 mm diameter rotating at 60 rpm for 600 revolutions. Also, three different values of normal applied load (F_n) were tested (0.4, 0.8 and 1.2 N) with 1/32 (wt. %) hydrated silica suspension to evaluate the influence of loading. Three experiments were performed per test condition.

4.2.3. Volume loss

The volume loss of tested samples was estimated based on wear scar diameter measurements and assuming that the morphology of the craters are similar to the shape of the test ball. Therefore, the volume loss can be calculated using Expression(4.1)[16]:

$$\Delta V = \frac{\pi \times b^4}{64R} \quad (4.1)$$

Where V is the crater volume, b is the crater diameter and R is the radius of the test ball where $b \ll R$. The diameter of each wear scar was measured by optical or scanning electron microscopy.

4.2.4. Microstructural characterization

After the micro-scale abrasion tests, samples were ultrasonically cleaned in propanol for 15 min and the worn surfaces were characterized using optical microscopy (Leica DM 2500M, Leica Microsystems, Germany) and field emission guns scanning electron microscopy (FEGSEM, FEI Nova 200) in secondary electron (SE) mode. Previously to FEGSEM characterization, PEEK samples were sputter-coated with gold-palladium.

4.3. Results and discussion

4.3.1. Micro-scale abrasion wear measurements

The volume loss recorded for PEEK and Ti6Al4V on ball-cratering tests at 0.4 N for different hydrated silica contents in distilled water is shown in Figure 4.3.

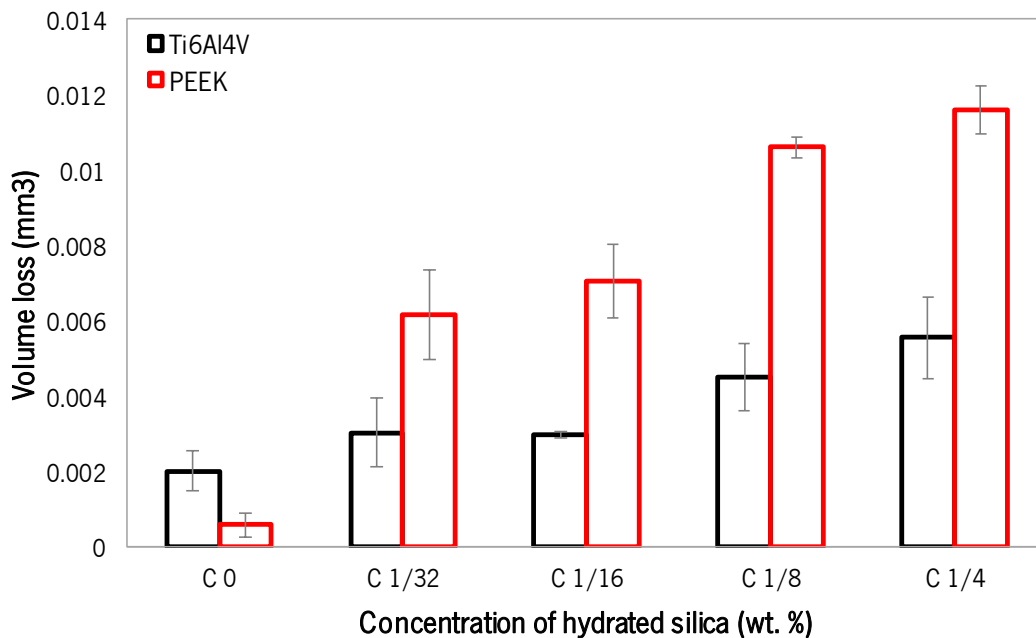


Figure 4.3 - Volume loss of PEEK and Ti6Al4V after micro-abrasion tests for different hydrated silica content in distilled water ($F_n=0,4 N$).

