

Chapter 6

The Effect of PLA/HA Coating Thickness on Crack Formation and Corrosion Performance



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Abstract Surface modification of metallic implants is often required to facilitate positive interaction between the implant and the surrounding hard tissue. In this study, a polymer-ceramic composite coating of polylactic acid/hydroxyapatite (PLA/HA) was successfully deposited on a Co–Cr–Mo alloy by the dip coating method in chloroform suspension at room temperature. The effect of various PLA/HA dipping layers was studied and the dip coating process parameters were optimized in order to obtain a homogeneous, crack free, densely packed and adhesive coating. It is found that PLA/HA-coated substrate with 3 dipping layers were denser and less crack sensitive compared to 6 dipping layers. Although it is hypothesized that a coarser coated surface helps to facilitate ingrowth of osseous tissue in human body, but current findings show opposite manners due to the fact that a higher corrosion rate was obtained. The coated substrate with 6 dipping layers also were found more profound to micro-cracks and delamination with a lower microhardness value compared to coated substrate with 3 dipping layers.

Keywords Co–Cr–Mo · PLA/HA coating · Biomaterial · Surface morphology · Dip coating

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6.1 Introduction

Co–Cr–Mo alloys are widely used for dental and orthopaedic prostheses owing to their favourable mechanical properties, low cytotoxicity, good corrosion resistance and biocompatibility [1, 2]. One of the main requirements for implant longevity is high corrosion resistance. The formation of an oxide layer on Co–Cr–Mo surface occurs rapidly upon contact with atmosphere. This oxide layer is considered instrumental in decreasing the dissolution rate of toxic metal ions in the biological environment [3, 4]. Moreover, the presence of an oxide layer also enhances the bioactivity of Co–Cr–Mo in body fluid as it provides sites for the deposition of calcium and phosphate compounds via an ionic exchange process with apatite from the bone tissue [5]. However, the oxide layer does not promote the formation of a hydroxyapatite layer, which is integral for the rapid fixation of an implant.

Several studies have reported excessive levels of Co, Cr and Mo ions in the vicinity of the implanted Co–Cr–Mo implants. The released of these ions will later combine with biomolecules and result in adverse biological reaction [2]. The coating of bioactive ceramic on metal implants is an effective approach to solve corrosion related problems and improve the biocompatibility of metallic implants. Hydroxyapatite (HA) is a synthetic material, which promotes osteointegration and thus accelerates tissue fixation at the implant surface during the early stages of implantation [6]. Dip coating is a promising technique which consists of three stages; dipping, withdrawing and drying (Fig. 6.1) [7]. This technique offers numerous advantages such as inexpensive setup, process simplicity, uniformity of deposition, low processing temperature and the ability to coat complex shapes and patterns. Additionally, the coating amount and thickness can be controlled by adjusting the concentration of suspension, the number of dips and varying the withdrawal speed. Heat treatment of

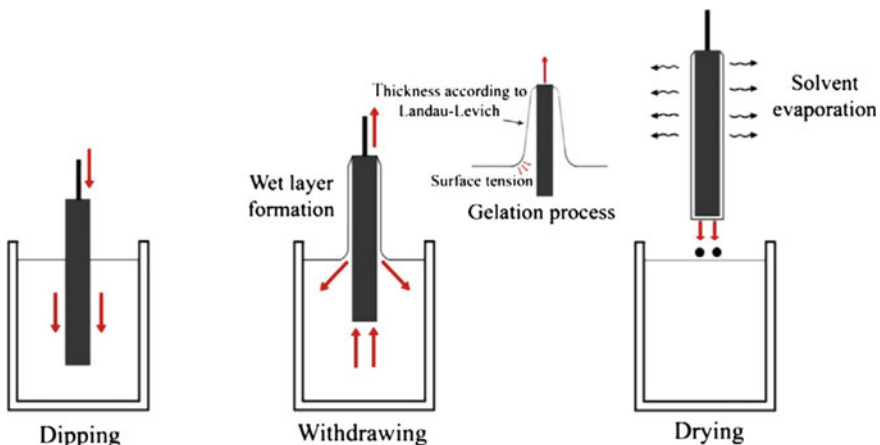


Fig. 6.1 Schematic diagram of dip coating process

coated substrate is often required to densify the coating layer, to increase the coating-implant bonding and eliminate porosity. However, too high a sintering temperature can lead in degradation of the metallic substrate and also phase transformation of HA into a non-crystalline phase which increases the dissolution rate in body fluid [8, 9]. Furthermore, thermal stresses originating from the difference in thermal coefficient between the ceramic coating and metallic implant result in the formation of micro-cracks and delamination of the coating from the substrate. Polylactic acid (PLA) is a semi-crystalline aliphatic polymer with good biocompatibility, sustained biodegradability and remarkable mechanical properties [1, 10]. With regards to aforementioned evidences, therefore this study was presented to report the deposition of highly compact polymer-ceramic composite coating of PLA/HA onto Co–Cr–Mo alloy, which does not require post-depositional heat treatment for densification. The effect of the PLA/HA coating thickness on the corrosion rate was also studied using the potentiodynamic polarization test in circulated simulated body fluid.

