# Dental Implant (CpTi) Performance: Electrochemical and

# Tribocorrosive Investigation

ΒY

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# THESIS

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### DEDICATION

This thesis is dedicated to my family: my parents, sister, husband, and children. Without the constant encouragement, support, and high expectations set by my parents, I could never have achieved as much as I have thus far. Some say I have an unhealthy relationship with my sister, Gaya, because so much of my sense of self is wrapped up in her. To that I say, if your sister were half as awe-inspiring as mine, you would do the same. To my husband, what can I say, you are my rock, and the only person in this world that I truly trust to take care of me. To my children, Kalyani and Annesley, I hope I inspire you to achieve to your fullest potential. I have such high hopes for the two of you, but my greatest hope is that I continue to be the mother you deserve.

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### LIST OF ABBREVIATIONS

C <sub>dl</sub>	Double Layer Capacitance (F)	
CE	Counter Electrode	
CPE	Constant Phase Element	
CPTI	Commercially Pure Titanium	
E <sub>corr</sub>	Corrosion Potential (V)	
EIS	Electrochemical Impedance Spectroscopy	
F	Faraday's Constant (96500 C mol <sup>-1</sup> )	
I	Total Current (A)	
I <sub>corr</sub>	Corrosion Current (A)	
I <sub>pass</sub>	Passivation Current Density (A)	
K <sub>c</sub>	Total Weight Loss Due to Corrosion (g)	
K <sub>w</sub>	Total Weight loss Due to Wear (g)	
K <sub>wc</sub>	Total Weight Loss Due to Wear and Corrosion(g)	
Μ	Atomic Mass (equivalent weight)	
OCP	Open Circuit Potential	
PD	Potentiodynamic	
PDL	Periodontal Ligament	
Q	Electric Charge Passed	
RE	Reference Electrode	
R <sub>p</sub>	Polarization Resistance (ohms)	
R <sub>sol</sub>	Resistance of Solution	
SCC	Stress Corrosion Cracking	
SD	Standard Deviation	
SEM	Scanning Electron Microscopy	
т	Exposure Time (sec)	

# LIST OF ABBREVIATIONS (continued)

W	Wear
WE	Working Electrode
Z	Number of Electrons Involved in Corrosion Process
ZCPE	Impedance of CPE

#### SUMMARY

The electrochemical corrosive nature and tribocorrosion nature of commercially pure titanium was investigated in this two-part, controlled, baseline study. Chapters 1 and 2 focus on defining the dental implant system as well as characterize the types of wear inherent in the system. In addition, titanium will be investigated as its use for dental implants in an effort to understand its corrosion mechanism. The use of titanium as a biocompatible metal for dental implants will be discussed, along with the tribocorrosive nature of titanium dental implants.

Chapter 3 is presented in the form of a paper already published in the Journal of Oral Implantology: Electrochemical Behavior of Dental Implants (CpTi): Influence of pH of Artificial Saliva (AAID-JOI-D-11-00054). In this first study, six pH levels were chosen (pH 3.0, 4.5, 6.0, 6.5, 7.5, 9.0) in order to simulate varying pH conditions within the oral cavity. The pH range was chosen based on studies previously done showing that the average pH of saliva is 6.3, but can drop to close to 3.0 when certain foods and beverages are ingested, and rise to pH 9.0 when certain oral conditions exist (chronic inflammation). Artificial saliva was chosen as a medium in order to simulate oral conditions with dental implant components, specifically titanium abutments, and the neck of the implant coming into contact with saliva or saliva-like substances via the gingival crevicular fluid once placed. Electrochemical testing techniques (open circuit potential, potentiodynamic, and electrochemical impedance spectroscopy) were used to provide a representative method of accelerated corrosion process. Initially, the evolution of open circuit potentials (OCP) was monitored during a period of 3600sec. OCP tests were performed in order to take a look at the corrosion tendency of the sample. EIS tests were performed before and after sliding in order to determine the corrosion rate. Then the samples were anodically polarized from -0.8 V to 1.8 V at a scan rate of 5mV/sec. PD tests were performed to substantiate Ecorr (corrosion potential), and lcorr (corrosion current). After the corrosion tests, surface characterization was performed by optical and scanning electron microscopy (SEM). Weight loss was estimated based on profilometry measurements of the wear scar (white light interferometry microscopy ((Zygo New View 6300, Middlefield, CT, USA)). Potentiodynamic curves were unique

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### SUMMARY (continued)

to each pH, indicating behavior dependent on pH. Results indicated neutral pH (pH 7.5) exhibited the poorest corrosion resistance.

While Chapter 3 laid the groundwork, Chapter 4, expanded the study into tribocorrosion and the effect of varying pH on the tribocorrosive nature of titanium. Chapter 4 is presented in the form of a paper to be published in the Journal of Biomedical Materials Research Journal: Influence of pH on the tribocorrosion behavior of CpTi in the oral environment: Synergistic interactions of wear and corrosion. This study provides a more clinically relevant look at corrosion of dental implants. Dental implants are subjected to constant load via mastication force, concentrated at the neck of the implant and abutment/implant interface. This same area is in constant contact with a saliva-like substance, via the gingival crevicular fluid. The second study again utilizes artificial saliva, but subjects titanium disc specimens to sliding tests at three representative pH values: 3.0, 6.0 and 9.0. The sliding system was chosen in order to mimic fretting forces realized at the abutment/implant interface. Electrochemical test methods were again used to determine peak degradation. This study suggests greatest material degradation of CpTi at near neutral pH, pH 6.0, in the presence of sliding motion.

In chapter 5, a discussion of the results produced by both papers will be correlated and its clinical application will be discussed. Chapter 6 discusses conclusions, limitations, and future work.

The corrosion experiments were performed at the Tribology Group, Department of Orthopedic Surgery in Rush University Medical Center (RUMC). This work was developed under the advisement of Dr. Mathew T. Mathew.

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#### 1. INTRODUCTION

#### 1.1 Background

Teeth are commonly absent from the dental arch either congenitally or as a result of disease (caries and periodontitis are the most common). It is not axiomatic that a missing tooth be replaced, but there are many indications to do so, for example, to improve masticatory function, speech, improve appearance, or to prevent harmful changes in the dental arches such as supereruption or tilting/drifting of teeth. Clinicians have long sought to provide their patients with an artificial analogue of the natural teeth. Dental implant therapy can reduce the rate of alveolar bone resorption, provide a stable prosthesis, and avoid the need for tooth preparation<sup>1-4</sup>.

Titanium is the material of choice for dental implant therapy because of its innate biocompatibility with human tissues<sup>5</sup>. In addition, the protective passive oxide film layer on the surface of titanium aids in osseointegration of dental implants for long-term survival. Long-term survival rates for dental implants are high, achieving a 97% rate<sup>6</sup>; however, little is known about survival beyond 10 years. A true understanding of why implants fail is not yet known.

The oral cavity is a harsh environment for non-noble metals, with saliva at varying pH levels, bacteria load, and temperature coming constantly in contact with their surface <sup>7</sup>. Several studies have been performed looking at the corrosive nature of titanium at an acidic pH (5 or less). Few have looked at the electrochemical corrosion of titanium in artificial saliva. One aim of this thesis was to investigate the corrosive behavior of CpTi in artificial saliva at 37°C, as a function of pH values (3-9) and to characterize the titanium surfaces as a result of the corrosion process.

Dental implants are not only subjected to electrochemical corrosion, but they are subjected to tribological (wear) effects due to mastication<sup>8</sup>. The lack of pdl around an implant fixture means that the implant must absorb vertical and lateral occlusal forces rather than transmit them. These absorbed forces results in stress of both the implant fixture and surrounding bone. Small stress concentrations may occur along the entire body of the implant at the bone to implant interface;

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however, studies show that the stress is concentrated at the neck of the implant, or first threads of the implant, and at the implant/abutment interface <sup>9</sup>. These stress concentrations at the neck of the implant, may also lead to fretting force or micromovements between several components: the implant and bone itself, the abutment and implant body, the final restoration (if cemented) and abutment, and the prosthetic screw and implant body <sup>10,11</sup>. The implant/abutment interface, when placed ideally, is located just subgingival to the crest of the alveolar bone. Once placed and restored, some degree of marginal bone loss is realized. Although roughened implant body surfaces result in less marginal bone loss than machined implant bodies, marginal bone loss on the order of 1-2mm within the first two years of placement is commonly experienced <sup>12</sup>. Fig 1 below shows a dental implant with minimal marginal bone loss. In clinical studies, an association between implant loading and marginal bone loss around implants, or complete loss of osseointegration has been stated<sup>13</sup>. Because the stress concentration is greatest at the neck of the implant, and the abutment/implant interface is located close to the crest of the bone, it is possible that marginal bone loss may be affected by the fretting forces causing wear and corrosion. Fig 2 shows a dental implant with poor esthetic result due to excessive marginal bone loss. The combination of fretting movement in the presence of electrochemically active saliva results in a tribocorrosive system with synergistic activity of wear and corrosion<sup>14-16</sup>. It is not fully understood how and when marginal bone loss occurs. It is possible that the tribocorrosion process leads to marginal bone loss (detrimental effect) due to the release of metal ions and wear/corrosion particles, or it may protect implants from excessive bone loss (beneficial effect) due to the growth of protecting passive surface layers. This thesis looked at the tribocorrosive nature of CpTi in the presence of artificial saliva with varying pHs from 3-9 in a controlled environment in order to investigate 1) if tribocorrosion is dependent on the pH and 2) if pH affects the amount of material loss, in an effort to begin to understand possible implant corrosion pathways. Artificial saliva was used as a controlled, stable solution, to mimic gingival crevicular fluid, and an existing sliding system was used to simulate movement between an implant abutment and implant body.



Fig 1. Implant indicating minimal marginal bone loss.



Fig 2. Implant indicating excessive marginal bone loss.

#### 1.2 Significance

The oral cavity is a harsh environment for titanium dental implant therapy due to its many corrosive pathways. It is an electrochemical cell due to the presence of saliva. This allows for current development, resulting in corrosion. It is also an unstable environment, because of a constantly changing pH due to ingesting food and drink and systemic health conditions, changes in bacteria load, temperature, ion concentration, and biomolecules <sup>17</sup>. In addition, there is the potential for galvanic corrosion, especially with implant therapy, where two dissimilar metals may contact creating a current which will cause the less noble metal to corrode. Finally, titanium dental implants rely on a stable passive film to be corrosion resistant; however they are subjected to constant mastication forces, with the average force of 70-150N<sup>18</sup>. The resulting movements may disrupt the passive film leading to wear and corrosion. There are many failure mechanisms for dental implants, and marginal bone loss is evident to some degree for each implant system available<sup>19</sup>. Many studies have looked at possible causes of marginal bone loss, including time of

loading, peri-implantitis, and implant surface; however few studies have looked to see if corrosion of titanium could lead to marginal bone loss<sup>20</sup>.

Only a few studies have looked at the corrosive nature of titanium used for dental implant therapy <sup>21</sup>. Even fewer have looked at the tribocorrosive nature, or synergistic effect of wear and chemical corrosion on titanium dental implants<sup>14,22,23</sup>. This study investigates the potential mechanism of tribocorrosion in an effort to understand its role as a potential source of delays in osseointegration and/or eventual marginal bone loss around implants.

#### 1.3 Specific Aim

Titanium is highly reactive. It oxidizes instantaneously when exposed to any amount of oxygen forming a thin oxide layer on the metal's surface. This oxide layer protects the surface from rapid oxidation and slows down the rate of corrosion if exposed to biological fluids. In addition, adherence of biomolecules to the oxide layer facilitate osseointegration of titanium dental implants.<sup>21</sup>. The oxide layer formation, however, is a dynamic process, involving ion exchange, oxidation, biomolecule adherence and desorption, and corrosion occurring simultaneously. The Pourbaix diagram shows a classical representation of titanium behavior at 25°C in H<sub>2</sub>O. It suggests that titanium is most reactive at anodic potential and lower pH<sup>24</sup>. However, the Pourbaix diagram does not take into account corrosion kinetics influenced by wear or friction, changes in temperature, presence of salts and/or proteins. Because of this we do not know its behavior how it will behave in different solutions or at body temperature. (37°C). The purpose of this study was: 1) to understand how pH can affect the retention and formation of the oxide film, and 2) to understand the synergistic effect of wear and corrosion as a function of pH.

#### 1.4 Hypothesis

In this two-part study, we speculated that a more acidic pH will cause greater material degradation of CpTi. We hypothesized that (1) the corrosive as well as (2) the tribocorrosive behavior of CpTi in artificial saliva at 37°C is affected by pH. This hypothesis was based on

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previous observations performed by Rocha et al. and Ribeiro et al. who found that acidification of solution improved the electrochemical response of the material. In addition, when considering the oral environment, peri-implantitis has been linked to marginal bone loss around dental implants. The microbial flora of biofilm present as greater peri-implantitis persists changes to have a greater concentration of acid-tolerating bacteria<sup>25</sup>. This causes the pH of the biofilm to drop. This would lead one to believe that a more acidic environment could lead to greater material degradation via tribocorrosion. This release of metal ions into the tissues could illicit an immune response resulting in marginal bone loss.

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#### 2. REVIEW OF LITERATURE

#### 2.1 Dental Implants

The use of dental implants has become a routine method for replacing missing teeth for surgical and restorative dentists. In the US, about 300,000 patients currently receive dental implants per year <sup>1-4</sup>. The dental implant system was developed by Branemark in 1952. He discovered that titanium, under conditions that were carefully controlled, could fuse to the bone so solidly that it could not be removed <sup>4</sup>. This process is known as osseointegration. The term osseointegration refers to a direct fixed connection between the dental implant and living bone without an intervening layer of connective tissue between <sup>5-10</sup>. In 1965, his theory was tested when Branemark successfully placed his first titanium dental implants. Branemark inserted four titanium fixtures into a patient's edentulous mandible. Several months later, he used the fixtures as the foundation for a fixed set of false teeth. The fixtures survived, the patient's life was transformed, and dentistry began to adapt a new treatment modality <sup>2</sup>. Today, implants are used to treat both edentulous and partially edentulous patients. For edentulous patients, implants can provide a more secure option to a complete denture, by either helping to retain the denture with the placement of a few implants, or by providing the patient with a fully fixed treatment option. The fastest-growing treatment indication is the single-tooth replacement with a 97% survival rate<sup>8</sup>.

The most common type of dental implant that is placed today is the "endosseous root form implant." These implants are designed to use a vertical column of bone for support, similar to the root of a natural tooth. The term "endosseous" refers to the fact that the implant is embedded into the jawbone. The bone of the jaw osseointegrates with the titanium of the implant body, essentially, the bone fuses directly with the surface of the implant <sup>11</sup>. An integrated implant differs from a natural tooth because it does not have a protective periodontal ligament (pdl) between the surface of the implant body and the bone. The pdl acts as a shock absorber transferring force away from the tooth/bone interface. Lack of a pdl means that proprioception will be less resulting in a difference of feel upon chewing when compared to natural teeth. The occlusal scheme must be altered in order to accommodate the lack of pdl <sup>12</sup>.