As seen in Figure 4.3, Ti6Al4V revealed a higher volume loss than that recorded on PEEK in 0% hydrated silica solution (only distilled water). This is in accordance with the results found by the authors for the same materials in reciprocating sliding tests against alumina in artificial saliva solution [23]. However, the volume loss gradually increased when hydrated silica was added to distilled water and PEEK revealed a lower abrasive wear resistance than that exhibited by Ti6Al4V. These results indicated a high sensitivity of PEEK to micro-scale abrasion wear compared to that on Ti6Al4V. That can be explained considering the lower hardness of PEEK (83 HV) [19] when compared to Ti6Al4V (350-370 HV) [7,20,21]. However, in the case of PEEK, the evolution of volume loss tends to stabilize for higher concentrations of hydrated silica. This trend could be explained by the decreasing of contact pressure between abrasive particles and PEEK for higher concentration of hydrated silica, thus reducing the intensity of micro-scale abrasion on the softer tested material. This observation can be related with the morphological features of worn surfaces as discussed in the next section.

The results of volume loss regarding the loading effect are shown in Figure 4.4. It can be seen an increase of the volume loss when the loading increased, that is in accordance with the fundamental laws of wear [22]. In addition, independently of the applied load, Ti6Al4V showed a higher abrasion resistance than PEEK as similarly noted on the variation of hydrated silica content (Figure 4.3).

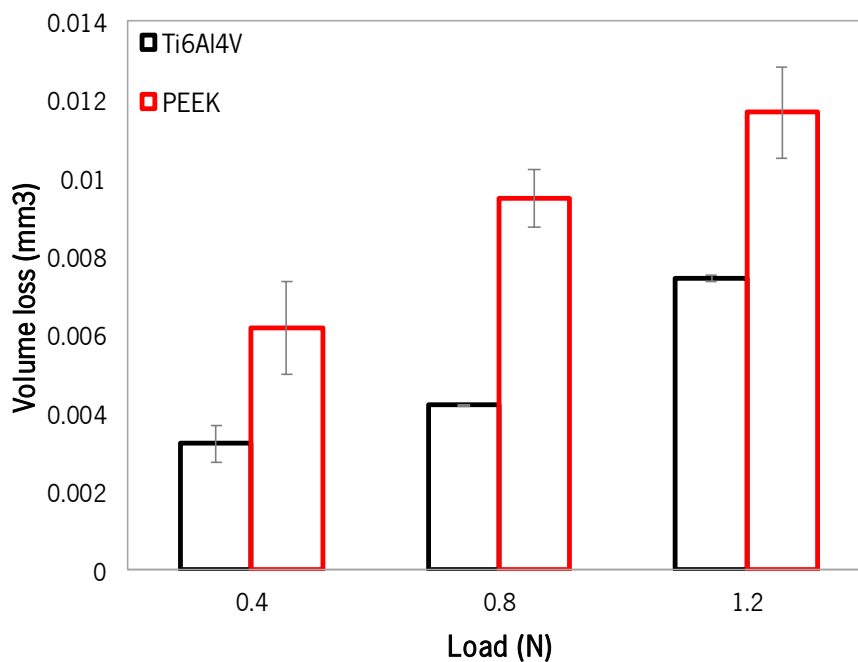


Figure 4.4 - Volume loss of PEEK and Ti6Al4V after micro-abrasion tests at constant concentration of hydrated silica (C1/32 wt. %) for different applied loads.

Considering the overall results, there is clear evidence that in presence of hydrated silica as abrasive suspension in distilled water, PEEK is more susceptible to micro-scale abrasion wear than Ti6Al4V. This behavior is mainly due to the lower hardness of PEEK when compared to Ti6Al4V. The same kind of wear response is expected to occur in dental applications involving these materials due to the micro-scale abrasion action promoted by the hard particles present in food or in tooth pastes. This is an important issue to be considered by dentists when choosing the appropriate material for specific oral parts of implants or prosthesis.

4.3.2. Wear scar morphology

The morphological features of worn surfaces in micro-scale abrasion tests are mainly determined by the nature, shape and size of the abrasive particles present in the slurry. In the present study, hydrated silica particles were used as abrasive agent, whose morphological features are shown in Figure 4.5. It can be seen that particles did not exhibit an overall spherical shape, having spikes on their surfaces. Concerning size, they varied from sub-micrometric particles to large particles having approximately 10 μm .

