PLLA coated WE43 Mg with a hydroxyapatite interlayer for enhanced adhesion and corrosion resistance

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Statement of Purpose: As a new generation of biodegradable implants WE43 magnesium alloy (yttrium-neodymium) has received a great deal of attention owing to its non toxicity and its low corrosion rate compared to other magnesium alloys [1]. However WE43 still degrades too fast and cannot maintain its mechanical integrity during the bone healing period. Poly-l-lactide acid (PLLA) has been introduced as a good protective coating layer because of its low degradation rate and biocompatibility [2]. In order to increase the bond between the coating layer and the substrate and therefore to prevent the risk of delamination, a hydroxyapatite (HA) layer was inserted between the substrate and PLLA. The roughness and bioactivity of HA were beneficial to improve the adhesion strength, the corrosion resistance and the biocompatibility of the structure.

Methods: For the HA formation, an aqueous solution containing 0.05M ethylenediaminetetra-acetic acid calcium disodium salt hydrate (Ca-EDTA) and 0.05M potassium dihydrogenphosphate (KH_2PO_4) was prepared and its pH adjusted to 9.3 with sodium hydroxide. The WE43 samples were immersed in the solution at 90°C for 2h and then rinsed with distilled water and dried in air. PLLA was dissolved into dichloromethane (DCM) at 10%wt and coated on the HA samples by dip coating technique under vacuum at a speed of 500 µm/sec. FESEM and FIB were used to observe the morphology and the thickness of the coating layer, respectively. Corrosion behavior was evaluated by immersing the samples into SBF (simulated body fluid) solution at 37°C and by measuring the pH evolution (n=3). Preliminary cell proliferation test was performed by DNA essay (n = 3) after 5 days culturing by using MC3T3 cells with a density of 1.10^4 cells/mL.

Results: Fig.1 shows the morphology and the thickness of the HA-PLLA coating layer. It can be seen that PLLA existed between the HA needles, indicating a good adhesion between the two. The total coating thickness was about 7 µm. Fig.2 presents the pH evolution of SBF solution for the different immersed specimens after a 6% extension. While bare WE43 corroded quite fast with a pH of 9.9 after 148h, the HA and PLLA coated samples showed a slower corrosion rate with a pH of 8.5 and 8.3 respectively. When HA is added as an interlayer in the PLLA coated sample, the corrosion decreased even more with a final pH value of 7.8. Fig.3 shows the DNA amount of MC3T3 cells cultured on the different samples for 5 days. The DNA amount of the HA-PLLA coated sample was almost twice of that of the PLLA coated WE43, indicating a clear improvement of its biocompatibility. On the inset image it can be seen a numerous amount of cells that are well spread out on the surface of the HA-PLLA coated WE43.

Conclusion: PLLA coated WE43 with an HA interlayer showed a better corrosion resistance and biocompatibility than the only PLLA coated WE43. The HA interlayer was effective in improving the corrosion of the Mg substrate by enhancing the bonding strength between the PLLA coating and the substrate.

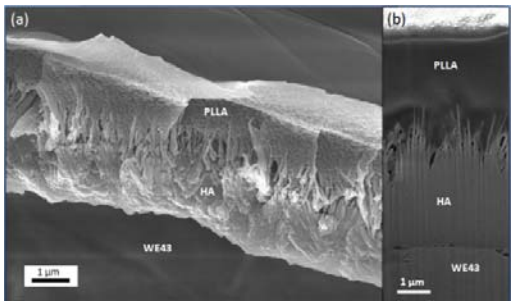

Figure 1: (a) SEM cross-sectional image of the WE43 coated PLLA with an HA interlayer; (b) FIB image showing the thickness of each coating layer and the good linkage between PLLA and HA.

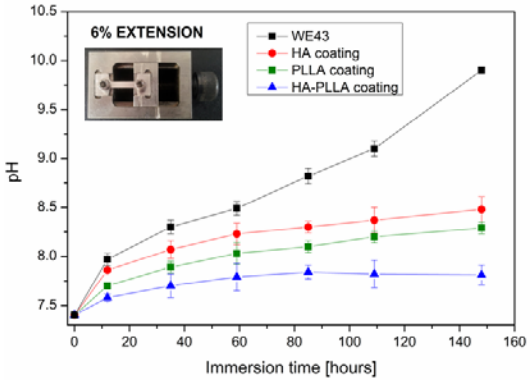

Figure 2: pH variation of SBF after immersion of bare, HA coated, PLLA coated and HA-PLLA coated WE43 samples for 148 hours. An applied strain of 6% was applied to the samples prior to the corrosion test.

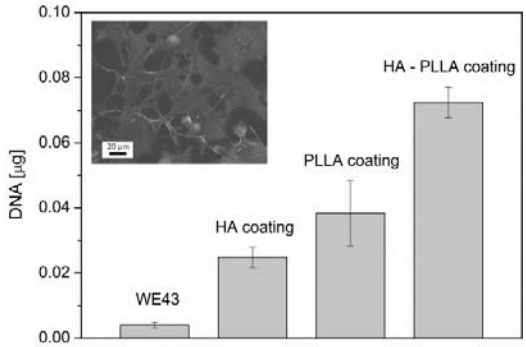

Figure 3: DNA amount of MC3T3 cells on bare, HA coated, PLLA coated and HA-PLLA coated WE43 after 5 days. The insert SEM image shows the cells attachment on HA-PLLA coated WE43 after 5 days.

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