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Implant companies differentiate their products by offering varied implant body design, surface textures, and thread design. The implant body can be conical, straight, and vary by length and diameter. The thread pitch, depth, angle, number of threads can all be varied. In addition, the surface treatment can be differentiated. Surface treatments such as acid-etching, surface roughening, titanium plasma spray, and hydroxyapatite coatings all aim to increase osseointegration during the first phase of healing upon placement. The clinical goal of dental implant therapy is to have a successfully integrated implant with hard tissue (surrounding alveolar bone) that will withstand axial and lateral forces subjected to the implant restoration. The tissue-implant interaction is managed by the surface characteristics of the implant itself <sup>15</sup>.

A dental implant is comprised of three components: the implant fixture, the abutment, and the final restoration. Fig 3. below shows a comparison between a dental implant and a natural tooth.



Fig.3 : Schematic representation of dental implant in the mouth <sup>15</sup>.

#### 2.1.1 The dental implant fixture

The fixture is the portion of the implant that is embedded in and becomes osseointegrated with the jawbone. It lies below the gum line. For all practical purposes the fixture can be considered to be an "artificial root."

Implant fixtures are constructed out of titanium and typically have a hollow or solid, straight or tapered shaped design. Each manufacturer will utilize a proprietary design for their implant fixtures. As a result, fixture surfaces are often machined, grit-blasted, etched or plasma sprayed, the number of threads vary from manufacturer to manufacturer, as does the angle and pitch of thread. The purpose of these treatments is to microscopically roughen the fixture's surface and increase its total surface area, thus providing a greater amount of bone to implant contact.

The surface of a fixture may also be coated with a biocompatible, bone-regeneration material such as hydroxyapatite. The thought associated with this coating is that it may enhance the osseointegration process by allowing it to occur at a more rapid rate. The optimal surface preparation and design is still a point of debate<sup>15</sup>.

#### 2.1.2 The dental implant abutment

The dental abutment aspect of a tooth implant is the portion that lies at and above the gum line. The dental crown or dental bridgework that the implant supports rests on top of the implant's abutment. An abutment is usually attached to the implant fixture via a screw, 3 to 6 months after it was initially placed.

#### 2.1.3 The dental prosthesis

The dental prosthesis refers to the final restoration that the implant supports. The final restoration can be fixed via cement or screw, or be removable. The restoration will connect into the implant via the abutment, transmitting axial and lateral forces thru to the implant.

A restored, single tooth implant can have a 10 year survival rate as high as 97% <sup>8-10</sup>. With high survival rates and the added benefits decreased caries risk of adjacent teeth, decreased risk of endodontic complications of adjacent teeth, and the psychological benefits to the patient of a relatively maintenance free treatment option, implant therapy has been the treatment of choice for

single tooth replacement. With its wide range of frequent use, understanding the true failure mechanism of dental implants has become paramount <sup>7-11</sup>.

#### 2.2 Effect of Mastication on Dental implants

The success of osseointegration depends on many known factors, including: bone quality, medical history of the patient, bone grafting, immediate loading, parafunctional habits, bacterial contamination, smoking habits, degree of surgical trauma, and implant surface characteristics<sup>16</sup>. Excessive surgical trauma and impaired healing ability, premature loading and infection are likely to be the most common causes for early implant losses, whereas progressive chronic marginal infection (peri-implantitis) and overload in conjunction with host characteristics are the major reasons for delayed failures <sup>16</sup>.

In the oral environment the high magnitude of forces due to mastication can lead to wear of dental implants. In adult humans, the average biting load is between 100-150N, being the maximum biting force reported 443 N. However it cannot be disregarded that biting forces can be different between individuals and in different regions of mouth. In the case of patients containing dental implants placed after 3.5 years, biting forces are around 50.1 N<sup>24</sup>. Forces developed by mastication can generate micro-movements on the implant/abutment, abutment/ceramic crown or in the implant/bone interface.

The engineering community has taken a great interest in understanding implant geometry in order to improve implant design to minimize mechanical failure caused by the extensive range of loading. For both early and late implant failures, loading is considered an important factor <sup>21</sup>. The distribution and magnitude of stresses within the implant are influenced by the implant dimensions <sup>17-21</sup>. Catastrophic mechanical failure of the implant may occur by implant fatigue <sup>17,19</sup> implant fractures, veneering resin/ceramic fractures or other mechanical retention failures <sup>18,20</sup>. The clamping force produced by a conical seal design of abutment to implant fixture can also cause stress on the implant fixture itself. A study by Rudi et al recently looked at how implant wall thickness effects stress load using finite elemental analysis<sup>22</sup>. It was found that masticatory

force is influential on implant stresses. In addition, the implant wall thickness significantly influenced the stress magnitude with the implant. It was found that when the wall thickness decreased (especially from 3.5mm), the stress concentration occurs at the internal and external threads at the neck of the implant as well as the sharp corners of the implant wall. An increase in measurable stress may lead to an increase in corrosion due to increased micro-movement of the implant fixture<sup>25</sup>.

#### 2.3 Titanium use for dental implants

Titanium has been widely used successfully as a dental implant material because of its excellent characteristics such as mechanical resistance, low density, absence of toxicity, resistance to corrosion and biocompatibility <sup>31</sup>.

Titanium is available as commercially pure and alloyed forms. Commercially pure titanium is the benchmark for medical applications because it allows for the greatest tissue compatibility. It is also the most corrosion resistant. The majority of dental implants are made out of commercially pure titanium, which is available in 4 grades depending upon the amount of carbon, oxygen and iron contained <sup>26</sup>. The mechanical properties of CpTi, including strength, ductility, formability, and weld ability vary with small additions of oxygen and iron. Grade 1 titanium contains the lowest levels of oxygen and iron producing the most formable metal. Higher grades have progressively greater oxygen contents for higher strength. Because titanium has a low Young's modulus in comparison to many other metals, it is well suited for the varied forces subjected go dental implants intraorally. A metal with a high Young's modulus, may result in bone resorption <sup>29</sup>.

Titanium has two allotropic structures, one hexagonal close packed (alpha) up to 882°C, and the other, body-centered cubic (beta) above 882°C. Titanium can undergo allotropic transformation; therefore, titanium alloys are stable as either alpha, beta, or alpha + beta alloys. Commercially pure (CpTi), grades 1 thru 4, are alpha alloys. Recently, grade 5 titanium has increased in use for the fabrication of dental implants. Grade 5 titanium, Titanium 6AL-4V, is an alpha+beta alloy<sup>27</sup>.

The Titanium 6AI-4V alloy contains 6% Aluminium and 4% Vanadium alloy is believed to offer similar osseointegration levels as commercially pure titanium. Ti- 6AI-4V alloy offers better tensile strength and fracture resistance because the addition of Aluminum tends to stabilize the alpha phase, improving the strength characteristics and oxidation resistance at high temperatures. Vanadium stabilizes the beta phase, creating a higher strength beta phase <sup>27</sup>. Alloying and heat treating yield a wide range of mechanical properties. It is almost always possible to balance the requirements of the medical field (most inert) with the preferences of the manufacturers who prefer stronger alloys for more economical fabrication. Nontoxic elements are favored for alloying including aluminum, vanadium, niobium, molybdenum, and zirconium, while elements such as nickel chromium, and cobalt are avoided due to potential toxicity. In general, the stronger beta alloys are used in low modulus of elasticity applications. Alpha + beta alloys are used when a greater modulus of elasticity is needed <sup>28</sup>.

Biocompatibility is defined as a state of mutual coexistence between the biomaterial and host environment, such that neither has an undesirable effect on the other <sup>29</sup>. The biomaterial should be used in the host for a specific function without eliciting a negative host response. Ideally, a dental material that is to be used in the oral cavity should be harmless to all oral tissues—gingiva, mucosa, pulp, and bone. Furthermore, it should contain no toxic, leachable, or diffusible substance that can be absorbed into the circulatory system, causing systemic toxic responses, including teratogenic or carcinogenic effects. The material also should be free of agents that could elicit sensitization or an allergic response in a sensitized patient <sup>29</sup>. Commercially pure titanium became known as the most corrosion-resistant non-noble metal, a property which results from the inert oxide layer that spontaneously forms on its surface. It also became apparent that similar resistance to corrosion could be achieved by some titanium alloys, such as titanium-6% aluminium-4% vanadium, which had far superior mechanical strength <sup>29</sup>. Although corrosion resistance is a prerequisite for biocompatibility, it does not necessarily guarantee it; other properties of the metal are of crucial importance. The reputation of titanium as a 'biocompatible' material was based on its excellent corrosion resistance, which severely limits the amount of titanium ions released into the tissue under most circumstances, and on its biological inactivity, sometimes termed biological indifference, in that traces of the metal are not known to influence any part of the tissues <sup>30</sup>.

Titanium dental implants are capable of osseointegration only because of the oxide film that forms on the surface of the metal. The implant surface consists of a relatively thick titanium oxide layer which acts as the implant-tissue interface. The interface consists of long-range but weak van der Waals interactions and short-range, strong chemical bonds (ionic and covalent bonds)<sup>31</sup>. The biomolecules exposed to the surface are in a continuous exchange of molecules with the metal oxide. Fig 4 below shows a depiction of the transport mechanisms that take place at the implant/tissue interface. Corrosion via the dissolution of the protecting oxide layer and implant/tissue interface may lead to severe problems with some implant materials if the oxide layer does not reform at an acceptable rate. The chemical properties, and therefore the interface chemistry, are determined by the oxide layer and not by the metal itself<sup>32-37</sup>.



Fig 4. Schematic of various transport and chemical processes that take place at an implant/tissue interface <sup>32</sup>.

#### 2.3.1 Corrosion Resistance of Titanium

Corrosion is a special concern for metallic materials in dental implantology because implants are subject to the oral cavity where electrolyte and oxygen consumptions differ from that of tissue fluids<sup>38</sup>. In addition, the pH can vary significantly in areas with plaque and within the everchanging oral cavity. This increases the range of pH that implants are exposed to in the oral cavity compared with other tissue sites within the body<sup>39</sup>.

The combination of high magnitude of stress (occlusal forces) plus simultaneous exposure to a corrosive environment (oral cavity), can result in the failure of metallic materials by stress corrosion cracking (SCC)<sup>40</sup>.

Elemental titanium belongs to a group of high-reactive elements, indicated by its reduction potential (-1.539V). However, in the presence of any amount of oxygen, the titanium reduction potential changes significantly and can reach (+0.4V) making it extremely unreactive<sup>39</sup>.

The corrosion resistance of titanium is due to its protective oxide film, which forms and reforms naturally in the presence of even trace amount of any form of oxygen. The film is highly adherent, thought to be insoluble, and chemically non-transportable, preventing reaction with the tissue it contacts. The passivation film, which is present on the surface of titanium, is made up of mostly TiO2, but also contains TiO and Ti2O3 to a much smaller degree. The thickness of the passive oxide film can reach up to 50-60 Å after long exposure to air<sup>32</sup>.

#### 2.3.2 Oral Environment – Corrosion of Titanium

The magnitude and variety of components within the oral environment can make it very harsh, leading to eventual degradation of biomaterials. The oral environment is the habitat of microbial species that are kept wet by saliva. Saliva incorporates several viruses, bacteria, yeast, fungi and their products, such as organic acids and enzymes, epithelial cells, food debris, and components from gingival crevicular fluid<sup>41</sup>. Moreover, saliva is a hypotonic solution containing bioactonate, chloride, potassium, sodium, nitrogenous compounds, and proteins. Therefore, the oral tissues are exposed to a veritable bombardment of both chemical and physical stimuli as well as metabolism of about 30 species of bacteria (the total salivary bacterial count is said to be five thousand million/ml of saliva)<sup>42</sup>. The pH of saliva varies from 5.2 to 7.8. Finally, there is a larger temperature variation within the oral cavity than most other parts of the body, coping with cold of ice (0°C) to hot coffee and soup<sup>43</sup>.

Factors such as temperature, quantity and quality of saliva, plaque, pH, protein, and the physical and chemical properties of food and liquids as well as oral health conditions may influence corrosion. Corrosion, the graded degradation of materials by electrochemical attack is of concern particularly when a metallic implant, metallic filling, or orthodontic appliances is placed in the

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hostile electrolytic environment provided by the human mouth <sup>43, 47-49</sup>. For dental implants, biocompatibility depends on mechanical and corrosion/degradation properties of the material, tissue, and host factors. Biomaterial surface chemistry, topography (roughness), and type of tissue integration (osseous, fibrous, and mixed) correlate with host response. Biocompatibility of the implants and its associated structure is important for proper function of the prosthesis in the mouth. Corrosion can severely limit the fatigue life and ultimate strength of the material leading to mechanical failure of the dental materials <sup>44</sup>.

Upon insertion, dental implant fixtures are exposed to saliva for a prolonged period. The wide range of biochemical compounds in saliva may enhance electrochemical corrosion <sup>45</sup>.

The unstable nature of human saliva does not lend itself to being duplicated making it unusable for in vitro studies. Artificial saliva is used as long as it reacts in a similar manner as natural saliva to the testing material <sup>46</sup>.

#### 2.4 Corrosion Mechanism

Corrosion is the degradation of an engineered material into its constituent atoms due to electrochemical reactions with its surroundings. There are two forms of corrosion, chemical corrosion, which occurs under dry conditions, and electrochemical corrosion, occurring under wet conditions <sup>50</sup>. In the oral cavity, electrochemical corrosion occurs due to the presence of saliva. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion controlled process, it occurs on exposed surfaces. All metals have the potential to corrode in an electrolytic solution, ie. saliva. When the oxide-free surface of a metal becomes exposed to the solution, positively charged metal ions tend to pass from the metal into the solution, leaving electrons behind on the metal surface. Metallic ions are brought to the surface of the metal, and subsequently released into solution via an anodic reaction, the oxidation of the metal (1). The accumulation of negative charge on the metal due to the residual electrons leads to an increase in the potential difference

between the metal and the solution. This potential difference is called the electrode potential, or the potential of the metal, which thus becomes more negative as the diffusion of metal ions progresses. In an electrolytic solution, this process is slowed because the electrons generated from the anodic reaction are consumed via two cathodic reactions, i.e. the reduction of hydrogen (2) and the dissolution of oxygen (3).



O2 + 4H+ + 4e- → 2H2O (3)

The surfaces of all metals (except for a completely inert metal such as gold) in air are covered with an oxide film. When such a metal is immersed in an aqueous solution, the oxide film will change. For some metals, in a highly acidic solution, the oxide film may dissolve completely leaving a bare metal surface leading to high levels of corrosion. In near-neutral solutions, the solubility of the oxide will be much lower; therefore, the extent of dissolution will be smaller. The underlying metal may only be exposed for short period of time until the oxide layer reforms, or it may be exposed only in areas of discontinuity in the metal, ie grain boundary or an inclusion. If the near-neutral solution contains inhibiting anions, the dissolution of the oxide film may be suppressed and oxide film is stabilized to form a passive oxide film layer. This passive oxide film layer will protect the metal from corrosion.

Methods to reduce the activity of the exposed surface, such as passivation , can increase a material's corrosion resistance. In addition, steps should be taken to limit corrosion by minimizing pits, crevices, grain size, inclusions and porosities. The metal should have good wear resistance and have the ability to repassivate at a high rate <sup>51-53</sup>.