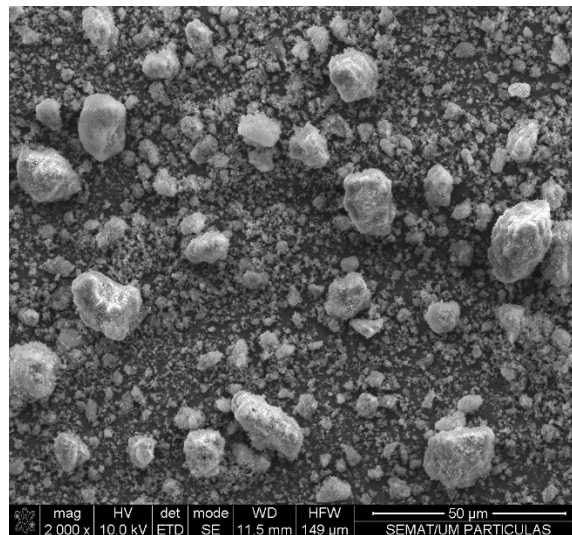


Figure 4.5 - FEGSEM micrograph of hydrated silica particles.

Figure 4.6 (A-D) shows representative morphologies of worn surfaces of Ti6Al4V and PEEK after micro-scale abrasion tests in presence of pure distilled water and in presence of 1/4 (wt. %) hydrated silica suspension.

