IMPROVEMENT OF TRIBOLOGICAL AND BIOCOMPATIBILITY PROPERTIES OF ORTHOPEDIC MATERIALS USING PIEZOELECTRIC DIRECT DISCHARGE PLASMA SURFACE MODIFICATION

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ABSTRACT

Joint and disc replacement via knee and hip, are growing considerably due to the increasingly aging population as well as the higher demand for an active lifestyle in the elderly population. However, the longevity of implants is significantly limited by wear performance, corrosion, biocompatibility and post-surgery infection. These factors are correlated to each other and effectively addressing any of them can dramatically improve the quality of prosthetic performance and lifespan. To this end, presurgical measures should be taken to maximize the performance of joint and disc implants. Thermal stabilization, electron beam and gamma irradiation are the most conventional approaches employed for enhancement and engineering of biomaterials. However, these methods are accompanied with drawbacks such as degradation of bulk properties (toughness, fatigue and tensile strength) but do improve the surface features and characteristics. This degradation in bulk properties could cause catastrophic failure in some implants under high cyclical loads or extreme loading conditions, such as knee prosthesis. Additionally, more recent techniques like Ar plasma modification require thermal stabilization that tends to negatively affect bulk properties. Furthermore, the conventional plasma coating methods are not cost efficient and require extremely large machinery, rendering them inappropriate for clinical applications. During the last decade, nonthermal plasma has been widely investigated mostly because of the associated antimicrobial effects and surface sterilization capabilities. However, most studies on this subject have been performed on polymeric materials while the tribological behavior of nonthermal plasma treated surfaces has remained uninvestigated. Piezoelectric direct discharge (PDD) plasma is categorized as a novel nonthermal plasma generating method in which the cold plasma is produced due to a direct discharge in a piezoelectric transformer. In this method, a compact hand-held device can be used to produce cold plasma (< 50 ºC) without the requirement of external gas cylinders. Similar devices are suitable for healthcare and clinical applications due to the safety and ease of operation. Yet there are still no published studies that thoroughly examine the potential surface enhancements of PDD for prosthetic applications.

Ti6Al4V is an extensively employed material in highly corrosion resistant and biocompatible α-β titanium alloy with high strength-to-weight ratio. However, poor wear properties of this alloy under cyclic loadings restrict its effectiveness as an implant in high-load bearing areas like in the knee and hip. As a result, researchers are working on a wide variety of surface enhancements and coatings to mitigate this issue. It has been shown that the formation of titanium oxide on the surface of Ti6Al4V improves the physico-chemical properties of this alloy for biomedical applications. Accordingly, creation of a thin oxide layer on Ti6Al4V can significantly improve its biocompatibility as well as the wear resistance properties.

GUR1020, on the other hand, is an ultra-high molecular weight polyethylene (UHMWPE) in prosthetic applications due to its high biocompatibility, high toughness and ease of fabrication methods. These properties degrade over cyclic loading conditions because of poor wear resistance. Therefore, the lifespan of GUR1020 implants is limited to less than ten years after surgery. Subsequently, the implant needs to be replaced with a new one to prevent infection and potential pain caused by the worn-out debris of the prosthesis. Hence, several coating methods (such as γ irradiation, ion irradiation and plasma surface modification) have been proposed to extend the longevity of GUR1020 implants by improving the tribological properties. However, these methods are impractical at the clinical level due to the complexity and size of machinery, safety issues, and detrimental effects on bulk properties of the prosthesis.

In this study, we have investigated the potential surface modification of Ti6Al4V and GUR1020 by means of a hand-held PDD plasma generator to scrutinize surface changes through the treatment process and their effect on tribological, corrosion and biological properties. This study explores new horizons for clinical applications of nonthermal plasma research and pioneers the introduction of a practical surface treatment method that can be utilized prior to prosthetic surgeries in a clinical setting.

Plasma treatment of surface reduced the water contact angle from 79.2º to 13.1º for Ti6Al4V and from 91.8º to 38.1º for GUR1020 samples. Accordingly, both metal and polymer proved to become considerably hydrophilic due to plasma exposure (~ 6X reduction in contact angle for metallic, and ~ 2.5X reduction in contact angle for polymer sample). Furthermore, contact angle becomes almost constant after 20 min of plasma exposure which indicates the treatment saturation point for metal and polymer. The lifespan of coating was measured by conducting the aging experiment. As a result, two stages were observed during

the "aging process". The first stage illustrates the existence of a temporary coating that degrades after about 10 hours of aging. The second stage shows a permanent coating that does not degrade over time. Therefore, all the experiments, including biocompatibility tests, were performed right after the plasma exposure without any further delays.

To realize the effective depth of PDD plasma on metal and polymer specimens, time dependent Ar ion etching was employed along with XPS analysis to quantify the depth of penetration. Firstly, Ar etching depth was measured by means of SRIM simulation package. By comparing the SRIM and XPS results, the effective depth of plasma penetration for GUR1020 was measured to be ~ 220 nm. effective depth of PDD plasma for surface modification of Ti6Al4V was measured to be ~ 130 nm.

From tribological experiments we realized that when both the disc (GUR1020) and pin (Ti6Al4V) are treated for 20 min each, the amount of wear rate was reduced by ~ 60X compared to the untreated case. This type of surface treatment enhances the wear properties by providing better wettability on the surface. In addition, the increase in microhardness as well as the enhanced wettability improve the tribological properties and reduce the wear volume. Therefore, it can be concluded that the presence of surface oxides, the formation of a hydrophilic layer and an increase in microhardness results in wear reduction.

Corrosion resistance is a significant factor for biological materials: a poor corrosion resistance increases the risk of implant rejection. It is well-known that Ti and its alloys form a surface oxide layer which improves the corrosion resistance. In order to evaluate the corrosion behavior of the samples before and after the surface treatment, open circuit potential (OCP) and Tafel curves were obtained. Tafel curves for untreated and treated samples clearly indicate a decrease in corrosion rate and a more noble potential. For the treated sample, the Tafel curve is shifted to the lower values of current density (0.158 µA/cm2) and more positive values of potential (-0.402 V). As a result, it can be concluded that the nonthermal plasma surface treatment increases the lifetime of the alloy in body fluid has no negative effect on the corrosion properties of Ti6Al4V.

We evaluated the osteogenic stem cells study at three times points: day 7, day 14 and day 21 respectively. From the results, it was observed that the percentage of viable cells after 20 mins of plasma exposure was 82 % for treated GUR and 56 % for treated Ti, whereas it was significantly lower for the control ranging from 24% to 27 % in control GUR and control Ti respectively. One tailed, paired students T-test analysis between the plasma treated groups revealed a strong statistical significance with $p<0.01$. These results can be corroborated from the physicochemical results mentioned in the characterization section, showing that plasma treatment creates a hydrophilic layer and enhances the surface properties.

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