#### 2.4.1 Corrosion of Titanium

Titanium itself is a highly reactive metal. Its corrosion resistance is due entirely to the formation of a stable, protective, strongly adherent oxide film <sup>67</sup>. This film forms instantly (due to the high reactive nature of Ti) on the surface when a fresh surface is exposed to air or moisture. The oxide film formed can be 10-16 Angstroms thick, and if left undisturbed, can continue to grow slowly over time. The composition of the film varies from TiO<sub>2</sub> at the surface to Ti<sub>2</sub>O<sub>3</sub> and TiO at the metal interface. Oxidizing conditions promote the formation of TiO<sub>2</sub> so that in such environments the film is primarily TiO<sub>2</sub> <sup>54</sup>. The film is transparent and not detectable visually.

The Pourbaix diagram for titanium shows that it is thermodynamically a very reactive metal; however the protective oxide passive film is very stable for a wide range of potentials<sup>55</sup>. The oxide film provides corrosion resistance and may enhance the osseointegration process when in contact with alveolar bone.

Kuphashak C et al, studied the electrochemical corrosion tendencies of titanium and titanium alloys in 37°C Ringer's solution<sup>56</sup>. It was found that the commercial pure titanium was most resistant to corrosion, but that alloys such as Ti-6AI-4V were the least resistant to corrosion. Many implant manufacturers use titanium alloys, specifically Ti-6AI-4V to fabricate dental implants for the increase in fracture toughness and modulus of elasticity.

The fluctuating pH and ion concentration in saliva is thought to be a factor affecting the corrosion behavior of titanium<sup>57</sup>. The pH of the mouth can vary from person to person. In addition, it can change as a result of ingestion of food and drink. It is thought that in the oral cavity, these interactions with saliva and altering pH can cause corrosion of the titanium alloy, resulting in degradation of the implant itself. Several studies have looked at the effect of fluoride concentration at various pH levels of artificial saliva on titanium and found that the surface of titanium corrodes at higher levels when subjected to high concentrations of fluoride ions <sup>57-61</sup>. There are few studies looking at the influence of pH on the electrochemical behavior of dental implants. This is one of the aspects studied in this thesis.

#### 2.4.2 Oxide Layer

The oxide layer may be disrupted, resulting in more rapid corrosion. It the dissolution process is higher than the reprecipitation rate of the oxide layer, the metal ions will gradually be released in the tissues <sup>62</sup>. The release would be slow due to the immediate nature of oxide reformation for titanium. However, over time, the accumulation of metal ions in the oral tissues and bone surrounding the dental implant may lead to adverse reactions such as toxicity, bone resorption, or allergy in the patient <sup>63-65</sup>.

The passage of metal ions through an oxide film takes place very slowly and so the current due to metal ions leaving the metal becomes very small when the surface is completely covered with an oxide film. The metal is thus protected against corrosion by a passivating oxide film <sup>62-65</sup>.

#### 2.4.3 Fretting Corrosion

There are many forms of corrosion that metallic materials can be exposed to: fretting, galvanic, crevice, pitting, and intergranular. Fretting corrosion seems to have the greatest effect on dental implants. Fretting corrosion occurs when two surfaces are in contact and experience low amplitude movements resulting in the damage of the contact surfaces. Dental implants are subjected to fretting movements constantly due to transmission of force between the implant restoration, connecting abutment, and implant fixture<sup>67</sup>. Fretting corrosion is a direct result of micromotion inherent within the implant system. Micromotion is a result of masticatory forces subjected onto the implant restoration which in turn is transmitted through the implant body<sup>31</sup>. Micromotion transmitted through the implant system can range anywhere from 30-150µm, with the average value being 50µm. Fretting corrosion is observed at the implant/abutment, implant/bone, and the final restoration/abutment interfaces. Each time any surfaces rubs against the titanium implant, the protective passive film layer is penetrated. The passivation layer reforms upon exposure to air and/or fluid. However, the instant the oxide layer is rubbed away, the risk of metal ion release into the tissues is high<sup>68</sup>. It is unknown how the body will react to the accumulation of metal ions in the tissue<sup>31</sup>.

#### 2.4.4 Galvanic Corrosion

Titanium has been chosen as the material of choice for endosseous implantation. Even though titanium alloys are exceptionally corrosion resistant because of the stability of the TiO<sub>2</sub> layer, they are not inert to corrosive attack. When the stable oxide layer is broken down or removed and is unable to reform on part of surface, titanium can be as corrosive as many other base metals <sup>69</sup>. Galvanic coupling of titanium to other metallic restorative materials may also generate corrosion. Hence, there is a great concern regarding the materials for suprastructures over the implants<sup>70</sup>.

When two or more dental prosthetic devices/restorations made of dissimilar alloys come into contact while exposed to oral fluids, the difference between their corrosion potential results in a flow of electric current between them. An *in vivo* galvanic cell is formed and the galvanic current causes acceleration of corrosion of the less noble metal. The galvanic current passes through the metal/metal junction and also through tissues, which causes pain. The current flows through two electrolytes, saliva, or other liquids in the mouth and the bone and tissue fluids <sup>70</sup>.

The differential surface of a metallic restoration may have small pits/crevices. Consequently, stress and pit corrosion occurs. The mechanical and notched sensitivity, stress corrosion cracking, torsional, and smooth and notched corrosion fatigue are properties of titanium materials used for implant <sup>70</sup>.

#### 2.5 Wear Mechanism

Tribology is the science of surfaces interacting during motion. When two surfaces are in constant contact, wear results. Wear can lead to eventual material loss. In the oral cavity, teeth during mastication exhibit a tribological scenario which can result in wear of enamel over time. When

translated to implant therapy, mastication forces may result in wear of the implant restoration. The implant fixture may undergo wear in the form of fretting as discussed before <sup>71</sup>.

#### 2.5.1 Wear of Titanium

The surfaces of titanium and of all commercially produced alloys of titanium have relatively poor wear resistance. In particular, titanium surfaces in contact with each other or with other metals readily degrade under conditions of sliding contact or fretting <sup>72</sup>. Even with light loading and little relative movement, complete seizure of surfaces can occur. This situation is caused by adhesive wear in which microscopic asperities on the metal surfaces come into contact as a result of relative sliding and they tend to weld together forming a bond at the junction which can have a rupture strength greater than the strength of the underlying metal. Fracture then takes place at one of the asperities causing metal to be transferred from one surface to the other. The debris formed gives rise to the accelerated wear that occurs with titanium <sup>56</sup>.

The wear resistance of titanium depends on the thickness of the naturally occurring oxide film, the structure of the oxide film, and the surface topography. Maximizing the oxide film thickness increases wear resistance; therefore, implant manufacturers attempt to increase the layer of the film via heating applications, or coating the surface (i.e. plasma spray)<sup>73</sup>.

#### 2.6 Tribocorrosion mechanism

Tribocorrosion deals with interaction of mechanical (wear) and chemical (corrosion) degradation processes leading to performance degradation and system failure. Tribocorrosion is an irreversible degradation process. Tribological processes, whether involving solid particle erosion, sliding wear, fretting, or micro-abrasion, involve many different material loss phenomena. When these wear processes occur in the presence of corrosion, the extent of material loss may be much greater than the processes acting separately <sup>74-78</sup>.

Although the history of tribocorrosion (tribo-electrochemistry) dates back to 1875, when Edison observed a variation in friction coefficient at various applied potentials, the field has not received attention until recently<sup>74</sup>. Researchers from various fields within science and engineering, and medicine have begun to focus on tribocorrosion due its practical importance, health impact and economic benefits.

Factors affecting the tribocorrosion process and mechanisms are the properties of the contacting materials, the mechanics of the tribological contact, and the physico-chemical properties of the environment. The microstructure of the materials and the presence of defects like phase distribution, grain size and orientation, non-metallic inclusions, segregations, dislocation density etc, are critical for the mechanical behavior of the materials. The rate of tribocorrosion for a given metal-environment combination depends on the applied forces and the type of contact: sliding, fretting, rolling or impact. The other factors include: sliding velocity, type of motion, shape and size of contacting bodies, alignment, and vibration. The physico-chemical properties of the environment influence the system in the form of the medium at the interface i.e., solid, liquid or gaseous and its corresponding properties like viscosity, conductivity, pH, corrosivity, and temperature <sup>74-78</sup>.

While tribocorrosion phenomena may affect many materials, they are most critical for metals, specifically the corrosion resistant or passive metals. These metals are "passive" due to their highly reactive nature, forming passive oxide films. As discussed earlier, titanium falls into this category. For passive metals, such as titanium, the total material loss due to tribocorrosion will be much higher than the sum of ear and corrosion measure independently. This is because the rate of tribocorrosion is not simply the addition of the rate of wear and the rate of corrosion. There is a synergistic effect between the mechanical and chemical mechanisms, resulting in greater degradation or loss of material. This synergism can have positive or negative effects depending upon the specific reaction products formed on the surface of the materials. The

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reaction products can protect the surface as in the case of self-lubricating and/or self-healing layers or can aggravate the material degradation process causing more material removal <sup>77</sup>.

#### 2.6.1 <u>Electrochemical techniques in tribocorrosion systems</u>

The tribocorrosion mechanisms can be observed effectively using electrochemical techniques. A Tribometer has the facility to measure the evolution of frictional forces. Electrochemical techniques are used to monitor the corrosion response from the test system <sup>79</sup>. A schematic diagram of the basic methodology of a tribocorrosion test system is shown in Fig 5 <sup>80</sup>.



Fig 5. Basic methodology in a tribocorrosion study<sup>80</sup>

Electrochemical interfacing consists of a potentiostat and three electrode attachments: a reference electrode (RE), a standard calomel electrode (SCE) and a counter electrode (CE) such as platinum wire or a graphite rod. The sample tested is the working electrode (WE)<sup>80</sup>.

The general steps for tribocorrosion tests are explained in the schematic diagram Fig 6. <sup>81-83</sup>. The selection of parameters depends on the application and research interest. For example, this thesis focused on how the pH of the solution could play a role in passive film degradation.

	Tribometer	Interfacing	Corrosion (Potentiostat)	
Parameters	load, sliding velocity, sliding distance, frequency		Different solutions, pH of the solutions, electrode potentials	
Techniques	Force measurements, Friction coefficient values		<ul> <li>Open circuit potential (OCP)</li> <li>Potentiodynamic curves</li> <li>Electrochemical Impedance spectroscopy (EIS)</li> <li>Electrochemical noise measurements</li> </ul>	
Online output parameters	Evolution of friction coefficient values, forces		Evolution of current or potentials	
Final results         Total-wear volume         Surface and micro         Solution with wear destructural characterizations		o Solution with wear debris and erizations corrosion products		
Analysis	Analysis Understanding the mechanisms, synergism or antagonism, individual contributions			

Fig 6. Basic steps in a typical tribocorrosion study <sup>81-83</sup>.

The surface state of the sample can be determined by electrochemical techniques such as open circuit potential, polarization and impedance measurements. Open circuit potential (OCP) measurements provide the evolution of potential and potential changes in the system with respect to standard electrodes (ie standard calomel electrode). It gives information about the electrochemical state of the material, if it is in an active or passive state. During a tribocorrosion test OCP is an average value determined by factors as the ratio of active-to-passive material in the wear track, the repassivation kinetics of the base material in the wear track, the contact frequency and load. Variation of the open circuit potential of materials in tribocorrosion systems can thus be correlated with variations in the surface of the material <sup>78-80</sup>.

Potentiodynamic polarization tests are useful in tribocorrosion studies because they give information on changes in electrochemical reactions kinetics induced by sliding, and also the influence of surface reactions on sliding conditions in the contact region. Polarization tests can give detailed information about mechanical depassivation or worn surfaces, corrosive wear rates, and the mechanism of mechanical wear. In addition, the corrosion current evolution can be studied at a constant potential from the system <sup>84</sup>.

Electrochemical impedance spectroscopy (EIS) can be used to understand the properties or characteristics or films formed at the contact zone. Usually, EIS measurements are taken before and after the sliding or tribotest. It gives information about the properties of the passive film, and allows the study of the intermediate species adsorbed on the materials' surface. In tribocorrosion tests, EIS permits the determination of the electrochemical reactions and the interaction between friction and corrosion <sup>85,86</sup>.

For titanium, with electrochemical techniques, it is possible to measure in real time, the amount of titanium transformed into oxide or into dissolved ions. This is accomplished by using current measurements during the entire tribocorrosion test. Following the evolution of corrosion potential and current, it is possible to understand the starting of rubbing: the open-circuit potential suddenly decreases to lower values, and an increase in current is observed, with the disruption of the oxide film. This allows a fresh active titanium surface to be exposed to the solution for repassivation.


Fig 7. Synergism of mechanical and corrosion effects of tribocorrosion.

The most important aspect of the tribocorrosion analysis of a system is to understand the individual effect of tribology (wear) and corrosion along with their interaction in order to determine if it is detrimental or beneficial. Fig 7 above illustrates the basic concept of linking the tribological events and corrosion process in order to understand the synergistic effect of tribocorrosion <sup>80,87</sup>.

# 2.6.2 Wear quantification in Tribocorrosion systems

The total wear volume in an electrochemical tribocorrosion study can be determined by measuring the worn material before and after an experiment. The total wear can be characterized as the loss due to corrosion (electrochemical oxidation), the mechanical wear volume, and the loss due to the synergistic effect<sup>88</sup>.

 $W_{total} = W_{mechanical} + W_{corrosion} + W_{synergistic}$ <sup>88</sup>

#### 2.6.3 <u>Tribocorrosion of dental implants</u>

Corrosion is a concern for metallic materials in dental implantology, because implants are exposed to a whole host of ever-changing corrosive elements. Upon placement into the alveolar bone, implant bodies can come into direct contact with saliva, blood, tissues varying in oxygen and electrolyte composition. In addition, the pH can vary significantly in areas within the oral cavity and from patient to patient <sup>89-92</sup>.

As mentioned previously, the corrosion and wear processes that act on a tribocorrosion system are controlled by the properties of the oxide layer formed on the titanium surface and the interaction of the oral environment with the surface. If the oxide layer is disrupted due to a tribocorrosion effect, several detrimental results could occur. It could lead to accumulation of titanium metal ions in the tissues. In addition, the metal debris could act as third body particles accelerating wear due to their abrasive nature <sup>89-92</sup>.

#### 2.6.4 Effect of tribocorrosion products on the oral environment

Because titanium is the most widely used metal in dental implantology, there has been growing concern as to effect of electrochemical corrosion of titanium in the oral cavity. The release of particles (third body particles) from metal structures into the biological milieu may be the result of the combined affect of electrochemical processes (corrosion) and mechanical disruption during insertion, abutment connection or removal of failing implants, i.e. tribocorrosion <sup>90-92</sup>.

A recent study conducted by Olmedo et al. looked at the response of the oral mucosa to titanium cover screws. One-hundred and fifty three biopsies of the supra-implant oral mucosa adjacent to the cover screw of submerged dental implants were analyzed. Histologic studies were performed to analyze epithelial and connective tissue as well as the presence of metal particles, which were identified using microchemical analysis. Langerhans cells, macrophages and T lymphocytes were studied using immunohistochemical techniques <sup>93</sup>. The surface of the cover screws was evaluated by scanning electron microscopy (SEM). Forty-one percent of mucosa biopsies

exhibited metal particles in different layers of the section thickness. Particle number and size varied greatly among specimens. Immunohistochemical study confirmed the presence of macrophages and T lymphocytes associated with the metal particles. Microchemical analysis revealed the presence of titanium in the particles. On SEM analysis the surface of the screws exhibited depressions and irregularities. The study concluded that the biological effects seen in the mucosa in contact with the cover screws might be associated with the presence of titanium or other elements, such as aluminum or vanadium (common alloying elements). It has been hypothesized that the corrosion products from dental implants may behave as haptenes, generating a hypersensitivity reaction with release of inflammatory mediators known as cytokines and macrophage recruitment <sup>94</sup>. Metal particles may be ingested by macrophages, stimulating the release of cytokines that contribute to bone absorption by activating osteoclasts. In addition to increasing bone reabsorption, the metal particles may suppress the osteoblast function, reducing bone formation and contributing to osteolysis <sup>94</sup>. The potential long-term biological effects of particles on soft tissues adjacent to metallic devices is unknown, but should be further investigated since these effects might affect the clinical outcome of the implant <sup>95</sup>.