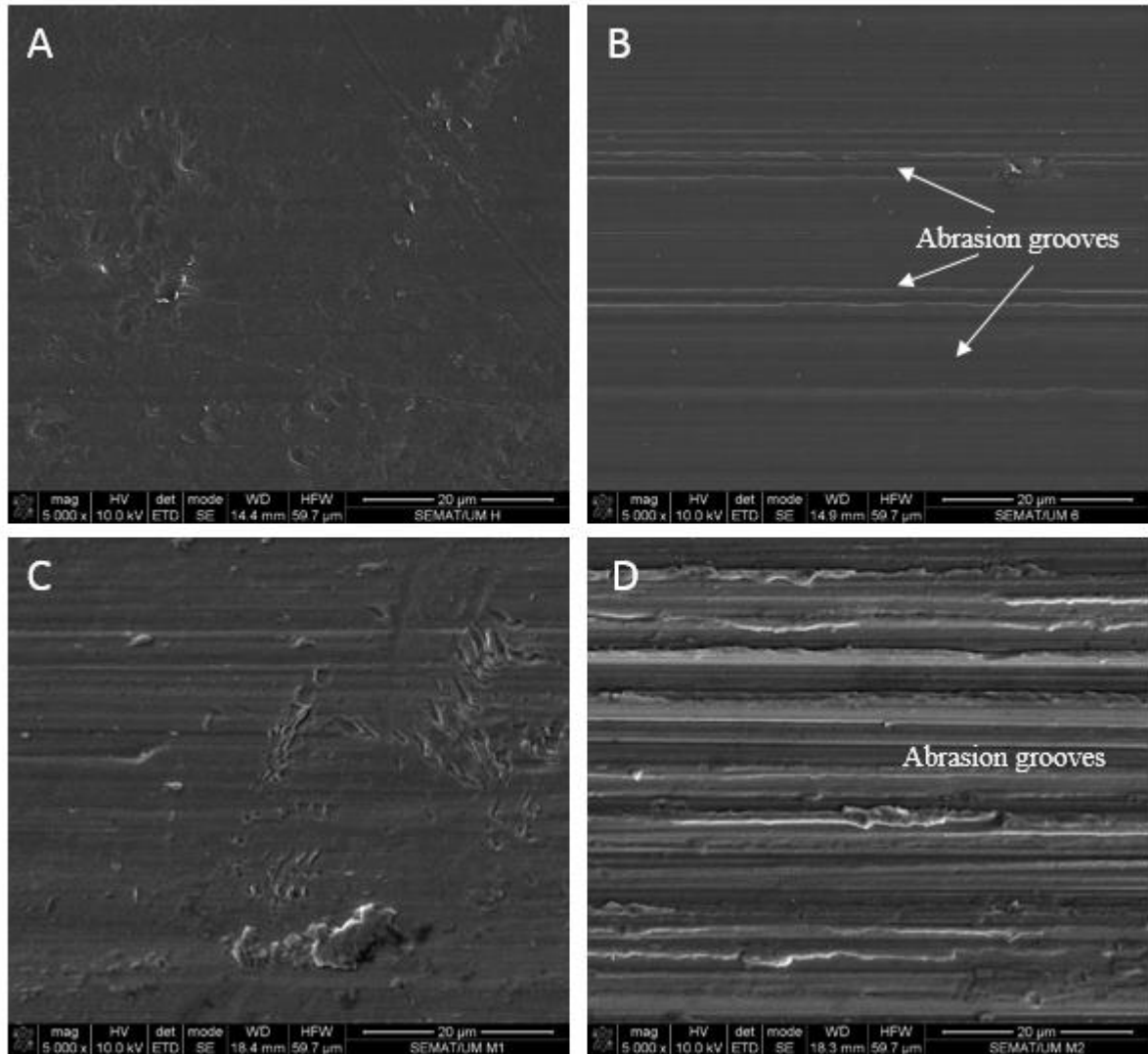


Figure 4.6 - FEGSEM images of the worn surfaces of PEEK (A and B) and Ti6Al4V (C and D) after micro-abrasion tests in presence of distilled water (A and C) and in distilled water with a concentration of 1/4 (wt. %) hydrated silica (B and D) ($F_n=0.4$ N).

As seen in Figure 4.6 (A and C), PEEK and Ti6Al4V worn surfaces are relatively smooth after micro-scale abrasion tests in distilled water without hydrated silica particles. The wear mechanisms were determined by the water lubricated sliding contact between the smooth surface of the bearing stainless steel ball and the tested sample. Nevertheless, the worn surface of PEEK (Figure 4.6(A)) evidences a smoother appearance than that of worn Ti6Al4V surface as in accordance with the results of volume loss in distilled water (Figure 4.3). Adhesion to the stainless steel ball counterface and two-body abrasion were the dominant wear mechanisms noted on Ti6Al4V (Figure 4.6(C)). On the tests performed in the presence of silica suspension, abrasion grooves aligned along the sliding direction are expected due to three-body abrasion action. That is shown in Figure 4.6 (B and D) although distinct morphologic aspects are

dependent on the nature of the tested sample. Abrasion grooves alternated with large flat regions on PEEK (Figure 4.6(B)) while the presence of abrasion grooves dominated on Ti6Al4V (Figure 4.6(D)). The volume loss of PEEK was significantly higher than that for Ti6Al4V (Figure 4.3) although a fine scale polishing mechanism was active on PEEK. This effect resulted in the smoothing at the flat regions of the polymeric wear scar with continuous removal of material, thus overlapping the intensity and quantity of abrasion grooves and contributing to the increase of wear volume.

The morphology of worn surfaces after micro-scale abrasion tests at different loads in presence of slurry with 1/32 (wt. %) hydrated silica is shown in Figure 4.7(A-F). It can be seen that all surfaces were abraded. The relatively low weight percentage of hydrated silica particles (1/32 wt. %), caused scratches due to ploughing and cutting on Ti6Al4V for higher loads, 0.8 and 1.2 N (Figure 4.7(C and E)). Thus, abrasion becomes more intense with the increasing of load. Wear grooves were more visible on Ti6Al4V than on PEEK as previously reported and discussed.

