

Reduction of corrosion behavior of Magnesium alloy by PCL surface treatment

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Introduction:

Metallic implants are often used for fracture fixation. However, stress-shielding effect may be resulted in some cases and thereby leading to bone loss around the implant¹. Therefore those metallic implants may need to be removed after the tissues have healed. The use of degradable metallic materials such as magnesium alloy is a promising candidate that may avoid second surgery. Hence, it helps reduce costs to health care system and morbidity to the patients. However, the major obstacles are the rapid degradation inside the human body and hydrogen gas release upon degradation. The corrosion rate has to be carefully controlled so as to make the alloys available for orthopaedic implantation. Surface modification is used since this method will not alter the bulk properties of magnesium alloy. Various surface treatments such as Plasma Immersion Ion Implantation and Deposition (PIII&D)² and plasma anodisation³ are applied so that the corrosion resistance of material can be enhanced. Our group has recently developed a unique method to deposit a biodegradable polymer named polycaprolactone (PCL) on the magnesium surface. Previous *in-vitro* studies suggested that the rate of degradation of the magnesium alloy has been delayed. Hence, this study aims to investigate the degradation and new bone formation of the coated magnesium alloy under *in-vivo* conditions.

Methods:

Polymer treated magnesium alloy was prepared by gas spraying. The polymer solution was prepared by dissolving the PCL granules into a solvent called dichloromethane. Two concentrations named PCL1 and PCL2 were prepared by dissolving 1g of polymer granules into 20ml and 30ml solvent respectively.

Two of each PCL1, PCL2 and untreated AZ91 magnesium alloy with 3mm diameter and 6mm long were then implanted into the great trochanter of three New Zealand White rabbits respectively. The animals were sacrificed at the second month of post-operation. The bone tissues with implants were harvested and fixed in 10% buffered formalin. All the samples were then embedded in methyl-methacrylate. The corrosion morphology and sectioning of the implants were examined by micro-computed tomography. After scanning by micro-CT, 2D planes were reconstructed by using NRecon software (Skyscan Company) and the 3D models were generated by CTVol which was a program for realistic 3D visualization. The total volume of implanted magnesium rod and new bone volume were calculated by using CTAn program which was used to analyze micro-CT datasets for morphometry and densitometry. Afterwards, the embedded tissue blocks were sectioned and ground to 50µm. Gimesa staining was then applied to the slides for histological analysis. The on-growth of new bone and the integration of material to host tissue were observed under optical microscope.

Results:

From the reconstruction images as shown in Figure 1, corrosion was found on untreated samples (red arrows) but not observed on PCL1 and PCL2 samples. By observing the 3D reconstruction models as shown in Figure 2, all the samples demonstrated the new bone formation on the material surface (white in colour). The actual values of the remaining implant volume and newly formed bone volume were displayed on Table 1. By comparing the treated and untreated samples, the untreated magnesium alloy showed the least volume of new bone formation and largest volume reduction of the implant after 2 months implantation, whereas PCL2 sample has the highest bone volume. The histological analysis confirmed that the newly formed bone tissue was observed around all of the implants. New bone (yellow arrows) and osteoblasts (green arrows) were observed in Figure 3.

Discussion:

In order to visualize the corrosion morphology and to quantify the *in-vivo* corrosion rate, micro-CT scan was employed. The micro-CT images showed that both PCL1 and PCL2 coatings were able to protect the magnesium alloy even under *in-vivo* conditions. Moreover, with the use of micro-CT, the volume changes of all samples were quantified. The result suggested that the untreated implant had the fastest corrosion rate but the polymer treated samples showed no

degradation at two months time point.

Furthermore, bone formation could also be observed and quantified by using micro-CT analysis. Newly formed bone was found around the implants of both treated and untreated samples in which these observations proved their biocompatibility. No adverse effect was found after implantation. Although corrosion occurred on the untreated sample, new bone formation was still observed around the implant. The result was found to be comparable with others' findings. Both Witte et al.⁴ and Xu et al.⁵ suggested that although corrosion occurred on their magnesium based alloys, newly bone formation was found around the implant. However, by comparing the new bone volumes in our present experiment, it was found that the untreated sample got the least amount of new bone formation than the treated samples. This was mainly related to the magnesium ion release. As demonstrated in the previous *in-vitro* cytotoxicity test, the osteoblastic activity was affected by the magnesium ion concentration. During corrosion, large amount of magnesium ion released may inactivate new bone formation. Therefore less new bone was formed around the untreated sample.

For the histological analysis, since gimesa also contained eosin, apart from staining nucleus, cytoplasm could be stained as well. For the area that was purple in colour was the mixture of blue and red colours, it represented the new bone growth area. Moreover, large amount of osteoblast was found around the polymer treated samples which led to more bone formation. Furthermore, no inflammation was found around the implants which suggested that no harmful effect occurred to the surroundings.

From the *in-vivo* animal study, it could be concluded that the polymer treated magnesium alloy was able to improve the corrosion resistance properties of the magnesium alloy significantly. Although the preliminary animal study showed successful result, longer time point is still needed so as to confirm the effectiveness and the degradation rate of the polymer coating with longer implantation time.

Sample	New bone volume	Implant volume change
Untreated	1.36 mm ³	0.33%
PCL1	6.71 mm ³	0
PCL2	10.79 mm ³	0

Table 1. Values of the new bone volume and the remaining implant volume

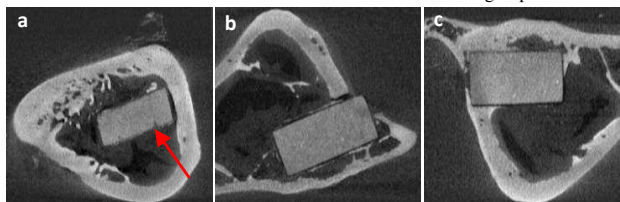


Figure 1. Micro-CT image of the implants after reconstruction. (a) untreated; (b) PCL1 and (c) PCL2

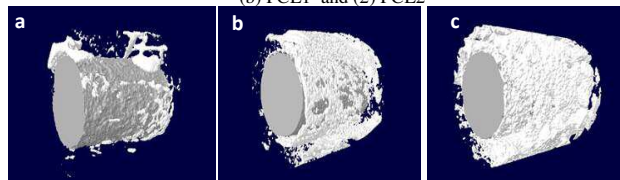


Figure 2. 3D model of the implants with newly formed bone. (a) Untreated; (b) PCL1 and (c) PCL2

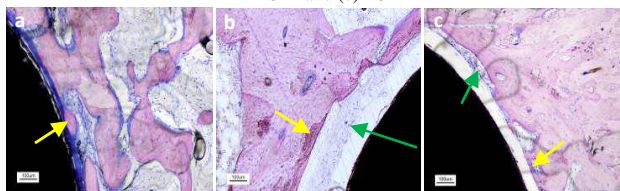


Figure 3. Histological photographs of gimesa stained of the bone tissue formed around the implants. (a) Untreated; (b) PCL1 and (c) PCL2

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