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# 3. Electrochemical Behavior of Dental Implants (CpTi): Influence of pH of Artificial Saliva

#### Abstract

Titanium is the most common material chosen for dental implants because it is highly corrosion resistant. This is due to the constant reformation of a protective passive film layer. The formation and composition of the passive film layer is dependent on the environmental conditions. If the stable oxide layer is damaged, corrosion of the titanium surface underneath can occur. Objective: The purpose of this study was to determine if basic corrosion of CpTi alloy in artificial saliva was affected by pH and to understand the corrosion kinetics/mechanisms of CpTi as a function of pH. Methods: In this study, titanium alloy discs were subjected to corrosion tests. Before the tests, all samples were cleaned and polished using standard metallographic preparation methods. Artificial saliva was used as the testing medium. The following pH values were tested: 3.0, 4.5, 6.0, 6.5, 7.5, 9.0. Different pH values were achieved by adding lactic acid (acidic) or NaOH (basic) in appropriate amounts. Results: Potentiodynamic curves indicated behavior change at each pH. In addition, the lcorr value determined from the potentiodynamic curve exhibited poorest corrosion resistance for pH 7.5. The Nyquist plot (from the electrochemical impedance spectroscopy (EIS) results) indicated that pH 7.5 had the poorest resistance. Scanning electron microscopy images indicated pHs 6.5, 7.5 and 9.0 had considerable surface corrosion. Conclusions: The results showed significant influence of pH of the media on the corrosion behavior of CpTi. The poor corrosion behavior at the neutral pHs invites some concerns, and highlights the need for further study.

Keywords: Titanium, corrosion, biocompatibility, artificial saliva, electrochemical impedance spectroscopy

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# 3.1 INTRODUCTION

Titanium is the most widespread material used for dental implants due to its mechanical properties, exceptional corrosion resistance and biocompatibility.<sup>1-3</sup> Although titanium alloys are highly corrosion-resistant because of the stability of the TiO<sub>2</sub> oxide layer, they are not inert to corrosive attack. When the stable oxide layer is broken down or is incapable to reform on parts of the surface, titanium can be as corrosive as other base metal alloys.<sup>4-8</sup> In addition, the oral cavity can simulate an electrochemical cell because saliva acts as a weak electrolyte. Electrochemical corrosion of titanium alloys may lead to surface corrosion of dental implants, and ultimately release the corrosion products into the system over time.<sup>9, 10</sup> It is unknown as to whether or not corrosive products may be beneficial or harmful to osseointegration.

The corrosion resistance of titanium results from the formation of an extremely stable, continuous, highly adherent, and protective oxide film on the metal's surface.<sup>3</sup> The nature, composition and thickness of the protective surface oxides that form on titanium alloys depend on the environmental conditions.<sup>3,7,8</sup> Recent studies have shown that the corrosion resistance of titanium (Commercially pure titanium (CpTi) and titanium alloys) becomes weaker with exposure to a varying fluoride concentration, NaF solution with a concentration of 0.5%. In addition, pH has been known to have a strong influence on the corrosion resistance of Cp titanium and titanium alloys.<sup>1-3, 11, 12</sup> Understanding the corrosion behavior of titanium in dental implants is very important, because it can negatively affect the biocompatibility and mechanical integration leading to failure of dental implants over time.<sup>9, 13, 14, 15</sup>

In the oral environment, titanium implants are constantly exposed to saliva. Upon placement, the entire surface of the implant can be contaminated with saliva. Once placed, the implant interface is continuously washed with saliva via the gingival sulcus. The presence of electrolytes in saliva can create damage by inducing crevice corrosion, which has been found in many dental implants.<sup>16, 17</sup>

In addition to the constant contamination, the pH of saliva can vary around dental implants. Many factors can change the pH of saliva. Infection can acidify the pH of saliva.<sup>11</sup> Food, oral hygiene products, age, periodontitis, oral habits such as smoking, systemic disease, and salivary gland radiation can also contribute to the changes of pH of saliva.<sup>17-22</sup> The normal, resting pH of saliva in the mouth does not fall below 6.3. The average saliva pH range for a healthy adult is 6.3 to 7. However, the resting pH of saliva can temporarily decrease to an average of 3.5 if acidic beverages are ingested, or increase to 8.3 if certain alkaline foods are taken in, such as vegetables and grains. Add three references The pH of saliva may contribute to the corrosion of dental implants.<sup>22, 24-28</sup>

Many studies have investigated the influence of pH in artificial saliva on the corrosion behavior of titanium.<sup>1, 3, 11, 12, 18, 22, 27</sup> However, most of the studies were performed using pH 5 and lower, which do not replicate the normal clinical situation. In addition, the interaction between titanium and the oral environment gives rise to electrochemical reactions.<sup>22, 24</sup> Within the corrosion studies of dental alloys, the knowledge of the electrochemical environment of the oral cavity is limited.<sup>24</sup> It is hypothesized that a lower saliva pH level induce greater corrosive damage on titanium, and as the pH level increases from 3 to 9, the amount of corrosive damage will reduce. Hence, the aim of this study was to investigate the corrosive behavior of CpTi in artificial saliva at 37°C, as a function of pH values (3-9) and to characterize the titanium surfaces as a result of the corrosion process.

#### 3.2 Materials and Methods

#### 3.2.1 Materials and solutions

In the current study, twenty-five CpTi alloy discs (American Elements, Los Angeles, CA) Ø12 mm and 7 mm thickness were used. The tests were conducted in artificial saliva with different pHs: 3, 4.5, 6, 6.5, 7.5, and 9. The forming of the artificial saliva and the electrolytes were based on

studies by Fusayama and Meyer.<sup>28, 29</sup> The composition of this solution, as seen in Table I, closely resembles that of human natural saliva. To obtain a more acidic artificial saliva

Component	Quantity (g/L)		
KCl	0.4		
NaCl	0.4		
CaCl <sub>2</sub> .2H <sub>2</sub> O	0.906		
NaH2PO4.2H <sub>2</sub> O	0.690		
Na2S.9H <sub>2</sub> O	0.005		
Urea	1		
To achieve lower pH (acidic) lactic acid is added			
To achieve high pH (basic) NaOH is added			

TABLE I.			
COMPOSITION OF ARTIFICIAL SALIVA.			

solution, lactic acid was added in 1mL increments, and to obtain a more basic artificial saliva solution, NaOH was added in 1mL increments.

Before the test, all the samples were polished and cleaned using standard metallographic methods. The samples were first mounted in mounting cups (Buehler, Lake Bluff, IL) with clear orthodontic resin (Dentsply, Milford, DE). The samples were cured under 20 psi. Samples were removed and rough polished using 8" 320 grit SiC paper to ensure that the sample was flat. The intermediate polishing step was accomplished using a TexMet polishing cloth and 9micron diamond polishing paste suspended in Meta-Di fluid (Buehler, Lake Bluff, IL). Once all deep scratches were removed from the surface, the final polishing step was accomplished using a Chemomet polishing cloth and colloidal silica (Buehler, Lake Bluff, IL). Both the intermediate and final polishing steps were conducted for 10 minutes. Fig 8 below shows the difference between an unpolished sample and a final polished sample.



Fig. 8. Unpolished and final polished specimens

Specimens were cleaned using 70% Isopropyl alcohol for 15 minutes, then dionized water for 15 minutes in an ultrasonic bath prior to testing. Specimens were dried using a hot air gun.



Figure 9. Electrochemical experimental set-up.

# 3.2.2 Electrochemical test methods

The tests were conducted in an electrochemical cell (Figure 9) and performed in triplicate for each group. The corrosion cell held 150ml of artificial saliva solution. All measurements were made in a standard three electrode cell system. A saturated calomel electrode (SCE) was used as the reference electrode (RE) and a graphite rod as a counter electrode (CE). A Gamry

potentiostat (Gamry Instruments, Warminster, PA) was used to carry out the corrosion measurements. After mounting the samples, a time period of 30 minutes was allotted for the initial stabilization and heating of the solution to 37C, to mimic the normal body temperature. Initially, the evolution of open circuit potential (OCP) was monitored during a period of 3600sec. The 2 hour electrochemical impedance spectroscopy (EIS) test was conducted following OCP. The EIS measurements were performed in the frequency range from 100 KHz to 0.01 Hz, with AC sine wave amplitude of 10 mV applied to the electrode at its corrosion potential. These values were used to determine the real (Z') and imaginary (Z'') components of the impedance, which were plotted with the Nyquist plot. The total impedance (|Z|) and phase angle were seen in a Bode plot as a function of the frequency. Impedance data is frequently interpreted in terms of an "equivalent circuit" based on a plausible physical model where the circuit elements represent electrochemical properties of the metal and its oxide film.<sup>23</sup> The EIS data was modulated into equivalent electrical circuits using the Zview2 corrosion software (Scribner Association Inc., Southern Pines, NC) in order to better understand the pH effect on CpTi. Finally, the samples were anodically polarized from -0.8 V to 1.8 V at a scan rate of 5mV/sec. Potentiodynamic measurements were carried out in order to determine the initiation and propagation of local corrosion, which is associated with the breakdown of the passive (protective) film. The electrochemical corrosion properties of CpTi at each pH were measured, in terms of corrosion potential (E<sub>corr</sub>), corrosion current density (I<sub>corr</sub>) and passivation current density (I<sub>pass</sub>). Fig 10 below shows the test protocol followed.



Fig 10. Test Protocol

#### 3.2.3 Surface characterization

Surface characterization was conducted using scanning electron microscopy (SEM) (Joel JSM-6490 LV, Oxford Instruments, Oxford, UK).

# 3.2.4 Statistical Analysis

The corrosion parameters, including  $E_{corr}$  (corrosion potential),  $I_{corr}$  (corrosion current density),  $C_{dl}$  (capacitance of double layer),  $R_{sol}$  (resistance of solution) and  $R_p$  (polarization resistance), were statistically analyzed using one-way analysis of variance (ANOVA) for analyzing how pH affects the corrosion parameters. Tukey's HSD test ( $\alpha = 0.05$ ) was chosen as the multiple-comparison technique when necessary (Statistical Package for the Social Sciences, version 17.0; SPSS Inc, Chicago, IL).

# 3.3 Results

# 3.3.1 Electrochemical impedance spectroscopy (EIS) data

The Nyquist (Figure 11) and Bode plots (Figure 12) provide the corrosion kinetics (impedance and frequency information). The Nyquist plot shows the electrochemical resistance of the Ti surface.



Fig 11. Representative Nyquist plot from EIS results for CpTi in artificial saliva as a function of pH.



Fig 12. Representative Bode plot from EIS results for CpTi in artificial saliva as a function of pH.

From the Nyquist plot, it can be noted that pH 7.5 had the poorest electrochemical resistance, followed by pH 9.0. For both pH 7.5 and 9.0, there was an increase in the semicircular diameter of the capacitance loop (as indicated by the Nyquist plot). An increase in capacitance leads to a decrease in the overall corrosion resistance. The corrosion resistance appeared to be highest at pH 3.0. Unlike the Bode plot, the Nyquist plot did not account for frequency. The Bode plot also suggested that the resistance of pH 7.5 is the poorest because of the lower  $R_p$  value (resistance of the passive film). Only one time constant was observed at each pH, indicating the formation of a homogenous passive film.<sup>32</sup>

Figure 13 represents the Randles equivalent circuit employed to model the corrosion behavior based on the EIS results. The components of the equivalent circuit are:  $R_s$  (resistance of the solution),  $R_p$  (polarization resistance) and  $C_{dl}$ . Mean values at each pH are compared in Table II.



Fig 13. Equivalent circuit used for fitting the experimental data.

# 3.3.2 Potentiodynamic curves

The results of the cyclic potentiodynamic polarization curves for the Ti alloy are presented in Figure 13. All samples revealed an active-to-passive behavior for each pH. However, the varying potentiodynamic curves indicated a behavior change dependent on pH. This was exhibited by the unique curves for each pH represented in Figure 14.



Figure 14. Representative polarization curves at each pH for CpTi in artificial saliva.

A summary of the corrosion data obtained from the cyclic potentiodynamic polarization curves and EIS modeling is provided in Table 2.

# TABLE II

CORROSION PARAMETERS OBTAINED FROM POTENTIODYNAMIC POLARIZATION CURVES AND FROM EIS MODELING OF CPTI IN ARTIFICIAL SALIVA AS A FUNCTION OF						
pH	pH3.0	pH4.5	<u>рп</u> рН6.0	pH6.5	pH7.5	pH9.0
E <sub>corr</sub> (V)	-0.40 ± 0.16	-0.39 ± 0.11	-0.35 ± 0.014	-0.37 ± 0.13	-0.38 ± 0.18	-0.40 ± 0.18
I <sub>corr</sub> (A/cm2)	8.33E-08 ± 6.81E- 09	9.47E-08 ± 1.46E- 09	1.27E-07 ± 5.60E- 08	1.31E-07 ± 6.89E- 08	1.65E-07 ± 6.81E- 08	1.17E-07 ± 5.98E- 08
I <sub>pass</sub> (A/cm2)	2.1E-0.5	3.1E-05	1.5E-05	1.0E-05	4.2E-05	3.2E-05
C <sub>dl</sub> (F)	2.66E-05 ± 6.72E- 06	1.74E-05 ± 1.63E- 06	1.69E-05 ± 3.54E- 07	1.61E-05 ± 7.07E- 07	2.06E-05 ± 7.07E- 08	1.68E-05 ± 2.55E- 06
R <sub>sol</sub> (Ωcm2)	359.65 ± 14.64	391.40 ± 14.42	390.55 ± 26.52	402.70 ± 11.31	451.70 ± 9.05	364.90 ± 7.92

From the cyclic potentiodynamic polarization curves, the following values were determined:  $E_{corr}$ ,  $I_{corr}$ , and  $I_{pass}$  (current passivation). Mean values for each pH are compared in Table 2.

Results of one-way ANOVA showed that pH had a significant influence on the  $E_{corr}$ ,  $I_{corr}$ ,  $C_{dl}$ , and  $R_{sol}$  values (p<0.05). The change in  $C_{dl}$  was significant when comparing pH 3.0 to all other pH (p<0.05).  $E_{corr}$  was significant when comparing pH 3.0 to all other pH (p<0.05).  $I_{corr}$  was significant for pH 6.0 and 7.5 when compared to pH 9.0 (p<0.05). The polarization resistance ( $R_p$ ) showed no significance when comparing between tests pHs (p>0.05).  $I_{pass}$  values, although not statistically significant, indicated greater current required for development of the passive film layer at neutral pH.