6.2 Methodology

In the present study, a cobalt-chromium-molybdenum alloy (Co–Cr–Mo) bar with ASTM standard of F1537 and chemical compositions of (in wt%): C: 0.24; Cr: 29.6; Mo: 6.5; Si: 0.7; Ni: 0.1; Fe: 0.12; Mn: 0.7; N: 0.16 and Co: balance was used. The alloy bar was cut using a precision cutter into disc shape with dimension of 14 mm diameter and 2 mm thickness (Buehler, Isomet 4000). The variation in surface roughness was reduced using #500 grit SiC paper in wet grinding method. The surface roughness of the alloy discs was then measured using a surface profilometer (Mitutoyo SJ-301) and $0.1 \pm 0.02 \mu\text{m}$ surface roughness was achieved. Then PLA/HA coating deposition process was carried out using a HTWL-01 Desktop Dip Coater (MTI Cooperation, USA) at room temperature and under controlled humidity. The substrates were assigned for dipping and withdrawal steps in the prepared PLA/HA slurry with fixed speed of 200 mm/min. This step was repeated for 3 and 6 dipping layers with an interval of 1 min for drying step in every cycle. This step is mainly used to obtain a desired coating thickness of PLA/HA on the substrates. The substrates were then left to dry in the vacuum furnace at a temperature of 50 °C for 1 h to evaporate the residual solvent and densify the coating layer. This step is crucial to improve the bonding strength of PLA/HA coating onto the surface of the Co–Cr–Mo substrate. Substrates that were coated with 3 layers and 6 layers of PLA/HA coating will be recognized as PLA3 and PLA6, respectively. Single Vickers hardness indentation method was performed at five different locations on the coated PLA3 and PLA6 substrate to obtain the average hardness of the coated layer. A load of 5 N with dwell of 10 s was applied in this test. Meanwhile, for the corrosion testing, potentiodynamic polarization diagrams were determined using a classical three-electrode cell with specimen as a working electrode with an exposed area of about 0.402 cm², a saturated calomel electrode (SCE) as a reference electrode and graphite as a counter electrode by employing Princeton Applied Research, US potentiostat (VersaSTAT

3-300). The coated PLA3 and PLA6 substrates were exposed to the simulated body fluid (Hank's solution) at circulated condition for 30 min prior to generation polarization. Megastudio Software measured the impedance in the frequency range of 5 MHz to 100 kHz, using a perturbation amplitude of 20 mV around the corrosion potential. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were calculated from the intersection of the cathodic and anodic Tafel curves using the Tafel extrapolation method. The test was repeated for three times for each of sample condition.

6.3 Results and Discussion

Representation of the FESEM images of the PLA/HA coating on Co–Cr–Mo alloy is shown in Fig. 6.1. The surface morphology and cross-section of PLA3 substrate clearly shows that there were no micro-cracks or undulation noticed in the substrate (Fig. 6.1a) and the coating surface looks more uniform as compared to PLA6 substrate (Fig. 6.1d). Further observations on the cross-section of PLA3 substrate and PLA6 substrate showed that the thickness of PLA/HA coating formed at 3 dipping layers and 6 dipping layers was 49.14 μm and 76.39 μm , respectively. Based on Fig. 6.1b, the PLA/HA coating with 3 layers is denser which is indicating the formation of a compact composite material on the substrate. This compact structure is proven to be highly essential to provide better barrier to prevent harmful ions such as Co and Cr, migrating from implant to the host tissues [11, 12]. In Fig. 6.1c, the micro-cracks were evident on 6 dipping layers of PLA/HA coating and widely spread on the surface. This phenomenon occurs due to cohesive strength between PLA and HA which becomes weaker as thicker coatings were applied. It is believed that failures happened at the PLA-HA interfaces due to weaker chemical bonding. Similar findings were also reported by other researchers [1]. Closed-up image on micro-cracks in PLA6 substrate was profound towards the metal substrate (Fig. 6.2).

Table 6.1 shows the hardness measured on the coated substrates surface after the dip coating process. Based on the data obtained, the hardness of PLA3 substrates is about 2 times higher compared to PLA6 substrate which is 8.02 N and 4.18 N, respectively. This happened due to PLA6 substrate has massive surface cracks and pores on the coated surface. The polarization test was employed to study the corrosion resistance performance of two different PLA/HA dipping layer on Co–Cr–Mo alloy surface. The related polarization curves are plotted in Fig. 6.4. While the values of the corrosion current density (i_{corr}) and corrosion potential (E_{corr}) obtained from the curves analyses were summarized in Table 6.2. It is observed that the E_{corr} for PLA6 substrate (-221.404 mV) is much higher than PLA3 substrate (-110.169 mV). It is also observed that Co-Cr-Mo substrate with 3 dipping layers of PLA/HA has lower corrosion rate compared to substrate with 6 dipping layers (0.015743 mmpy vs. 0.049434 mmpy). This phenomenon happened due to the denser and uniform PLA/HA coating on the PLA3 surface as mentioned in earlier discussions. The dense

