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Adhesion and Scratch Testing of Antibiotic Loaded Poly-Lactic Acid Biocomposite Thin Films on Metallic Implants

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Abstract. Surface modifications have been progressively applied in order to improve the mechanical, biological and chemical properties of metallic dental and orthopedic implants. Therefore, the novel and multifunctional biocomposites coating matrices, which also consist of local and targeted drug delivery systems, are the most recent applications in the medical field. In this study, gentamicin antibiotic containing HAp bioceramics were utilized in a biodegradable poly-lactic acid thin film matrix which was applied to Ti6Al4V metallic implant surfaces. Nano-indentation and scratch test methods were applied. It was observed that, bonding between coating and the substrate is strong enough to be used in implant applications. Additionally, it was observed that the hardness and young modulus values of uncoated Ti6Al4V disc which were 4.3 and 125.2 GPa, respectively. However, under the same testing conditions, it was also observed that the H values (0.6-0.8GPa) and the E (50-60 GPa) values of PLA-HAp biocomposite coated samples are slightly higher than the H values (0.4-0.6 GPa) and the E values (40-50 GPa) of only PLA coated sample.

Introduction

Metallic implantable devices have been used most frequently in the field of orthopedics and dentistry because of their properties and biocompatibility, in particular, because of their high strength and corrosion resistance [1].

The most commonly used metallic biomaterials are Co-Cr-Mo alloy, pure Ti and Ti alloys. The reasons of high demand of Ti and Ti alloys for orthopedic and dental implant applications are their biocompatibility, easily applicable production and shaping methods, high strength, low weight, and good mechanical properties. Although Ti6Al4V has a relatively high strength and low weight when compared to other metallic alloys, the release of metallic ions is similar to other metallic implants. During the last few decades in order to prevent these problems, various types of surface modification methods were utilized according to implant types and treatments [1-4].

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The design of multifunctional coating materials is the most recent example of surface modification studies [5]. They combine drug delivery systems to prevent post-operative complications on implants and treat certain bone diseases, such as osteomyelitis and inhibit metallic ion release from metallic implants.
The novel nanocoatings and thin film coatings whose matrix materials consist of bioceramics, such as calcium phosphates, and natural or synthetic polymers, such as PLA, have been proposed by in some of the most of recent studies [6].
In our previous study we developed and reported a dental Ti6Al4V implant, which was coated with gentamicin (Gm) and gentamicin loaded coralline hydroxyapatite (HAp-Gm) within a poly-lactic acid (PLA) matrix for a multifunctional implantable system. Additionally, their surface morphology and structural characterization were reported [7].
In addition to their biocompatibility, mechanical properties of the substrate, coating material and also their combination are also important during implant insertion and their long-term survival. Dental and orthopedic implant are exposed to a range of biomechanical stresses and external functional loads that, the combination of coating material and substrate properties, and a fracture resistance and strength level of coating are crucial points during their design and use.
Therefore the measurement of mechanical properties, specifically by nano-indentation and scratch tests, are most important to determine coating and substrate properties for the long-term performance with the physiologic environment. Whilst the scratch test is applied to define the adhesion strength of the coating and the substrate material interface, nanoindentation tests are used to obtain Young's modulus (E) and Hardness (H) values of the coating [8-10].
In this current research, the suitability of a biocomposite containing an antibiotic against post-operative infections and regenerative drugs were examined, and their mechanical and adhesion properties of the coating materials and the bonding strength between coating material and the substrates were determined.

Experimental

Materials

All chemicals were obtained from Sigma Aldrich, Australia. Coral samples were obtained from the Great Barrier Reef, QLD, Australia. High purity Ti-Al-V discs were obtained from the Good Fellows UK.

Methods

Hydrothermal Conversion & Drug Loading

The coral pieces were cleaned with the diluted bleach solution to remove organics. After a cleaning process they were ground with a ceramic ball mill. The coral microspheres were converted to hydroxyapatite HAp by hydrothermal method at 220C within a Parr Hydrothermal converter (USA). The hydrothermal method was reported previously by Ben-Nissan *et al.* [11]. Coralline HAp (cHAp) microspheres were used as an appropriate drug carrier system for sustained release of Gm because of their nano- and meso-pores. Gm antibiotic powder was embedded into the cHAp microspheres using a rotary evaporator at 60C.
Gm loaded HAp particles were incorporated within biodegradable PLA thin films in order to produce PLA biocomposites using the solvent-casting method [6].