# 3.3.3 Surface examination of corroded surfaces

SEM images taken after the electrochemical tests suggest surface corrosion at pH 6.5, 7.5 and 9.0 (Figs. 16e, f and g respectively, arrows). Considerable evidence of surface corrosion represented by surface damage can be seen particularly at pH 7.5. Negligible surface corrosion existed at pH 3.0, 4.5 and 6.0 with respect to the control sample (Figs. 15a-d). The control sample was not subjected to the electrochemical tests.



Fig. 15 (a-g). SEM images of CpTi samples after electrochemical tests were performed taken at 3000x. (a: control, b: pH: 3.0, c: pH: 4.5, d: pH: 6, e: pH 6.5, f: pH: 7.5, g: pH: 9).

# 3.4 Discussion

Pure Ti and Ti alloys are highly reactive; therefore, when they are exposed to fluid media or air, they quickly develop a layer of titanium dioxide ( $TiO_2$ ). This layer of titanium dioxide, also known

as a passive film, acts as a protective interface between the metal structure and biological medium, i.e. saliva.<sup>4, 9</sup> The thickness and composition of the passive film layer is dependent on the environment the titanium is subjected to. Once formed, the passive film layer is constantly broken down and reformed in the oral cavity due to the existence of electrochemical reactions present in the saliva and mechanical actions caused by mastication and micro-movements. The combination of chemical reactions and mechanical actions can lead to a complex degradation process of the passive film layer which can ultimately lead to surface corrosion.

This study showed that the hypothesis was not valid; the pH does have an affect on the corrosion behavior of CpTi in artificial saliva.  $E_{corr}$ ,  $I_{corr}$  and  $I_{pass}$  values suggested that artificial saliva at neutral pH (6.0, 6.5, and 7.5) led to greater corrosion of the CpTi discs. This was indicated by the decreasing  $E_{corr}$  values, increasing  $I_{corr}$  values and increasing  $I_{pass}$  values for all three pH values.

All three testing values ( $E_{corr}$ ,  $I_{corr}$  and  $I_{pass}$ ) suggested an increase in current is required for the development of the passive film layer. This behavior can indicate that although a passive layer is forming, defects in the oxide film may form as well, i.e., there is a tendency towards the formation of a more irregular or porous oxide layer.<sup>2, 8, 30</sup> The defects can eventually lead to dissolution and subsequent release of metal ions into the system.

The results from the Nyquist and Bode plots indicated that the oxide film formed on the surface of CpTi is thinner at the neutral pH 7.5 (higher corrosion kinetics). If the passive film is thinner, it is easier to penetrate, also leading to an increase in potential pitting. Although the Nyquist and Bode plots agree with potentiodynamic results for pH 7.5, they do not support the results of potentiodynamic tests for pH 6.0 and 6.5. In addition, only the C<sub>dl</sub> value for pH 7.5 (capacitance was higher for 7.5) is in agreement with potentiodynamic and SEM results. A increase in capacitance is associated with an decrease in the thickness of the passive layer over time.<sup>23,31,32,33</sup> A possible explanation, is that the EIS tests performed in this study were conducted over a short period of time, only two hours. Over a prolonged period of time (days, weeks, years)

the passive film layer at pH 6.0 and 6.5 may increase in thickness, improving the overall corrosion resistance. However, as noted by the SEM images, during the short time of the potentiodynamic test performed in this study, breakdown of the passive film layer was possible. Earlier studies also reported such particular behavior of heavy surface damage, even pitting, on Ti under the influence of surrounding media, particularly pH level and amount of dissolved oxygen. <sup>8, 13</sup>

A previous study by Souza et al suggested that the protective passive film on Ti alloys at lower pH is less protective.<sup>22</sup> The study evaluated the effect of pH on the electrochemical behavior of titanium alloys in Ringer solution and found that, contradictory to the current study, Ti alloys tend to be more corrosive at a lower pH. In their study two Ti alloys were compared (Ti-13Nb-13Zr and Ti-6Al-4 V), not CpTi, at only two pH values, 5.5 and 7.0. In addition, Ringer solution differs greatly in electrolytic composition from artificial saliva. <sup>8, 13, 15, 16, 30, 32</sup>

This study had several limitations. It was limited by the small number of samples tested and large range of pH values. In addition, acidic or basic components within the artificial saliva solution may have contributed to the corrosion at more neutral pH. Future work will look at close pH intervals of artificial saliva in order to identify the pH value with the greatest electrochemical corrosion. Galvanic studies should be incorporated, as well as combining the chemical and mechanical components of corrosion via tribocorrosion studies of the implant system. <sup>33, 34</sup>

This study provided a novel and systematic approach in studying corrosion of titanium in the oral environment, by employing different electrochemical techniques, particularly impedance measurements.<sup>30</sup> Understanding the corrosion process of titanium alloys is crucial in predicting the long-term effects of current implant therapy. Corrosion products may have a beneficial or potentially detrimental effect on osseointegration of dental implants.<sup>10</sup> Further studies via electrochemical studies and tribocorrosion<sup>33,34</sup> will continue the corrosion investigation and ultimately lead to the most effective treatment for patients.

## 3.5 Conclusions

The results from this study exhibited that there was a significant influence of pH of the media on the corrosion behavior of CpTi. The following conclusions were drawn:

- I<sub>corr</sub> values indicated that neutral pH 7.5 had inferior corrosion resistance. This finding
  was supported by the impedance results of the Nyquist plot and R<sub>p</sub> value determined via
  the Bode plot.
- E<sub>corr</sub>, I<sub>corr</sub>, and I<sub>pass</sub> values suggested a greater corrosion potential at more neutral pH:
   6.0, 6.5, 7.5. EIS results did not support greater corrosion kinetics at pH 6.0 and 6.5.;
   however it did support greater corrosion kinetics at pH 7.5.
- 3. SEM images showed considerable surface damage under pH: 6.5, 7.5 and 9.0.
- The weak corrosion behavior at neutral pH invites some concerns and highlights the need for further study.

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#### 4. Influence of pH on the Tribocorrosion behavior of CpTi in Artificial saliva

#### Abstract

Dental implants made of titanium alloys have been used as a predictable therapy approach to replace missing teeth. The oral environment subjects titanium implants to varying conditions like changes in pH, temperature, and saliva contamination leading to chemical corrosion together with mastication process. **Objective:** In this study, the combined effect of chemical corrosion and wear (so called tribocorrosion) in the degradation of dental implant material (cpTi) under varying pH oral environment was investigated. Methods: Titanium (cpTi) discs were subjected to sliding tests in artificial saliva at varying pH: 3.0, 6.0 and 9.0. A custom made tribocorrosion apparatus was used to carry out the tests. The tribological system consisted of a ceramic ball of 28mm diameter articulating against the flat face (titanium). Results: EIS results indicated an increase in electrochemical double layer capacitance (C<sub>dl</sub>) at pH 3.0 and 6.0 after sliding. Surprisingly, in the presence of tribological stresses the measured current evolution was highest and fluctuated the most at pH 6.0. In addition, the greatest weight loss was measured at pH 6.0. Conclusions: Despite reports of cpTi being electrochemically stable down to pH 2.0, this study suggests degradation peaks at near neutral pH pH values in the presence of motion. At pH 6.0 the passive film layer, typically protecting the surface of titanium may not be reformed cohesively, resulting in more tribocorrosion products at the surface, which are easily sheared off. These findings elevate concern with regards to dental implants because the average pH of the oral cavity is 6.3. Key words: Tribocorrosion, Dental implants, Electrochemistry, Synergism

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#### 4.1 INTRODUCTION

The use of dental implants is a routine method for replacing missing teeth. In the US, about 300,000 patients currently receive dental implants yearly <sup>1</sup>. Titanium is the most common material used for dental implants due to its biocompatibility, mechanical properties and excellent corrosion resistance <sup>2-4</sup>. The corrosion resistance of titanium results from the formation of a very stable, continuous, highly adherent, and protective oxide film on the metal's surface. The nature, composition and thickness of the protective surface oxides that form on titanium alloys depend on environmental conditions <sup>4</sup>.

Although titanium alloys are highly corrosion-resistant because of the stability of the TiO<sub>2</sub> oxide layer, they are not inert to corrosive attack <sup>5</sup>. When the stable oxide layer is broken down or is unable to reform on parts of the surface, titanium can be as corrosive as many other base metal alloys <sup>6</sup>. In the oral environment, once placed, the implant interface is continuously washed with saliva via the gingival sulcus. The oral cavity can simulate an electrochemical cell because saliva acts as a weak electrolyte <sup>7</sup>. Electrochemical corrosion of titanium alloys due to the electrolytic nature of saliva, may lead to crevice corrosion of dental implants, and ultimately the release of corrosion products into the body<sup>8</sup>. In addition to constant contamination, the pH of saliva can vary in areas around dental implants. Many factors can change the pH of saliva. Infection can acidify the pH of saliva<sup>11</sup>. Food, oral hygiene products, age, periodontitis, oral habits such as smoking, systemic disease, and salivary gland radiation can also contribute to the changes of pH of saliva <sup>12-21</sup>. The normal, resting pH of saliva in the mouth is in the range of 6.3 to 7.0. However, the resting pH of saliva can fall below 6.3 to an average of 3.5 temporarily if acidic beverages are ingested or be raised to 8.3 if certain alkaline foods such as vegetables and grains are taken in <sup>13</sup>. The pH of saliva may contribute to the corrosion of dental implants <sup>7, 22-26</sup>. The pH level is known to have a strong influence on the corrosion resistance of titanium (cpTi) and titanium alloys (e.g. Ti6Al4V)<sup>22, 26-28</sup>. Previously, a clinical report by Willert et al <sup>34</sup> on crevice corrosion of cemented titanium alloy stem in hip joints revealed the presence of high acidicity (even up to pH 2.0) around the proximity of corroded stem. Authors also observed corrosion marks on the surface next to sliding tracks, which eventually shows both the mechanical change and chemical influence on the degradation. This demonstrates that the simultaneous actions of wear and corrosion (tribocorrosion) may influence overall performance of implants <sup>32, 35-37</sup>.

In oral cavity, during mastication, a dental implant is exposed to both axial and lateral movements, in addition to the corrosive environment. All of the forces subjected to dental implants generate micro-movements on the implant/abutment, abutment/crown and the implant/bone interface. Each time the two surfaces rub against each other, their protective passive film may be removed leading to surface corrosion and eventual release of corrosion products into the system. These corrosion products likely induce inflammatory reactions that provoke the release of inflammatory mediators from macrophages which lead to bone resorption <sup>29, 30</sup>. Numerous studies have attempted to investigate the chemical corrosion of titanium surfaces, however, very few have reported on the effect of combined chemical and mechanical action, which resemble the clinical oral environment <sup>31-33</sup>.

Therefore, the objective of the current work was to study the tribocorrosion behavior of Ti as a function of the varying pH levels of solution. We hypothesized that Ti is more susceptible to tribocorrosive wear at lower pH values.

#### 4.2 Materials and Methods

#### 4.2.1 Specimen Preparation

CpTi alloy discs (American Elements, Los Angeles, CA) of 12mm diameter and 7mm thickness were used. The tests were conducted in artificial saliva with different pHs: 3.0, 6.0, and 9.0. The electrolyte reference used was Fusayama and Meyer's artificial saliva <sup>22-23</sup>. The composition of this solution, Table II, closely resembles that of human natural saliva. To obtain a more acidic artificial saliva solution, lactic acid was added in 1 mL increments, and to obtain a more basic

artificial saliva solution, sodium hydroxide (NaOH) was added in 1 mL increments. Before the test, all the samples were polished and cleaned using standard metallographic methods. Final surfaces finish of Ra < 10 nm was attained and maintained within  $\pm 2$  nm SD.

TABLE I COMPOSITION OF ARTIFICIAL SALIVA			
Component	Quantity (g/L)		
KCI	0.4		
NaCl	0.4		
CaCl2.2H2O	0.906		
NaH2PO4.2H2O	0.690		
Na2S.9H2O	0.005		
Urea	1		
To achieve lower pH (acidic) lactic acid is added			
To achieve high pH (basic) NaOH is added			

# 4.2.2 Initial corrosion tests

The tests were conducted in a custom made electrochemical cell. The cell held 150 ml of solution. All measurements were made in a standard three electrode cell system <sup>37</sup>. A saturated calomel electrode (SCE) was used as the reference electrode (RE) and a graphite rod as the counter electrode (CE). A Gamry potentiostat was used to carry out the corrosion measurements. After mounting the sample, a time period was allotted for the initial stabilization and to achieve the temperature of 37°C. Initially, the evolution of open circuit potentials (OCP) was monitored during a period of 3600sec. Then the samples were anodically polarized from -0.8 V to 1.8 V at a scan rate of 5mV/sec. The potentiodynamic tests were started -0.3V below the lowest obtained OCP value . After the corrosion tests, surface characterization was performed by optical and scanning electron microscopy (SEM).

# 4.2.3 Tribocorrosion tests

A specially made tribocorrosion set-up was employed for the current study as shown in Figure 16.



Figure 16. Tribocorrosion test apparatus.

It consists of pin-on-ball tribo-system <sup>38-40</sup> where a ceramic ball of 28 mm diameter, articulates against the flat face of the cylindrical titanium sample. At the beginning of each test, the ball surface was cleaned and the surface checked for any damage. The ball was then placed to articulate with a fresh surface against the metal disc. Tests with varying pH were conducted randomly. In the current study, the focus was on the influence of pH values of the solution and mechanical stress from the tribological system on the tribocorrosion behavior of titanium. Therefore, the type of corrosion test selected was a potentiostatic test to measure the evolution of current. As this study was conducted at corrosion potential ( $E_{corr}$ ), the effect of the unworn area has been neglected because the current contribution is deemed insignificant in the presence of a passive film <sup>41</sup>.

To imitate oral contact conditions, the load (constant 20 N, corresponding to the Hertzian contact pressure of 372 MPa at the start of the experiment) and motion frequency (1.2 Hz) was adjusted to reflect the stresses and movements during the mastication. Tests were conducted for 2000 cycles, representing normal daily mastication activity of a person. Table III provides details on the tribocorrosion test set-up and test parameters.

TABLE III TEST MATRIX FOR TRIBOCORROSION				
Material	CpTi (Titanium)			
Ball	Ceramic			
Load	20N			
рН	3 (artificial saliva +lactic acid			
	6 (artificial saliva +lactic acid			
	9 (Artificial saliva + NaOH)			
Frequency	1.2 Hz			
No of cycles	2000 cycles			
Amplitude	5°			

The testing protocol consisted of three phases: initial stabilization, sliding phase which was a potentiostatic test conducted at corrosion potential ( $E_{corr}$ ) in order to evaluate the current evolution as a function of time and pH, and a final stabilization period. The initial stabilization period was kept to 1- 2 hours. During the sliding phase, the potentiostatic test was performed at  $E_{corr}$  for each pH, the evolution of current was monitored as a function of time. The  $E_{corr}$  measurement were made during the initial stabilization period of each tribocorrosion test and validated using the value determined from the initial potentiodynamic test (Figure 18 below) using the same solution and testing conditions. During the potentiostatic test, the evolution of current was monitored as a function of time. Before and after sliding, EIS measurements were performed in the frequency range from 100 kHz to 0.01Hz, with AC sine wave amplitude of 10 mV applied to the electrode at its corrosion potential ( $E_{corr}$ ). For EIS data simulations the Zview2 software was used. Three test replicas (n=3) were used for this study. Weight loss was estimated based on profilometry measurements of the wear scar (white light interferometry microscopy ((Zygo New View 6300, Middlefield, CT, USA))

#### 4.2.4 Estimation of weight loss due to wear and corrosion

As explained below, a simple model<sup>16</sup> was used to identify the contribution of corrosion and wear to the total weight loss:  $K_{wc}$ =  $K_w$  +  $K_c$ , where  $K_{wc}$  is the total weight loss due to wear and corrosion (tribocorrosion),  $K_w$  is the total wear loss due to sliding wear, and  $K_c$  is the total wear volume loss due to corrosion. In this setup, the  $K_w$  is determined via "before" and "after" testing weight measurements. The weight loss due to corrosion can be estimated by using Faraday's Law:  $K_c = Q/ZF$  and  $K_c = MIt/ZF$ , where:

- Q = charge passed
- F = Faraday's constant (96500 C/mol-1)
- Z = number of electrons involved in the corrosion process (assumed to be 2)
- I = the total current
- T = the total exposure time
- M = the atomic mass of the material or equivalent weight.