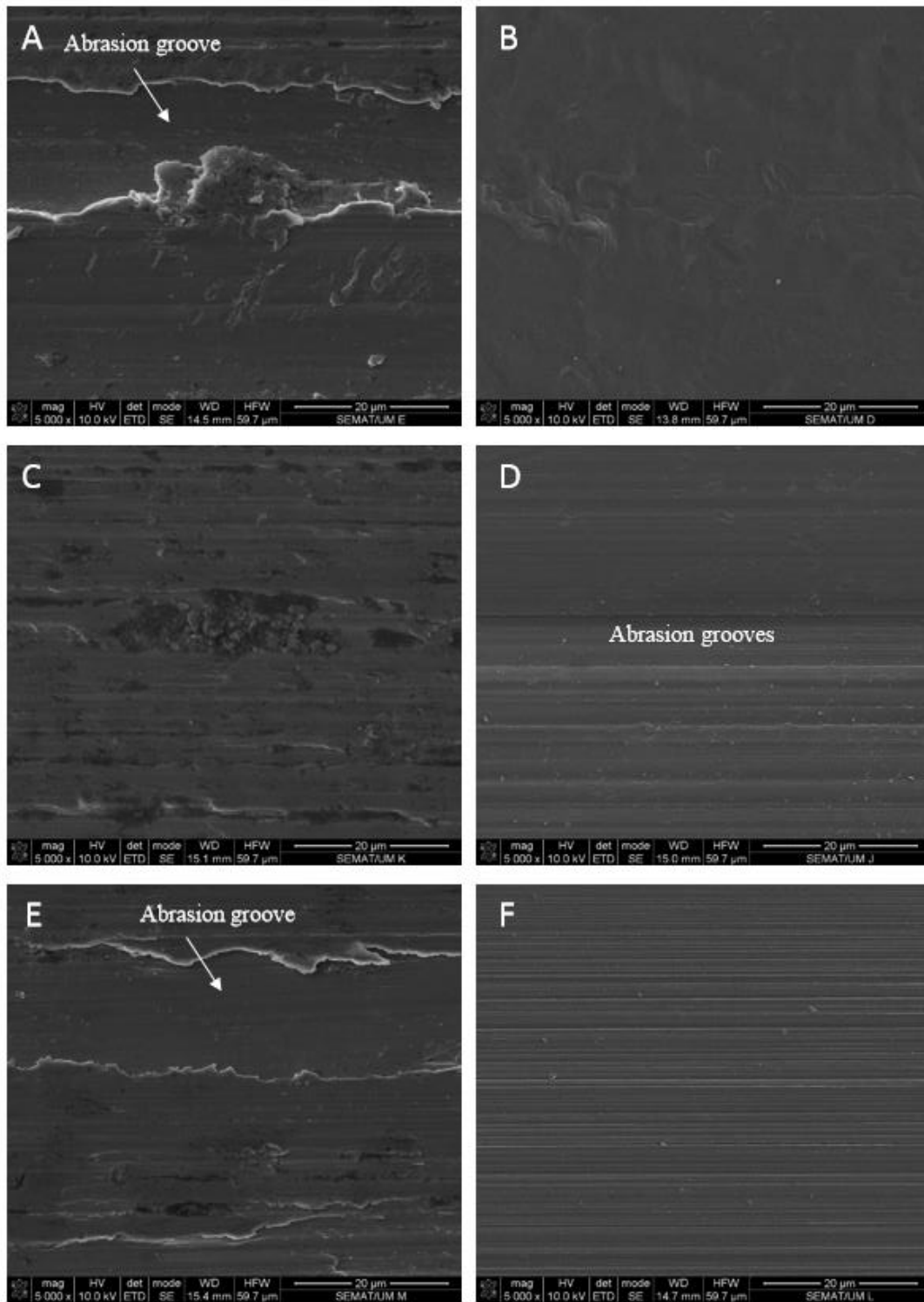


Figure 4.7 - FEGSEM images of the Ti6Al4V (A, C and E) and PEEK (B, D and F) worn surfaces after micro-abrasion tests in presence of slurry with 1/32 (wt. %) hydrated silica suspension at different loads: (A and B) 0.4 N; (C and D) 0.8 N; (E and F) 1.2 N.

On three-body abrasion, abrasive particles could roll instead of being permanently in cut [22]. This is a beneficial effect that contributes to the decreasing of wear volume. Figure 4.8 presents a particular detail of Ti6Al4V worn surface evidencing a wear groove that was suddenly interrupted possibly due to the rotation of an abrasive particle. This mechanism, being active on Ti6Al4V, was not found on PEEK wear scars. That view supports the higher abrasive wear resistance of Ti6Al4V than PEEK in micro-scale abrasion tests in contact with hydrated silica suspension.