The PLA-HAp Biocomposites Coating method on Ti6AL4V Discs.

Dip and spin coating methods were used for the Ti6Al4V substrates. Ti6Al4V discs were coated with PLA biocomposites incorporating Gm antibiotic and Gm loaded coralline HAp particles by the dip coating method at a constant speed. The mechanical properties of PLA film and PLA biocomposite coating on the metallic implant surface were determined by micro-scratch test and nano-indentation tests.

The Characterization of Mechanical Properties.

For the scratch test (Hysitron Inc., USA), 160μN constant force and 150nm constant indentation depths were applied for each sample. For the nano-indentation test (Hysitron Inc., USA), max. 90mN load was applied by using Berkovich indenter for each sample.

Results and Discussion

The development and characterization of the coated Ti6Al4V surface were reported in our previous studies by Macha *et al.* [5]. Although the in vitro studies are important in order to control drug release rate, the determination of the mechanical properties is pertinent for the long-term survival of the implants. For this reason, nano-indentation was applied to determine the properties of the coating material, and the scratch test was used to obtain information on the adhesion strength between the substrate and the coating material.

The thickness of the coating material is an important parameter regarding the mechanical properties of the samples. Therefore, the thicknesses of the PLA biocomposite thin films were measured by using a profilometer and it found to be approximately 400nm for both dip and spin coated samples.

It is well established that during scratch testing an increase of the normal force (F_N) reduces the surface friction coefficient for soft coatings [12]. The indentation depth (d_I) is also found to affect the surface friction coefficient.

In this study, the scratch test was applied with a constant F_N, which was 160μN, and a constant depth d_I, which was approximately 150 nm. The scratch tests were applied to the coated samples to observe the adhesion and bonding strength differences between the dip and spin coated samples and between the only PLA and PLA biocomposite thin film coating matrices

Surface friction coefficients versus lateral displacement graphs for the three different samples are shown in Fig.1. In Fig.1-A, the friction coefficient of spin coated sample is found to be slightly lower than dip coated samples.

Additionally, the surface friction coefficient differences between PLA thin film and PLA biocomposite thin film coated samples are shown in Fig.1-B. Note that the friction coefficient of the PLA biocomposite matrix is slightly lower than that of the PLA matrix. However, as expected plastic deformation is obtained for all coated samples, and a reasonably good bonding between substrate and coating matrix is observed.