#### 4.2.5 Surface Characterization

Worn and corroded surfaces were examined by using optical, white light interferometry and scanning electron microscopy (SEM) techniques (Joel JSM-6490 LV, Japan). This is helpful to determine the wear/corrosion mechanisms based on surface damage and compositional changes.

#### 4.3.6 Statistical Analysis

The corrosion parameters, including  $E_{corr}$  (corrosion potential) and  $I_{corr}$  (corrosion current density), were statistically analyzed using one-way ANOVA for analyzing how pH affects the corrosion parameters. Tukey's HSD test ( $\alpha = 0.05$ ) was chosen as the multiple-comparison technique when necessary (Statistical Package for the Social Sciences, version 17.0; SPSS Inc, Chicago, III, USA).

#### 4.3 Results

#### 4.3.1 Evolution of electrochemical parameters

Figure 17 shows the potentiodynamic curves of CpTi, in the presence of artificial saliva with pH 3.0, 6.0 and 9.0. The values of  $E_{corr}$ ,  $I_{corr}$ , and  $I_{pass}$  (Table IV) show the least corrosion resistance at pH 6.0. One-way ANOVA demonstrates that pH has a significant influence on  $E_{corr}$  and  $I_{corr}$  (p<.05). Post-hoc analysis shows that  $E_{corr}$  is significantly higher for pH 6.0 compared with other pH (p<0.05).  $I_{corr}$  is significantly raised for pH 6.0 when compared to pH 9.0 (p<0.05).  $I_{corr}$  is significantly lower for pH 3.0 when compared to pH 6.0 and pH 9.0 (p<0.05).  $I_{corr}$  is significant, indicate greater current required for development of the passive film layer at neutral pH. During the tribocorrosion, the potentiostatic test was performed at the  $E_{corr}$  value for each pH. Performing potentiostatic tests enabled the measurement of the evolution of current at each specific pH. Figure 18 (a) shows the evolution of current at pH 6.0. From this figure, it becomes evident that once sliding begins; there is an increase in the current value as well as the fluctuation of current. Five cycles are highlighted in Figure 18(b) for direct comparison of pH effect on current evolution. For each pH, the same conditions were applied, only pH was varied. Figure 18(b) shows that pH 6.0 had the greatest current value and the greatest current fluctuation, suggesting some degree of surface damage.



Figure 17. Potentiodynamic curves of CpTi in presence of artificial saliva at pH 3,6,9. Curves and  $E_{corr}$  values are unique indicated a difference in behavior as a function of pH.

# TABLE IV

### CORROSION PARAMETERS OBTAINED FROM POTENTIODYNAMIC POLARIZATION CURVES AND FROM EIS MODELING OF CPTI IN ARTIFICIAL SALIVA AS A FUNCTION OF PH

	рН 3.0	рН 6.0	рН 9.0
Free potential (open			
circuit potential):			
E <sub>oc</sub> (V)	$-0.025 \pm 0.01$	$-0.5 \pm 0.08$	$-0.54 \pm 0.04$
<b>Corrosion potential:</b>			
E <sub>corr</sub> (V)	$-0.40 \pm 0.16$	$-0.35 \pm 0.014$	$-0.40 \pm 0.18$
Corrosion current: I <sub>corr</sub>			
(A/cm)	$8.33 \times 10^{-8} \pm 6.81 \times 10^{-9}$	$1.27 \mathrm{x} 10^{-7} \pm 5.60 \mathrm{x} 10^{-8}$	$1.17 \mathrm{x} 10^{-7} \pm 5.98 \mathrm{x} 10^{-8}$
<b>Passivation current:</b>			
$I_{\text{pass}}$ (A/cm <sup>2</sup> )	$2.1 \times 10^{-5} \pm 3 \times 10^{-6}$	$1.5 \times 10^{-5} \pm 1 \times 10^{-6}$	$3.2 \times 10^{-5} \pm 2.2 \times 10^{-6}$



Figure 18(a). Representative evolution of current at pH 6.0 indicates development of current upon sliding.

Figure 18(b). Highlighted 5 cycles in order to observe pattern variation as a function of pH. pH 6.0 has greatest current value and fluctuation of current.

## 4.3.2 Weight loss distribution as a function of pH

The variation of weight loss as a function of pH is shown in Figure 19 (a) & (b) and Table V. Figure 19(a) shows the  $K_{wc}$ , the total weight loss (combined effect of wear and corrosion), as a function of pH. A one-way between-groups analysis of variance was conducted to explore the impact of pH on material degradation for  $K_{wc}$ . There was a statistically significant difference for the three pH groups (p=0.001). Post-hoc comparisons using the Tukey HSD test indicated that the mean score for pH 3.0 (M=280, SD=52.9) was significantly different from pH 9.0 (M=110, SD=10). pH 6.0 (M=333.33, SD=45.092) was significantly different from pH 9.0 (M=110, SD=10).

# TABLE V

# EIS PARAMETERS AT TESTED pH VALUES (pH 3.0, pH 6.0 and pH 9.0), BEFORE SLIDING (BS) and AFTER SLIDING (AS). Rs: SOLUTION RESISTANCE ( $\Omega$ ), POLARIZATION RESISTANCE (Rp), WARBURG COMPONENT (Wo), CAPACITANCE (C), X<sup>2</sup> VALUE AT BEST FIT ACHIEVED

Test conditions	Rs (Ω)	Rp(Ω)	Wο(Ω)	Cf (F)	X <sup>2</sup>
pH 3-BS	214.9± 10.7	25672±1283	-	$2.69 \text{ x}10^{-5} \pm 1.3 \text{ x}10^{-6}$	$2.2 \times 10^{-3} \pm 1.1 \times 10^{-4}$
pH 3-AS	199.2± 9.9	39647±1982	-	$8.22 \text{ x}10^{-5} \pm 4.3 \text{ x}10^{-6}$	$6.1 \times 10^{-3} \pm 3.1 \times 10^{-4}$
pH 6-BS	168± 8.5	27853±1392	$3.0 \pm 0.2$	$8.01 \times 10^{-5} \pm 4.1 \times 10^{-6}$	$1.7 \times 10^{-3} \pm 8.5 \times 10^{-5}$
pH 6-AS	177.5± 9.8	27458±1567	5068±254	$9.60 \text{ x}10^{-5} \pm 4.8 \text{ x}10^{-6}$	$1.1 \times 10^{-3} \pm 5.5 \times 10^{-5}$
pH 9-BS	225.7±11.5	23696±1487	45406±2278	$1.16 \text{ x} 10^{-5} \pm 5.8 \text{ x} 10^{-7}$	$3.2 \times 10^{-3} \pm 1.6 \times 10^{-4}$
pH 9-AS	178.3± 7.2	30645±1665	62295±4012	$9.53 \text{ x}10^{-6} \pm 4.7 \text{ x}10^{-7}$	$2.5 \times 10^{-3} \pm 1.3 \times 10^{-4}$



Figure 19(a). (a) Evolution of Kwc (total weight loss due to combined effect of wear and corrosion) as a function of pH. (b) Evolution of Kc (total weight loss due to corrosion) as function of pH.
The evolution of K<sub>c</sub>, the mass loss due to corrosion as a function of pH, is shown in Figure 19(b). The K<sub>c</sub> value of pH 6.0 was significantly higher than those of pH 3.0 and 9.0. The pH 6.0 shows the greatest weight loss due to corrosion and total weight loss. Post-hoc comparisons using the Tukey HSD test indicated that the mean score for pH 3.0 (M=0.283, SD=0.06) was significantly different from pH 6.0 (M=97.4, SD=3.32). pH 6.0 (M=97.4, SD=3.32) was significantly different from pH 9.0 (M=33.7, SD=47.8).

#### 4.3.3 Evolution of EIS parameters as a function of pH

The data from the electrochemical impedance spectroscopy (EIS) before and after sliding are displayed through Nyquist graphs (real impedance vs. imaginary impedance). Nyquist plots for all three investigated pH-values are included in the Figure 20 (a-c). It is interesting to note that the impedance values were higher after sliding than before sliding, which was true for for all three pHs.



Fig 20 (a,b,c). Nyquist plot before and after the sliding for pH 3, 6, 9 (a,b,c respectively). Impedance value increased after sliding at all three pH values which may be result of test setup.

Close observations on the Nyquist results (Figure 20 (a-c)) indicate a more complicated behavior than what can be modeled with a simple Randle's circuit for pH 6.0 and pH 9.0. Hence, two separate EIS circuits were used to model the corrosion process, as presented in Figure 21 (a) and (b). For pH 3.0, a modified Randle's circuit was used (Figure 21(a), where the simple

capacitance component in the Randle's circuit is replaced by a constant phase element (CPE), to obtain a representative model of the actual electrochemical behavior <sup>45-47</sup>. It is thought that the CPE behavior can be linked to the heterogeneous properties of the surface, after tribocorrosion exposure. Further, Nyquist plots for pH 6.0 and pH 9.0 display a suppressed semicircle and a start of a diffusion tail (Figure 20(b-c)). Hence, a new model, Figure 21b, consisting of CPE and Warburg element (Wo) was employed for pH 6.0 and pH 9.0. Thus, the effect of surface heterogeneity and diffusion are separated from polarization resistance <sup>39, 48-49</sup>. The EIS data, solution resistance (Rs), polarization resistance (Rp), capacitance (Cf), and X2 values are presented in Table V. In general, low X2 values indicate a satisfying fit of the model <sup>46-47</sup>. Interestingly, the increase in the Warburg element for pH 6.0 and pH 9.0, clearly indicate the predominant influence of diffusion and surface heterogeneity at higher pH levels, particularly for the surface after the tribocorrosion exposure. Hence, the reported resistance and capacitance values are indicative of actual interfacial capacitance <sup>37, 38</sup>.

Figure 23(a) shows the variation in polarization resistance (Table V) as a function of pH and test conditions (before sliding (BS) and after sliding (AS)). The resistance increased after sliding in the pH 3.0 and pH 9.0 solutions. In case of pH 6.0, the resistance was very similar to resistance of before sliding. This supports the observed high weight loss at pH 6.0 and suggests the presence of an unstable passive film generated under tribocorrosion conditions. Figure 23(b) shows the variation in capacitance as a function of pH and test conditions. An increase in capacitance can be seen for pH 3.0 and pH 6.0, despite increased corrosion kinetics after sliding. The capacitance for pH 9.0 after sliding appears to not differ from the value before sliding.



Fig 21. The employed electrochemical impedance spectroscopy (EIS) circuits for EIS model. (a) Randle's circuit with CPE-pH 3.0, (b) EIS circuit with Warburg component- pH 6.0 and pH 9.0 Rs: Solution resistance, CPE: Constant phase element, Rp: Polarization resistance, Wo: Warburg element



Figure 22. EIS model results (a). Variation of polarization resistance ( $R_p$ ) as a function of pHs, before sliding (BS) and after sliding (AS). Greater resistance after sliding may be function of test set-up (b). Variation of capacitance ( $C_{dl}$ ) as a function of pHs, before sliding (BS) and after sliding (AS) pH 9.0 did not have increase in capacitance which may indicate greater passivation at basic pH. (error bar: ±SD)

#### 4.3.4 Surface Characterization

A typical wear scar obtained after the tribocorrosion exposure is shown in Figure 23. The SEM images of the worn surfaces taken at pH 3.0, 6.0 and 9.0 are provided in the Figures 24(a-f). Figure 24(a) & (b) SEM images of the worn surfaces, after tribocorrosion exposure at pH 3.0. The heavy mechanical deformation of the surfaces is clear from the Figure 24(b) at pH 3.0. The damaged surface at pH 6.0 is shown in the Figure 24(c) & (d). Figure 24(d) at (pH 6.0) indicates accelerated wear and deformation due to chemical corrosion as the changes in the surface appearance of cracks and delamination. Finally, the worn surfaces for pH 9.0 are presented in Figure 24(f) and (g), which shows similar observations.



Figure 23. A typical tribocorrosion wear scar.

 $\begin{bmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 2 \\ 1 & 2 & 1 & 2 & 2 \\ 1 & 2 & 1 & 2 \\ 1 & 2 & 1 & 2$ 

Figure 24 (a-f). SEM images of the worn surfaces, after tribocorrosion exposure. All show significant mechanical deformation. (d) pH 6.0 shows increased chemical deformation with the appearance of cracks.

### 4.4 Discussion

In the current study, the influence of pH on the tribocorrosive behavior of Titanium is investigated and synergistic interactions between wear and corrosion are analyzed.

### 4.4.1 Influence of pH on the electrochemical behavior of Titanium

The tribocorrosion results did not follow the general corrosive behavior of Ti degrading more at lower pH values. Instead, the highest weight loss was determined for pH 6.0, therefore, the hypothesis has to be rejected. The corrosion kinetics undergoes continuous changes in close association with tribological events (sliding or fretting). Subsequently this might impose changes in surface chemistry which are reflected in the high polarization resistance after sliding (Figure 22(a)).

Titanium is used for dental implants in the oral cavity due to its material property to oxidize quickly. The oxide film should serve as a protective interface between the metal structure and biological medium, i.e. saliva <sup>1-4</sup>. Hence, the results of the study are concerning because the average pH within the oral cavity is 6.3 <sup>15-16</sup>.

Further, the results (Figure (18)) clearly show that the evolution of the current is very sensitive to the characteristics of the tribological event. In this study, large spikes in the current evolution could be the result of passive film breakage and re-formation. According to Pourbaix <sup>50-53</sup>, pH 6.0 (at tested potential) promotes passivation, causing more current flow, than pH 3.0 and pH 9.0. Interestingly, as observed during the initial electrochemical test, pH 3.0 exhibits very minor variation. It is known that the magnitude of the current evolution largely depends on the passivation process (rate of growth and structure of the film) and fundamental electrochemical behavior (in a particular electrolyte) of the material <sup>5, 36, 43</sup>.