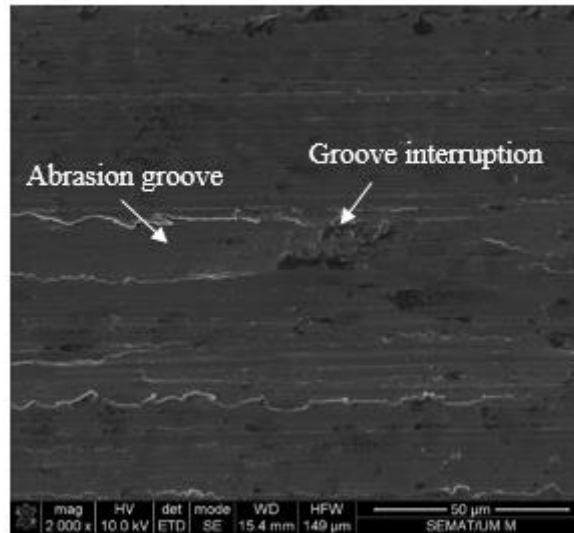


Figure 4.8 - SEM image of Ti6Al4V worn surface showing an abrasive wear groove that was interrupted due to rotation of the abrasive particle ($W= 1.2\text{ N}$; concentration of 1/32 (wt. %) hydrated silica).

4.4. Conclusions

The present study compared the abrasive wear on PEEK and Ti6Al4V by ball-cratering tests to evaluate the susceptibility to surface degradation in dental applications involving the contact in presence of abrasive suspensions commonly found in toothpastes. The main outcome of this work can be drawn as follows:

- In the absence of hydrated silica particles (two-body abrasion conditions in presence of pure distilled water), PEEK exhibited higher wear resistance than Ti6Al4V.
- PEEK revealed lower wear resistance than Ti6Al4V in the case of micro-scale abrasion tests using slurry consisting in distilled water with different contents of hydrated silica suspensions.

- An increase of the volume loss was noted on both tested materials when the slurry abrasive content or load was increased.
- The amount of abrasive particles present in the oral cavity during tooth cleaning or mastication play an important role on the degradation of dental restorative structures by wear, being this aspect more critical for PEEK than for Ti6Al4V dental restorative parts.

Acknowledgements

This work has been supported by FCT (Fundação para a Ciência e Tecnologia) in the scope of the project UID/EEA/04436/2013 and EXCL/EMS-TEC/0460/2012.

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Wear of PEEK/Ti6Al4V systems under micro-abrasion and linear sliding conditions

CHAPTER 5

GENERAL DISCUSSION

5. GENERAL DISCUSSION

When the dental implant is simultaneously exposed to mechanical stress (e.g. mastication loads) and chemical degradation (e.g. physiological environment), this synergy can be responsible for failures of implant systems.

As reported in the technical literature, titanium and its alloys are the first choice materials used to synthesize orthopedic and dental implant systems. The main problem with the metallic materials is the ions release to surrounding tissues, which stimulate peri-implant inflammatory reactions [1,2]. Then, veneering materials to titanium implant can be a potential strategy to avoid titanium degradation and ions release, as studied in the present work. Thus, PEEK becomes a very attractive material for biomedical applications, particularly for dentistry and orthopedic implants. The understanding of the wear and corrosion mechanisms of PEEK veneering Ti6Al4V is the key for the long-term performance of titanium in an oral environment.

Concerning previous *in vivo* and *in vitro* findings on the failure of implant systems, some relevant parameters on wear and corrosion were investigated in this work. Also, the PEEK veneering to titanium was evaluated regarding the tribocorrosion issue resulting in the following present studies: (i) tribocorrosion of hybrid samples of PEEK/Ti6Al4V in artificial saliva; (ii) micro-abrasion behavior of PEEK/Ti6Al4V systems in abrasive slurry (distilled water solution with hydrated silica in different proportions).