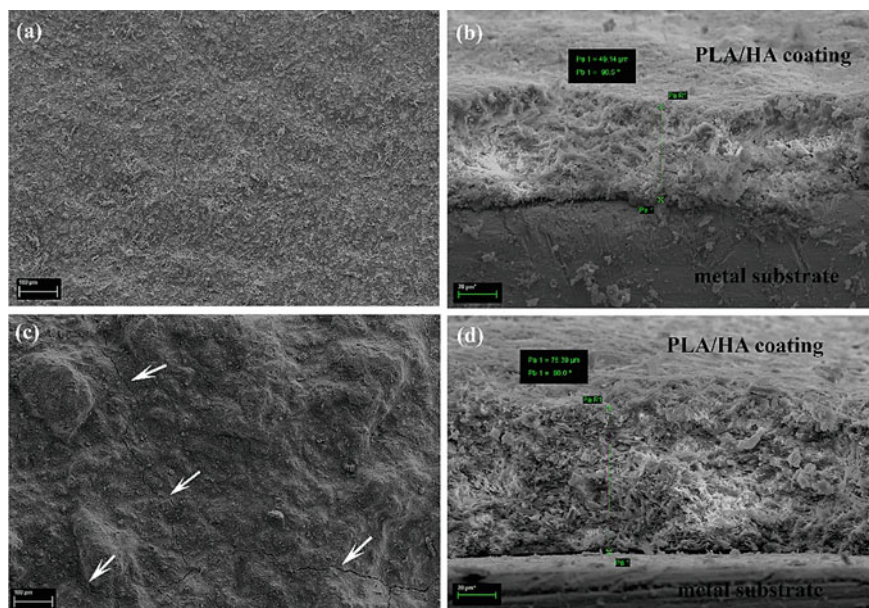


Fig. 6.2 Surface morphology and cross-section views of PLA/HA coating on Co–Cr–Mo alloy, **a** and **b** for PLA3 substrate, **c** and **d** for PLA6 substrate

Table 6.1 Vickers hardness measurement on PLA/HA-coated surface of Co–Cr–Mo substrate

Vickers hardness (HV) measurement			
Substrate	Applied load (N)	Average HV values	PLA/HA coating thickness (μm)
PLA3	5	8.02	49.14
PLA6	5	4.18	76.39

coating is believed to be able to act as a barrier to prevent chemical attack and thus protect the alloy from corrosion (Fig. 6.3).

Table 6.2 Tafel results for PLA3 and PLA6 substrates in Hank's solution

Dipping sample	E_{corr} (mV)	i_{corr} (nA)	Corrosion rate (mm/year)
3 dipping layers	−110.169	8.897	0.015743
6 dipping layers	−221.404	92.918	0.049434

Fig. 6.3 Closed-up images of micro-cracks in PLA6 substrate

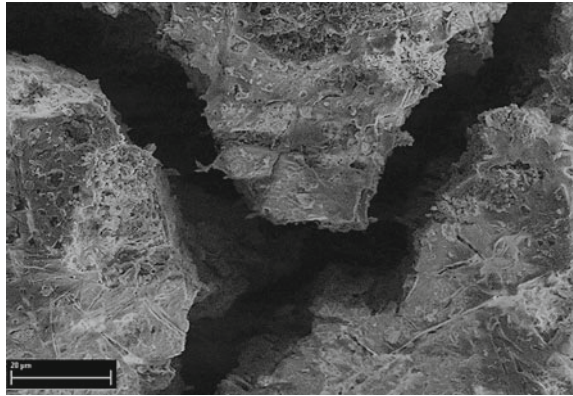
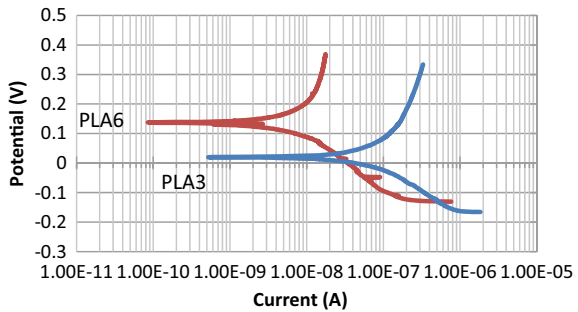


Fig. 6.4 Corrosion rate for PLA3 and PLA6 substrates in Hank's solution



6.4 Conclusion

The thickness of PLA/HA coating has a direct influence on the formation of micro-cracks as well as on the corrosion performance on the Co–Cr–Mo alloy. Thinner and denser PLA/HA coating on PLA3 substrate without micro-cracks is obtained on Co–Cr–Mo alloy which is able to reduce the corrosion rate (0.015743 mmpy vs. 0.049434 mmpy). Thicker and weaker cohesive strength on PLA6 substrate that consists with massive micro-cracks promotes higher corrosion rate. This phenomenon happened due to the simulated body fluid managed to penetrate into the bulk material and caused excessive release of metal ions.

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