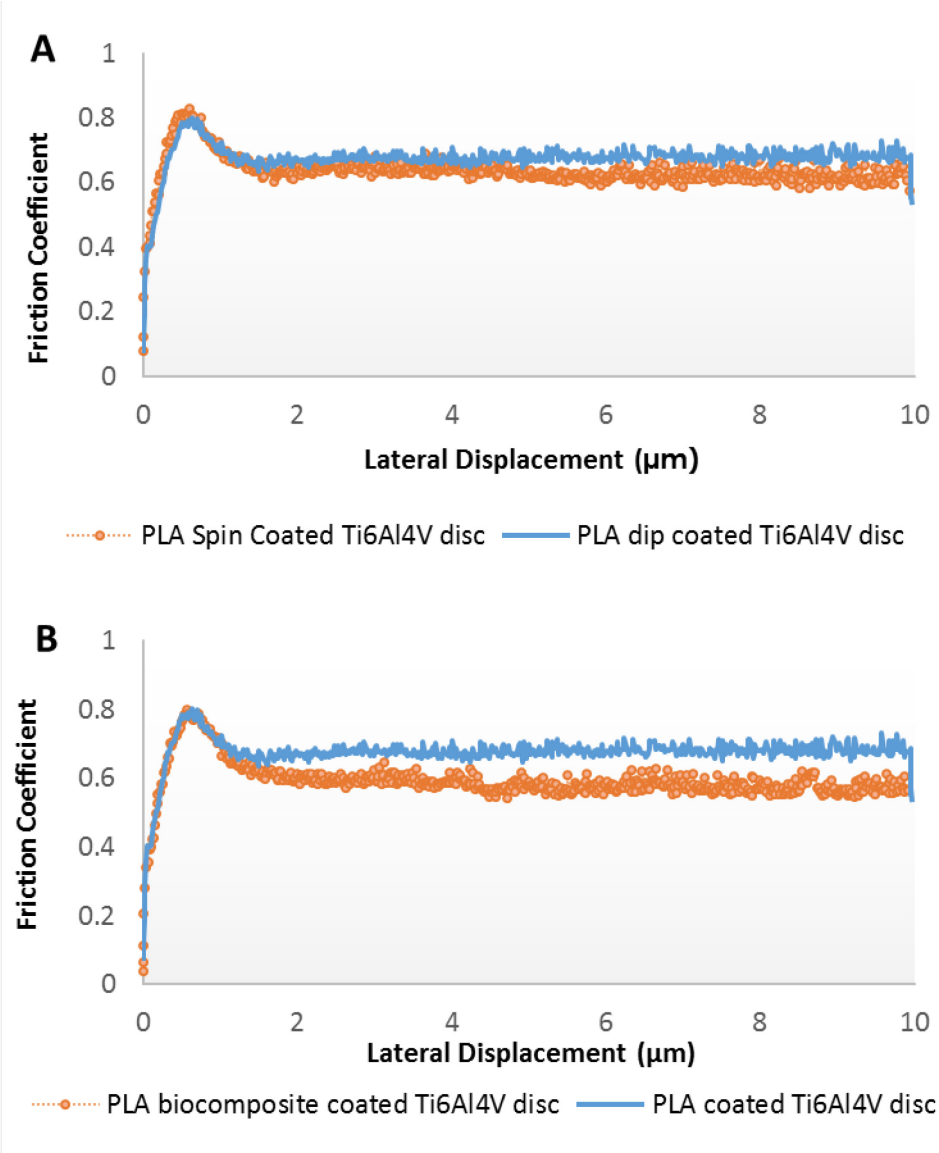


Fig.1 Friction coefficient vs. Lateral displacement results of the PLA dip and spin coated (A), and PLA biocomposite coated (B) Ti6AL4V discs.

Nano-indentation results showed clear differences between the hardness (H) and Young's modulus (E) values of the PLA biodegradable thin film coated and the uncoated Ti6Al4V discs.
The H and E values for the Ti6Al4V disc without PLA thin film coating are shown in Figure 2 (Fig.2-A), which were 4.3 GPa and 125.2 GPa, respectively.
As expected the H and E values of PLA (Fig.2-B) and PLA biocomposite (Fig.2-C) thin films were much lower than uncoated titanium alloy samples.
Under the same testing conditions, it was observed that the H values (0.6-0.8 GPa) and the E (50-60 GPa) values of PLA biocomposite coated samples were slightly higher than the H values (0.4-0.6 GPa) and the E values (40-50 GPa) of only PLA coated sample.