5.1. Corrosion measurements

In this study, Open circuit potential (OCP) of Ti6Al4V was measured before, during and after reciprocating sliding tests. Before the sliding tests, the OCP recorded on Ti6Al4V immersed in artificial saliva stabilized at quite constant values, as seen in Figure 3.4, page 47. Generally, an increase of the OCP with time is attributed to the thickening of the oxide passive layer, while a decrease of OCP might be associated with breaks or partial dissolution of the passive film [3]. After OCP stabilization, the alumina ball was loaded onto that passive film. An abrupt drop in the OCP curve was noticed when the sliding was started,

indicating the destruction of the passive titanium film (depassivation) that exposed the fresh active titanium in the wear track (Figure 3.4, page 47). A passive film can be partially damaged or totally removed when the titanium surface is rubbed, depending on the severity of the wear conditions [4]. Mischler et al. [5], reported that a major cause of the overall degradation is attributed to the wear accelerated corrosion due to detachment of the passive film. In fact, the OCP measured was a mixed potential which value depends on the state of undamaged and damaged materials. During the sliding period, the material was not able to recover its protective passive film while the mechanical action was in course. After unloading, the OCP immediately increased to the initial values following from re-growth of a passive film on Ti6Al4V in the wear track (repassivation) (see Figure 3.4 page 47). Souza et al. [6,7] and Licausi et al. [8], reported a similar behavior of the OCP recorded on Ti6Al4V in presence of artificial saliva solution. Galliano et al. [9], reported the tribocorrosion behavior of plasma nitrided Ti6Al4V in 0.9% NaCl solution, while Fernandes et al. [10], stated the tribocorrosion behavior of plasma nitrided and plasma nitrided + oxidised Ti6Al4V alloy in a 0.9% NaCl solution. In the studies of those authors, the results of OCP had a comparable trend, which was also corroborated by the results obtained in this work.

On veneering PEEK to Ti6Al4V structures, the OCP remained constant during the sliding that indicated the protective effect of PEEK against tribocorrosion (see Figure 3.4, page 47). Another previous study reported the protective effect of a bioabsorbable polymer (PDLLA) veneering to Ti6Al4V under tribocorrosion [7]. However, such protective veneer was removed after 9 min of sliding exposing the Ti6Al4V to the environment. Then, the decrease of OCP values indicated the partial destruction of PDLLA in the wear track and then the destruction of the passive titanium film. Even though the PDLLA did not protect the Ti6Al4V structure against wear and corrosion for a long term period, that could be enough during implant placement. In addition, this polymer could act as a lubricant layer coating titanium implants during its placement into bone. Then, PDLLA can be absorbed during the osseointegration process.

5.2. Reciprocating sliding wear of PEEK veneering to Ti6Al4V samples

The evolution of the coefficient of friction (COF) during sliding for both PEEK/Ti6Al4V and Ti6Al4V against Al₂O₃ ball is shown in Figure 3.5 (page 48). The value of the COF obtained for contacts involving titanium was about 0.36, while the COF recorded on PEEK against alumina was significantly lower (0.07). Additionally, PEEK revealed specific wear rate one order of magnitude lower than that on Ti6Al4V. This is

in accordance with the results obtained from OCP measurements. Previous studies [6,7] reported similar COF values for titanium immersed in artificial saliva. Regarding PEEK, Greco et al. [11] reported a lower COF on PEEK (0.07-0.16) in dry conditions. At high sliding speeds the coefficient of friction of PEEK and its composites had a decreasing trend with increased load. Davim et al. [12], studied the wear and friction of PEEK and PEEK reinforced with glass or carbon against steel, under extensive dry sliding. Concerning friction, the authors concluded that PEEK reinforced with glass fiber showed a higher COF (0.25-0.36) than that on PEEK (0.21-0.32) and PEEK reinforced with carbon fibers (0.18-0.21). Alternatively, PEEK showed a less wear resistance, comparatively to PEEK composites. Sumer et al. [13], showed a comparative study between PEEK and PEEK reinforced with glass fibers (GF), under dry sliding and water lubricated conditions, against a AISI D2 steel disc. It has been reported that PEEK-GF presented a lower COF (0.12-0.28) than pure PEEK (0.15-0.37).

Regarding the morphological aspects of worn surfaces obtained in this work, the presence of wear debris was detected by the adhesion of Ti6Al4V alloy on the alumina ball, as confirmed by EDS analysis (Figure 3.6, page 51). Also plastic deformation and grooves aligned along the sliding direction can be seen in Figure 3.6, page 51. PEEK revealed a relatively smooth appearance, with slight grooves aligned parallel to the sliding direction due to abrasion promoted by the ceramic counterface.