Once formed, the passive film layer is constantly breaking down and reforming because of electrochemical reactions present in the oral cavity via saliva, and mechanical actions caused by mastication and micro-movements. Once the oxide film is destroyed, further corrosion resistance is dependent on how quickly reformation takes place <sup>50</sup>. During the mastication process, the oxide film layer can be damaged; therefore, good corrosion resistance results from the ability of the metal surface to rapidly reform the protective oxide film <sup>37,50</sup>. The nature, composition and thickness of the protective surface oxide film as well as the rate of reformation are directly influenced by the environment condition, i.e. composition and pH of saliva <sup>50</sup>. The combination of chemical and mechanical actions can lead to a complex degradation process of the passive film layer which can ultimately lead to surface corrosion and potentially harmful metal ion release into the body <sup>51, 52</sup>. In the experimental set-up, the articulation of the ball removes the passive film leading to a sequence of corrosion mechanisms, such as depassivation, and repassivation. Hence, the surface, which is very active during the passivation process, possibly undergoes a defective reformation of the passive film at pH6.0. In literature, the Pourbaix diagram of titanium

provides a classical representation of titanium behavior at 25°C in water <sup>53</sup>. It depicts the wide range over which the monoxide, trioxide and dioxide of titanium is predicted to be stable, based on thermodynamic (free energy) consideration. From the Pourbaix diagram it would be expected to have corrosion of titanium at an anodic potential and lower pH. The Pourbaix diagram for Ti provides a general picture for understanding the corrosion behaviour of the metals, as a function of pH and electrode potentials. However, it does not take into account body temp (37°C) or different solutions, i.e. artificial saliva vs. water. In addition, the Pourbaix diagram does not take into account corrosion kinetics influenced by the wear and friction.

#### 4.4.2 Influence of pH on the tribocorrosion behavior: Mechanisms and synergism

The results showed the greatest current and fluctuation of current at pH 6.0. Greater fluctuation is an indication of greater surface damage via the tribocorrosion process. It appears that because the K<sub>c</sub> value at pH 6.0 is significantly higher than those of pH 3.0 and 9.0, that the increase in corrosion tendency at pH 6.0, significantly affects the weight loss. At pH 9.0, the passive film may be more easily reformed, leading to less total weight loss. Therefore, it seems that pH has a strong influence on the formation but also lower the degradation of the passive film. In addition, the weight loss decreases at pH 3.0 indicate the influence of wear enhanced corrosion under the tribocorrosion process rather than a pure electrochemical exposure. When a metal surface is subjected to severe rubbing or to a stream of impacting particles the passive film damage becomes continuous and extensive. The SEM images support the existence of greater corrosion due to tribocorrosion at pH 6.0 as evident by the appearance of cracks. At pH 6.0, the self-healing process via passive film formation, may no longer be effective, and in addition it requires a high rate of metal oxidation. The underlying CpTi will strongly corrode before the protective passive film is reformed, if at all. In such a case, the total material loss due to tribocorrosion will be much higher than the sum of wear and corrosion one would measure in experiments with the same metal where only wear or only corrosion takes place. This shows that tribocorrosion is not simply the addition of the rate of wear and the rate of corrosion, but it is strongly affected by synergistic and antagonistic effects between mechanical and chemical mechanisms <sup>42-44</sup>.

It was expected to see a decrease in corrosion resistance after sliding, however, according to the Nyquist plots, the corrosion kinetics improved after sliding for all three pHs. This may be due to special characteristics of this test system where the ball is contacting a small area on the sample; however, the entire sample surface is exposed to the pH solution. Because the entire sample is exposed to the solution, the passive film layer remains intact over a large area of the sample surface leading to an increase in corrosion kinetics. It is also interesting to note that at pH 6.0 and 9.0 the impedance values after sliding were significantly higher than before sliding. This may mean the sliding process and worn area may have contributed to the long-term improvement in corrosion resistance. Along with our EIS results of increased corrosion kinetics after sliding, there was an increase in capacitance for pH 3.0 and pH 6.0. The capacitance for pH 9.0 after sliding appears to not differ from the value before sliding. This could be a result of increased passivation at a basic pH. There was an increase in resistance for pH 9.0 after sliding which was in consistent with the capacitance value. The predominant influence of diffusion and surface heterogeneity at higher pH levels was clearly indicated, particularly after the surface was exposed to tribocorrosion <sup>45-49</sup>. This led to an increase of the Warburg element in the EIS model for pH 6.0 and pH 9.0 (Table V).

In evaluating the synergistic interactions between wear and corrosion, Stack et al.<sup>42-44</sup> formulated criteria according to the ratio of corrosion wear ( $K_c$ ) and mechanical wear ( $K_w$ ). The ratio ( $K_c/K_w$ ) provides a decisive factor for the magnitude of this synergism and indicates the possible dominant mechanistic region present in the tribocorrosion process, as shown below:

### TABLE VI

SYNERGISTIC (Kc/Kw) RATIO AND DEGRADATION MECHANISM

Synergistic (K <sub>c</sub> /K <sub>w</sub> ) Ratio Value	Degradation Mechanism
$K_c/K_w \leq 0.1$	Wear
$0.1 < K_c/K_w < 1$	Wear-corrosion
$1 \leq K_c/K_w \leq 10$	Corrosion-wear
K <sub>c</sub> /K <sub>w</sub> >10	Corrosion

Figure 25 displays the evolution of  $K_c/K_w$  ratio for tested pH values. Interestingly, the values of  $K_c/K_w$  for pH 3.0 and pH 9.0 are below 0.1, indicative of dominant degradation mechanism is mechanical wear. At pH 6.0,  $K_c/K_w$  is lies between 0.1 and 1. The clearly demonstrate prevalence of synergistic interaction between wear and corrosion as the dominating degradation mechanism. This is in agreement with other observations in this study (section 4.4.1).



Fig 25. Kc/Kw ratio for pH 3.0, 6.0, and 9.0. pH 6.0 shows combination of wear and corrosion as dominate degradation mechanism.

In tribocorrosion studies, combination of processes such as sliding, rolling, fretting, impact, erosion, etc., together with electrochemical or chemical attack (presence of saliva) can result in various forms of deterioration ranging from loss of material to delamination and cracking <sup>35,43</sup>.

When tribocorrosion occurs in a biological environment, such as in the oral system, the presence of biological species, such as saliva and bio film, creates further complexity in understanding the material's degradation kinetics and interplay of both driving mechanisms <sup>37, 54</sup>.

#### 4.4.3 Clinical relevance and future scope

The tribocorrosion results did not follow the general corrosive behavior of Ti, with an increase of corrosion at lower pH values <sup>34</sup>. Instead, the highest weight loss was determined for pH 6.0, which raises concerns for bio-tribological applications. The corrosion kinetics undergoes uninterrupted changes in close association with tribological events (sliding or fretting3). Subsequently this might impose changes in surface chemistry, which is reflected in the high polarization resistance after the sliding (Figure 22). The articulation of the ball removes the passive film leading to a sequence of corrosion mechanisms, such as depassivation, and repassivation. Hence, the surface, which is very active during the passivation process, possibly undergoes a defective reformation of the passive film and resulting in highest weight loss as observed at pH 6.0.

Although this study has several limitations, it provides a first look at a systematic approach in investigating tribocorrosion behavior of titanium in the oral environment. It is important to note that the components within the artificial saliva solution may have contributed to the corrosion at more neutral pHs. Further, the tribometer used was with a constant, unidirectional load, however in the oral environment, the load is varied both in magnitude and direction. The sample dimensions are different from implants. Other than general EIS measurement, localized approach at the tribocorrosion site could provide further insight about the specific effect of tribocorrosion on the impedance. In addition, hydration can alter oxide impedance properties over time. In future, a special tribocorrosion apparatus will be developed to mimic multidirectional fretting movement at varying loads by including other different types specimens for example Ti-6AI-4V alloy with a variety of surface treatments. Tribocorrosion studies will also be performed and the adherence of osteoprogenitor cells to the corroded and surfaces will be investigated <sup>5,6,54,55</sup>. Understanding the

synergistic effect of mechanical and chemical corrosion of titanium alloys is crucial to understanding the long-term effects of current implant therapy. Tribocorrosion products may have a beneficial or potentially detrimental effect on osseointegration. Further studies through electrochemical corrosion and tribocorrosion will be considered and ultimately lead to the most effective treatment for patients.

#### 4.5 Conclusions

In this study, tribocorrosion behavior of commercially pure titanium was investigated in the presence of artificial saliva as a function of pH. Evolution of current at all three pH values indicates the existence of damage to some degree to the passive layer during tribocorrosion. Titanium shows inferior performance in tribocorrosion at pH 6.0 as indicated by the total weight loss and SEM images. SEM images indicated greater tribocorrosion damage with appearance of cracks.

These findings are of concern with regards to dental implants because the average pH of the oral cavity is 6.3. The EIS results also agree with the surface changes, before and after the sliding. Better corrosion behavior after sliding may be due to the coupled action of the strong passive film formed in the unworn area, and chemical reaction in the worn area. Understanding the synergistic effect of mechanical and chemical corrosion of titanium alloys is crucial to understanding the long-term effects of current implant therapy.

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### 5. RESULTS and DISCUSSION

The aim of this master's dissertation was to study the tribocorrosion behavior, or combined effects of electrochemical corrosion due to saliva and wear, via the pin on ball tribological apparatus, of commercially pure titanium, at varying pH. Both the electrochemical and tribocorrosion results did not follow the general corrosive behavior of greater degradation of titanium at a strongly acidic pH value. The hypotheses must be rejected because in this study, the greatest weight loss was observed at pH 6.0.

#### 5.1 Electrochemical Results

The results from the initial study looking at the electrochemical behavior of CpTi at varying pH indicated that the pH having the poorest electrochemical resistance, therefore the greatest corrosion potential, was at neutral pH 7.5. The results from the tribocorrosion study also indicated greatest corrosion at close to neutral pH, but at a value of pH6.0. The tribocorrosion study was not performed at pH 7.5. Based on the electrochemical corrosion results, a greater tribocorrosion effect may be observed at pH 7.5.

#### 5.1.1 Current Evolution

The results for both the basic electrochemical corrosion study as well as the tribocorrosion study of CpTi indicate an active-to-passive behavior for each sample; however each potentiodynamic curve was unique to the pH. This shows that pH has an effect on the passivation process of titanium <sup>1</sup>. Ipass, although not statistically significant indicated that greater current was required to develop a passive film at near neutral pH for both the basic electrochemical corrosion study (at pH 6.0, 6.5, and 7.5) as well as the tribocorrosion study (at pH 6.0).

The potentiostatic tests performed at the Ecorr value for each pH enabled the measurement of the evolution of current at each specific pH. Once the sliding began, the current increased indicating an increase in surface corrosion. In addition to an increase in current, the fluctuation increased. The increase in current indicates that wear at any pH causes an increase in material degradation <sup>2,3</sup>. However, each pH exhibited a unique current value with unique fluctuation. This shows that the material degradation is dependent on pH, not simply on the addition of wear. pH 6.0 had greatest current value with the greatest fluctuation, meaning a more active surface. The large spikes observed at pH 6.0 could be the result of passive film breakage and re-formation. According to the Pourbaix diagram, pH 6.0 promotes greater passivation, causing more current flow. When subjected to wear and electrochemical corrosion, it is possible that because of the greater current flow present at pH 6.0 for titanium, with continued wear, the passive film breaks down and reforms at such a fast rate, that the current works against the system to degrade the material further rather than properly repassivate the surface.

#### 5.2 Tribocorrosion Results

The greatest total weight loss (Kwc) was observed at hibited by pH 6.0. This could be related to the formation of a greater number of third-body particles at pH 6.0<sup>4</sup>. The SEM images support the existence of greater corrosion due to tribocorrosion at pH 6.0 with the appearance of cracks. The SEM images from the basic electrochemical corrosion study also showed the greater amount of corrosion at more neutral pH (pH 6.5 and 7.5). At pH 6.0, there may have been a period of slow repassivation leading to greater wear resulting in an increase in third body particles, increased total weight loss, and an increase in current. A greater number of third body particles would result in an increase in the overall material degradation <sup>4</sup>. Because the corrosion resistance after sliding increased, the passive film layer that formed at the completion of the test may have better characteristics than the original oxide film formed before it was mechanically

damaged. The increased surface area due to wear may have led to a greater thickness of oxide layer leading to an increase in capacitance <sup>3</sup>. At pH 9.0, the resistance increased greatly which may mean that at more basic pH of artificial saliva, the oxide layer is at its most protective

The results from both of these studies do not follow the trend of the studies previously performed. From the Pourbaix diagram, it would be expected to see greater corrosion of Titanium at an anodic potential and lower pH  $^{5}$ . The problem of correlating the Pourbaix diagram to this study lies in the fact that the Pourbaix diagram does not take into account corrosion at 37°C, in a different ionic solution from water, or corrosion kinetics. Nakagawa et al reported that titanium loses its corrosion resistance at pH 4.2 with high concentration of Fluoride ions (452.4ppF in a 0.1% NaF solution)<sup>6</sup>. The results from the Nakagawa study indicated that the corrosion of titanium is enhanced in an acidic environment with high concentration of F- ions in solution because F- ions readily combine with H+ ions to form HF. The presence of HF accelerates corrosion of titanium. Fluoride was not added in this study to the artificial saliva solution. The results from this study show that in an unaltered Fusayama and Meyer artificial saliva solution at 37°C, the potential for greater electrochemical corrosion exists at more neutral pH (pH 7.5). In addition, under tribocorrosion sliding conditions, greater corrosion was seen at almost neutral pH of 6.0. More neutral pH may increase corrosion for a short time, leading to a lower potential, higher current evolution, and increased total weight loss. Because titanium repassivates almost instantaneously in the presence of oxygen, the passive layer most likely reforms. It may form a temporarily more stable, more protective passive layer, as evident by the increase in resistance after sliding; however with continued exposure to tribocorrosion, the passive layer will continually breakdown and reform. Over time, the greater corrosion rate and potential seen at pH 6.0 will lead to greater material degradation.

#### 5.3 Discussion – Clinical Relevance

There are many potential areas for tribocorrosion when considering dental implants in the oral cavity, the greatest area being at the abutment/implant interface <sup>7-10</sup>. At the abutment/implant interface, in many cases, two materials come into contact in the presence of gingival crevicular fluid, leading to tribocorrosion. Although the fit between abutment and implant body is tight, especially with the conical seal design, because the abutment is screwed into the implant with a prosthetic screw it is not a solid unit which lends itself to micromovement between the abutment and implant when subjected to axial and lateral occlusal forces <sup>9</sup>. This micromovement is also known as fretting <sup>10</sup>. Occlusal forces affect dental implants and the surrounding bone. According to bone physiology theories, there exists a certain threshold where the response mechanical stress will result in strengthening of the bone by increasing the bone density or apposition of bone <sup>11</sup>. On the other hand, stress above this threshold will result in bone resorption<sup>11</sup>. Many studies have shown that occlusal load may result in marginal bone loss around dental implants <sup>12-14</sup>. Because of the lack of pdl around a dental implant, occlusal force transmission is concentrated at the crest of the bone rather than the apex <sup>13,14</sup>. This combination of fretting force inherent in the system as well as the stress concentration at the neck of the implant due to the lack of pdl leads to the greatest amount of potentially detrimental fretting force at the abutment to implant interface.