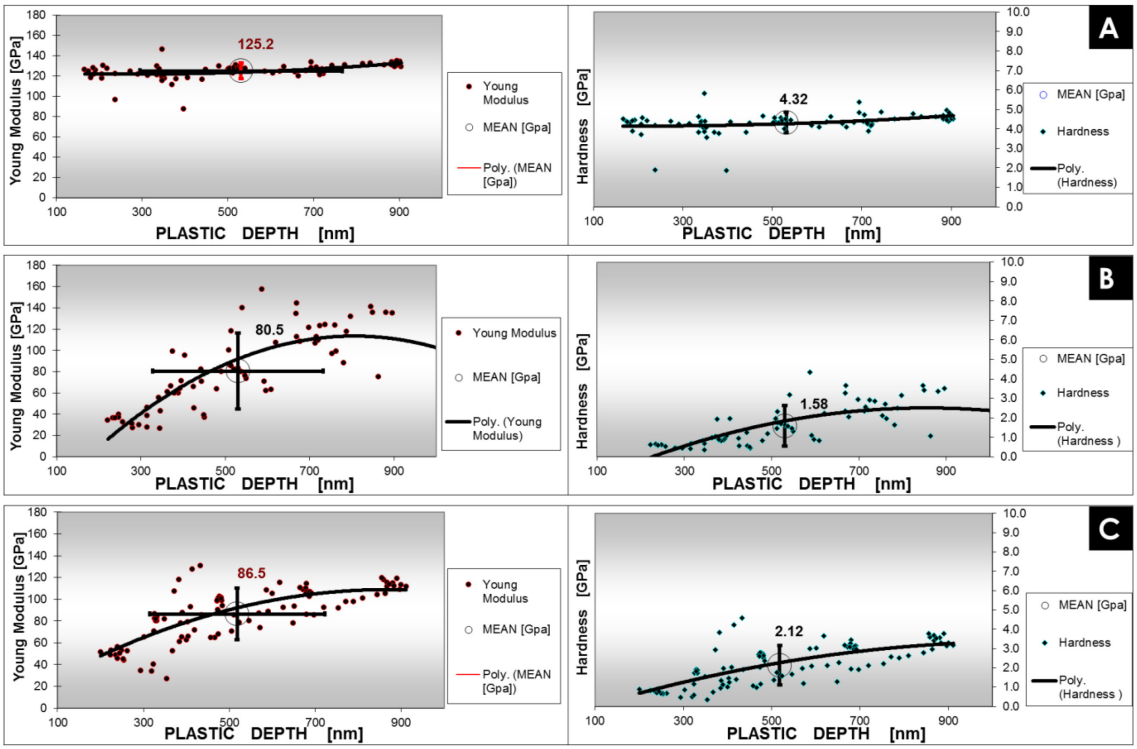


Fig.2 The Nano-Indentation Results for Uncoated (A), PLA coated (B) and PLA-biocomposite coated (C) Ti6Al4V discs.

The average H and E values of all samples are given at Fig.3. It can clearly be observed that both H and E values were decreased after coating.
It is thought that this can be a very advantageous condition for an implant design, because the Young modulus values of coated samples are closer to the bone Young modulus value whose range is 10-25 GPa [13] than uncoated Ti alloy implants.

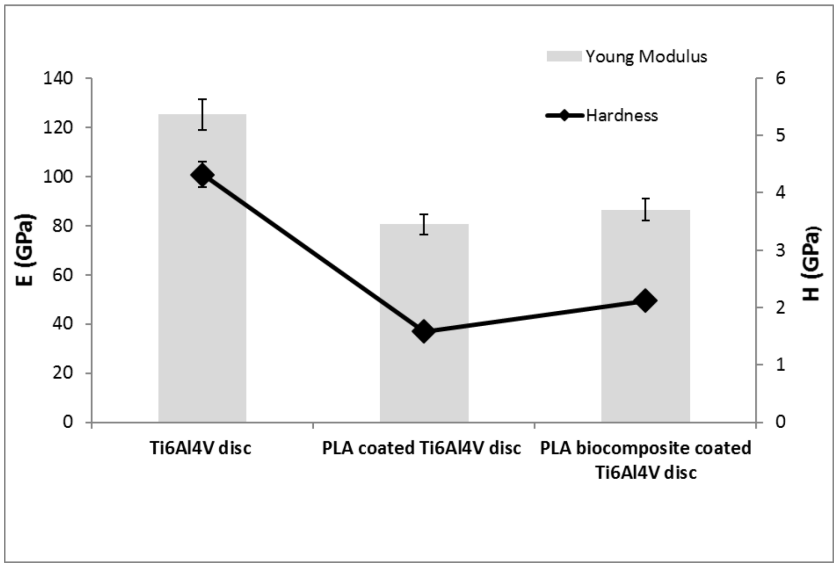


Fig.3 The hardness and Young's modulus values of uncoated, PLA coated and PLA biocomposite coated Ti6Al4V discs, respectively.

Conclusions

This PLA biocomposite coated slow drug delivery system developed has a multifunctional use; firstly they are biodegradable, in addition they may contain antibiotics or other therapeutic drugs such as bone forming additives, and their Young's modulus values at the interface is reduced and closer to bone E values and hence a gradient effect at the bone interface.

It was determined that the H and E values of uncoated Ti6Al4V disc were 4.3 and 125.2 GPa, respectively. However, under the same testing conditions, it was determined that the H values (0.6-0.8GPa) and the E (50-60 GPa) values of PLA-HAp biocomposite coated samples are slightly higher than the H values (0.4-0.6 GPa) and the E values (40-50GPa) of only PLA coated sample. Although further investigation and verification is recommended these preliminary results demonstrate that the bonding between implant and PLA biocomposite, determined by scratch and nano-indentation tests might be strong enough to withstand the stresses during implant insertion and functional movements.

Acknowledgments

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