5.3. Abrasive wear of PEEK veneering to Ti6Al4V

For micro-abrasion tests performed in this study, the volume loss of PEEK increased when hydrated silica was added to distilled water. PEEK revealed a lower abrasive wear resistance as compared to that of Ti6Al4V. This can be explained based on the lower hardness of PEEK comparatively to Ti6Al4V. Abrasion grooves were evidenced for both materials, although with more intensity on Ti6Al4V alloy (Figure 4.6, page 67). As expected, abrasion was more intense with increasing normal applied load (Figure 4.7, page 69).

Until now, there are no published works on microabrasion related to the materials considered in this work (PEEK and Ti6Al4V alloy). Trezona et al. [14], in their study about transitions between two-body and three-body abrasive wear on tool steel, analyzed the variation of wear volume after 30 m of sliding with different slurry concentrations and applied loads. One type of the realized tests was performed with F1200 SiC abrasive slurry against tool steel. With the increase of SiC volume fraction the wear volume increased up to a certain value, and then decreased. With the increase of applied load the wear loss also increased.

Gomez et al. [15] stated the effect of abrasive particle size distribution on the wear rate. SiC abrasive particles with average particle size on the order of 2 μm in one case and 6 μm in the other were used against ASTM 1020 carbon steel. The variation of wear volume as a function of active particles, showed similarities with Trezona et al. study [14] and also with the present work.

On three-body abrasion conditions, as it was the case of the present work concerning micro-abrasion tests, abrasive particles could roll instead of being permanently in cut [16,17]. This is a favorable situation comparatively with a two-body abrasion mechanism, decreasing the abrasion wear intensity. A particular detail revealing a wear groove that was interrupted possibly due to the rotation of an abrasive particle was evidenced on Ti6Al4V worn surface (see Figure 4.8, page 70).

5.4. References

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Wear of PEEK/Ti6Al4V systems under micro-abrasion and linear sliding conditions

CHAPTER 6

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

6. CONCLUSIONS AND SUGESTIONS FOR FUTURE WORK

6.1. Conclusions

The present study reported the tribocorrosion and micro-abrasion behavior of PEEK and Ti6Al4V in a comparative way and therefore the main outcomes of this work can be drawn as follows:

- Veneering PEEK to Ti6Al4V samples as hybrid structures were successfully synthesized by hot-pressing technique for tribocorrosion tests;
- Considering the tribocorrosion tests against an alumina ball, PEEK revealed a low coefficient of friction resulting in a higher resistance to sliding wear than Ti6Al4V. Thus, PEEK revealed high potential to be used as a veneering biomaterial to Ti6Al4V structures due to its biocompatibility combined with a low degradation by tribocorrosion mechanisms when immersed in artificial saliva;
- On the micro-abrasion tests, PEEK demonstrated a lower wear resistance than that obtained for Ti6Al4V in presence of abrasive particles. Thus, the amount of abrasive particles present in the oral cavity during tooth cleaning or mastication play an important role on the degradation of dental restorative structures by wear.
- Finally, it can be concluded that veneering PEEK on Ti-based substrate can be useful for biomedical joints considering that titanium provides a high mechanical strength while PEEK enables enhanced biocompatibility and tribocorrosion resistance to the assembly. In the case of abutment-implant or crown-abutment joints, such hybrid structure is able to support the masticatory forces combined with a high tribocorrosion resistance avoiding the release of metallic ions from the substrate.

6.2. Suggestions for future work

The experimental work on veneering PEEK to titanium structures should continue regarding the following issues:

- The influence of polymer thickness on the sliding and abrasive wear performance of titanium-based hybrid structures must be evaluated by reciprocating sliding tests concerning load and by micro-abrasion tests concerning abrasive particles content;
- The adhesion between PEEK and titanium-based substrate should be studied. Several surface treatments of titanium-based substrates can be performed in order to increase the bonding of PEEK to titanium;
- PEEK composites can be used to coat other metallic substrates than Ti6Al4V to increase the long term performance of dental or orthopedic prostheses and implants.