One of the major difficulties in tribocorrosion studies is the lack of standard testing apparati <sup>15</sup>. Because it is a relatively recent field of study, there are few tribocorrosion systems, or tribometers. In this study, a pin-on-ball tribo-system, was used where a ceramic ball of 28 mm diameter articulated against the flat face of a cylindrical titanium specimen while being submerged in the artificial saliva solution. This was to simulate the contact between two-bodies: abutment and implant in the oral cavity. Although the pin-on-ball tribometer has many limitations, specifically, it does not provide multi-directional forces, i.e. occlusal forces, as seen at the

abutment/implant interface, it does provide a controlled environment for investigating the combined corrosive effect of wear and electrochemical corrosion <sup>15</sup>. Using the pin-on-ball apparatus, wear and electrochemical corrosion are studied coincidentally. The results of this study, by This combined effect, or tribocorrosion, as evident by the results of this study may be leading to greater material degradation than previously thought based on basic titanium corrosion studies only<sup>16</sup>.

Electrochemical corrosion can occur when titanium comes into contact saliva, gingival crevicular fluid, and/or biofilm within the oral cavity. The main difference between the three substances is the overall pH value with a range of pH 3.0 to pH 9.0<sup>17</sup>. The average pH of saliva is 6.3, however it varies from pH3.0 to pH 9.0 based on food and drink as well as the overall systemic health of the patient <sup>18</sup>. When a highly acidic drink is ingested, such as soda, the pH of saliva can drop to an acidic pH (4.3 or lower) for 30-60 minutes, or as long as there is sugar present in the mouth for aciduric and acidogenic bacteria to metabolize <sup>19</sup>. In this study, three pH values were chosen to encompass this range: pH 3.0, 6.0 and 9.0.

Dental implants come into contact with saliva upon placement of the implant body. In addition, the abutment/implant interface is in constant contact with a saliva-like substance known as gingival crevicular fluid <sup>20</sup>. The junction of abutment to implant ideally lies subgingival with the crest of the bone apical to it. The gingiva does not attach to the implant or abutment; providing optimal emergence of the restoration from tissue <sup>21</sup>. With unattached gingival tissue, the abutment to implant interface is continuously washed with a saliva-like substance, known as gingival crevicular fluid <sup>21</sup>. Gingival crevicular fluid is an enzyme heavy, saliva-like substance. Because it has a high concentration of alkalinic enzymes, such as alkaline phosphatase, the pH range is 7.5-8.7 <sup>20</sup>. The pH of the gingival crevicular fluid is heavily influenced by the microbial flora present at the titanium surface due to the attachment of biofilm <sup>22</sup>. Biofilm is a complex

matrix of polymers of host and bacterial origin beginning with the pellicle formation: salivary proteins attaching to the titanium surface <sup>23</sup>. The pH can drop to below 6.0 for extended periods of time when acute inflammation is present <sup>24</sup>. Studies have been performed to evaluate the pH values of gingival crevices and periodontal pockets. These studies have suggested that the pH value is influenced by the condition of the surrounding tissue. Alkaline pHs as high as 9.06 for gingival crevices adjacent to sites of chronic gingivitis have been reported <sup>25</sup>. The pH measurements showed a tendency to be more acidic during an acute inflammation, dropping to pH 6.28, and shifted towards alkaline, increasing to pH 7.65, during chronic inflammation <sup>19</sup>. The mean pH sampled from successful implant sites was 6.8, and that for failing implant sites with chronic inflammation was pH 7.2 <sup>19</sup>.

This study looked at 3 representative pH values: pH 3.0, 6.0 and 9.0. pH 3.0 represented ingestion of highly acidic products, pH 6.0 represented a slightly acidic scenario indicative of acute inflammation, and pH 9.0 represented an alkalinic scenario common to chronic inflammation. Based on previous tribocorrosion studies artificial saliva was chosen as the medium due to its stability throughout testing<sup>26,27,1</sup>. Natural saliva is very active and hard to stabilize. In addition, because this was a baseline study performed to determine the effect of pH as the only variable, unaltered artificial saliva was used instead of adding bacteria or changing the ion concentration.

The results of greatest current evolution and material degradation at pH 6.0 are of great concern because pH 6.0 would be indicative of gingival crevicular fluid with acute inflammation. Periimplantitis has been linked to marginal bone loss <sup>28</sup>. It begins as an acute inflammatory process that progress to a chronic inflammatory process <sup>12</sup>. It is possible that at pH 6.0, the oxide layer cannot repassivate effectively when worn away (via tribology) leading to excessive material degradation. In fact, it may be that the higher current inherently present at pH 6.0 for titanium

may work to accelerate material degradation due to competition between repassivation and continued breakdown. This would be exemplified if an acute inflammatory response exists, i.e. with peri-implantitis, where aerobic bacteria and anaerobic bacteria exist and compete, leading to marginal bone loss <sup>29</sup>. Although the formulation of the artificial saliva used in this study differs from that of gingival crevicular fluid, its base is similar and pH range studied is applicable. Further studies should be performed in order to mimic gingival crevicular fluid with varying bacteria load, a more clinically relevant model.

Greater material degradation leads to an increased deposit of Ti metal ions into the surrounding tissues which would prompt an increase in host response. The increase in number of macrophages and T lymphocytes surrounding Ti metal ions would lead to eventual osteolysis, resulting in loss of bone surrounding the implant <sup>30</sup>. This is of great concern at pH 6.0 given that the average pH of saliva is pH 6.3 <sup>31</sup>. More importantly, the pH, as stated previously, of gingival crevicular fluid in acute inflammation can drop to close to pH 6.0 for prolonged periods of time. Peri-implantitis has been linked directly to marginal bone loss <sup>32</sup>. The SEM images support greater corrosion at more neutral pH with possible pitting corrosion visible on pH 7.5 when subjected to only electrochemical corrosion. Under tribocorrosion parameters, the SEM image from pH 6.0 shows the clear appearance of cracks. The appearance of cracks and the total material loss at pH 6.0 due to tribocorrosion leads to the conclusion that at more neutral pH, the synergistic effect of electrochemical corrosion and wear has a stronger effect on the rate and amount of corrosion.

This study was designed to provide a baseline of tribocorrosion of CpTi as a function of pH in the presence of artificial saliva. The test set-up provided a controlled experiment in order to minimize variables. This allowed for the determination, if the amount of material degradation due to tribocorrosion was dependent on pH. The results show this to be true with distinct values of

current evolution between all three pH values, material degradation and overall weight loss at each pH. Greatest material degradation at pH 6.0 is of great concern because gingival crevicular fluid, when in the presence of acute inflammation, has a more acidic pH of 6.0 or lower. It is possible that at this commonly experienced, slightly acidic pH the repassivation of titanium is slowed, allowing for greater destruction of the titanium surface. With prolonged exposure to pH 6.0, i.e. acute peri-implantitis, the degradation of titanium will lead to greater metal ion release into the tissues. This may compound the inflammatory response leading to osteolysis and significant marginal bone loss. Once the inflammation transitions from acute to chronic and the pH value raises to a more alkalinic level (greater than 7.0), the more destructive nature of tribocorrosion may be slowing. The oxide layer may be reformed at a faster rate, it may be more adherent or thicker at an alkalinic pH, as evident by pH 9.0 have little change of capacitance after sliding. Through this study, a potential corrosive pathway has been outlined as baseline. Through further investigation, using more clinically relevant models of a fretting tribometer and/or solutions closer in composition to gingival crevicular fluid, a direct link between tribocorrosion products and marginal bone loss or loss of osseointegration may be made.

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### 6. Conclusions

The results from the first study exhibited that there was a significant influence of pH of the media on the corrosion behavior of CpTi. The following conclusions were drawn:

- $I_{corr}$  values indicated that neutral pH 7.5 had inferior corrosion resistance. This finding was supported by the impedance results of the Nyquist plot and  $R_p$  value determined via the Bode plot.
- E<sub>corr</sub>, I<sub>corr</sub>, and I<sub>pass</sub> values suggested a greater corrosion potential at more neutral pH:
  6.0, 6.5, 7.5. EIS results did not support greater corrosion kinetics at pH 6.0 and 6.5.;
  however it did support greater corrosion kinetics at pH 7.5.
- SEM images showed considerable surface damage under pH: 6.5, 7.5 and 9.0.
- The weak corrosion behavior at neutral pH in artificial saliva invites some concerns and highlights the need for further study.

In the second study, the tribocorrosion behavior of commercially pure titanium was investigated in the presence of artificial saliva as a function of pH. The following conclusions can be drawn,

- Evolution of current at all three pH indicates the existence of damage to some degree to the passive layer during tribocorrosion.
- Titanium shows inferior performance in tribocorrosion at pH 6 as indicated by the total weight loss and SEM images. SEM images indicated greater tribocorrosion damage with appearance of cracks. These findings are of concern with regards to dental implants because the average pH of the oral cavity is 6.2.
- The EIS results also agree with the surface changes, before and after the sliding. Better corrosion behavior after sliding may be due to the coupled action of the strong passive film formed in the unworn area, and chemical reaction in the worn area.
- Understanding the synergistic effect of mechanical and chemical corrosion of titanium alloys is crucial to understanding the long-term effects of current implant therapy.
- Tribocorrosion products may have a beneficial or potentially detrimental effect on osseointegration.

Results from both studies indicate greater corrosion at more neutral pH. This invites great concern given that the average pH of the oral cavity is pH 6.2. From the tribocorrosion study, the results indicate that the passivation layer may be stronger after repassivation which may lead to overall protection, however with the constant transmitted masticatory force leading to continued mechanical wear, the passivation layer may not have time to repassivate completely. This could lead to greater material degradation over time, leading to the release of titanium metal ions into the tissues. Further study must be performed to understand the point of repassivation, the structure of passivation layer, and if a continuous layer is able to reform throughout the life of the implant. In addition, it is important to understand if the tribocorrosion pathway may lead to loss of implant due to the immune response to Ti metal ions in present in the surrounding tissues.

#### 6.1 Limitations

There were several limitations common to both studies.

- Only a small number of samples (n=3) were tested for each pH.
- There was a large range between pH values. In order to truly understand at which pH, the greatest amount of corrosion occurs, a very short range must be tested.
- The components within the artificial saliva may have contributed to the corrosion at more neutral pHs which may not be exhibited with human saliva. However, because of the unstable nature of human saliva, it will be very difficult to test.
- Although the pH of each solution was continuously tested throughout each test, it was difficult to maintain each specific pH. Additional lactic acid or NaOH needed to be added prior to starting several testing cycles due to instability within the solution itself.
- Although polishing was taken to a smooth finish, possible contamination may have been introduced during the polishing process. In addition, scratches from polishing may have been introduced, leading to greater wear.
- The tribometer used was with a constant, unidirectional load.

### 6.2 Future Work

Future work can be related to:

- Understanding the pH that has the greatest corrosion potential by looking at smaller range of pHs.
- Using a different medium i.e. gingival crevicular fluid, to mimic an integrated dental implant.
- Subjected titanium to fretting conditions as opposed to pin on ball tribocorrosion apparatus.
- Looking at various titanium surface treated samples in order to understand the potential for corrosion amongst the various implant systems available today.
- Performing tribocorrosion studies with the addition of osteoprogenitor cells in solution or after wear, in order to see the adherence of osteoprogenitor cells to the tribocorroded areas.
- Understanding the impact of biofilm on tribocorrosion.

It is important to continue to investigate the effect of tribocorrosion on titanium in a dental implant application in order to better understand the method of osseointegration and potential mode of failure. In addition, it is important to understand the long-term impact dental implant therapy may have on the human body.

# A. Development of OCP for Basic Corrosion of Titanium



# B. Potentiodynamic for Ti Basic Corrosion Trial #1



# C. Potentiodynamic for Ti Basic Corrosion Trial #2



# D. Potentiodynamic for Ti Basic Corrosion Trial #3



рН	Rs	%Error	Cf-T	%Error	Cf-P	%Error	Rp	%Error	X2
3.0	393.1	0.3349	1.1615E-5	0.5451	0.9551	0.1707	1.5066E14	0.09915	0.0025
4.5	409.2	0.3971	2.1437E-5	0.6543	0.9337	0.2175	1.5066E14	7.3118E-8	0.0033
6.0	480.9	0.4431	2.028E-5	0.7979	0.9221	0.2822	1.6983E14	87.23	0.0039
6.5	481.7	0.3523	1.7481E-5	0.5793	0.9217	0.1942	1.7351E14	5.7634E7	0.0024
7.5	481.7	0.3523	1.481E-5	0.5787	0.9272	0.1938	1.5066E14	6.6375E7	0.0024
9.0	525.4	0.4424	1.8261E-5	0.7261	0.9209	0.2454	1.5066E14	0.1541	0.0039

# E. Impedance Parameters for Ti

Capacitance values reveal that greatest corrosion occurring at pH4.5 and 6.0. Least

amount of corrosion at pH3.0.

# F. AFM Analysis for Ti



- AFM results show greatest roughness for pH6.0 and 3.0 samples; however AFM analyzes only a very small area of the total tested area.

# G. ANOVA Data for Basic Corrosion of Titanium

TiSpectroscopy

Туре		Sum of Squares	df	Mean Square	F	Sig.
Capacitance double layer Between Groups		.000	5	.000	12.827	.000
	Within Groups	.000	12	.000		
	Total	.000	17			
Ecorr	Between Groups	.099	5	.020	5.681	.006
	Within Groups	.042	12	.003		
	Total	.141	17			
lcorr	Between Groups	.000	5	.000	22.457	.000
	Within Groups	.000	12	.000		
	Total	.000	17			
Resistance solution	Between Groups	16346.320	5	3269.264	28.061	.000
	Within Groups	1398.090	12	116.508		
	Total	17744.410	17			

H. Tukey Test data for Ecorr from basic corrosion of Titanium

Type=Ecorr					
			Subset for a	alpha = 0.05	
	pН	N	1	2	
Tukey HSD <sup>a</sup>	9.0	3	- 4.625000000 00E-1		
	3.0	3	- 4.300000000 00E-1	- 4.300000000 00E-1	
	6.5	3	- 3.100000000 00E-1	- 3.100000000 00E-1	
	4.5	3	- 3.050000000 00E-1	- 3.050000000 00E-1	
	7.5	3		- 2.850000000 00E-1	
	6.0	3		- 2.700000000 00E-1	
	Sig.		.059	.054	

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.
## APPENDIX

I. Tukey Test Data for Icorr of Basic Corrosion of Titanium

Type=Icorr					
			Subset for alpha = 0.05		
	рН	N	1	2	
Tukey HSD <sup>a</sup>	3.0	3	.0000000860 0		
	4.5	3	.0000000870 0		
	6.0	3	.0000000995 0		
	6.5	3	.0000001325 0		
	9.0	3	.0000001450 0		
	7.5	3		.0000004250 0	
	Sig.		.665	1.000	

Means for groups in homogeneous subsets are displayed.

a. Uses Harmonic Mean Sample Size = 3.000.

## APPENDIX

J. Weight loss distribution, total weight loss ( $K_{wc}$ ), weight loss due to corrosion ( $K_c$ ) and weight loss due to wear ( $K_w$ ) from Tribocorrosion of Titanium

рН	<b>K<sub>wc</sub></b> (μg)	<b>Κ</b> <sub>c</sub> (μg)	<b>Κ</b> <sub>w</sub> (μg)	K <sub>c</sub> /K <sub>w</sub>
pH 3.0	230 ± 6.45	0.28± 0.06	229.7± 26.45	0.0012
pH 6.0	333.33 ± 45.09	97.43 ± 3.32	235.7± 35.34	0.432
pH 9.0	105 ± 10.21	3.75 ±0.49	101.3 ± 9.85	0.037

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