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Coating Systems for Biodegradable Magnesium Applications

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Abstract

Current research for degradable magnesium implants has shown a multitude of potential applications for these materials. Within various studies, the research focuses especially on Mg alloys' biocompatibility and also its mechanical and corrosive behaviour in *in vitro/in vivo* environments. In particular, the corrosive properties of Mg alloys often remain problematic, showing either a rapid or a burst degradation, limiting their applicability. Besides changing the alloy, a magnesium implant's initial corrosion properties can be improved and controllable by means of applied coatings. In general, a multitude of coating solutions (e.g. on basis of phosphates or degradable polymers) are already available for permanent implants. If these are applicable to Mg, the next step requires that they delay corrosion and inhibit burst corrosion. In this study, the applicability and corrosion-delaying properties of PLA and MgF_2 coatings on the magnesium alloy LANd442, respecting their singular and combined application, is shown. By means of corrosion tests in a simulated body fluid the use of combined coatings was proven to be advantageous regarding longevity and toughness of the coating system.

Introduction

Currently, magnesium alloys are being investigated as degradable biomaterials for use in stents, sutures, and orthopedic applications [1-3]. Biodegradable, resorbable materials are of interest because they eliminate the need for a second surgical procedure to remove a temporary implant or device [4]. However, as magnesium alloys often exhibit poor corrosion resistance, their use in medical applications has previously been limited. A rapid degradation of Mg implants compromises structural integrity and leads to the production of excess hydrogen gas and an increased pH in the implant's proximity. Fortunately, these effects can be minimized through alloying and by coating the implant with a corrosion resistant layer [2, 5].

One of the most critically investigated coatings is magnesium fluoride (MgF_2), since Mg and F are both naturally occurring elements in the body, and the components of degradation remain harmless as the layer corrodes [6]. Previous studies using an MgF_2 protective layer have shown significantly improved corrosion resistance in industrial applications, as well as slight improvements in *in vitro* and *in vivo* biological testing [7-10]. However, MgF_2 is known for its brittle and cracked surface characteristics and inappropriate behaviour in case of deformations [11, 12].

The application of resorbable polymer coatings to magnesium could be a good alternative, since polymers possess better plasticity. However, Chen *et al.* [13] discovered reactions between Magnesium base material and polymer coatings (PLA and PCL). Here, the coating's defects and diffusing processes allowed the surrounding fluid to react with the base material, resulting in the generation of H_2 and $Mg(OH)_2$. Chen *et al.* [13] suggested that H_2 accumulations in the bonding zone led to a decrease in bonding strength. Furthermore, they claimed that $Mg(OH)_2$ accumulations reacted with the adjacent polymer, where the hydroxide led to an increased production of polymeric acids that either further neutralized OH^- or reacted with $Mg(OH)_2$ [13]. Finally, the increased production of polymeric acids led to a decreased corrosion resistance since the Mg surface passivation by $Mg(OH)_2$ became suppressed. This consequently led to an increased production of H_2 and $Mg(OH)_2$, promoting the degradation of the polymer. A mutual acceleration of both materials' corrosion rates resulted [13]. The cascade of reactions of the Mg and PLA proximity in a corrosive environment is summarized in **Table 1**. Via pH measurements, the biomedical polymer films lead to a decreased initial corrosion rate of pure Mg [14].

Table 1: Reactions of Mg and Polymer

No.	Reaction	Description
1	$Mg + 2H_2O \rightarrow$ $Mg(OH)_2 + H_2 \uparrow$	Reaction of Mg and water [15]
2	$Mg(OH)_2 + 2Cl- \rightarrow$ $MgCl_2 + 2OH^-$	Reaction of magnesiumhydroxide and chloride ions from the SBF [13]
3	$(-COOR-)_n \rightarrow$ $R_1COOH+R_2OH$	Catalysed production of polymeric acids by means of $Mg(OH)_2$ [13]
4	$OH^- + R_1COOH \rightarrow$ $R_1COO^- + H_2O$	Reaction of polymeric acid and OH^-[13]
5	$Mg(OH)_2 + 2R_1COOH \rightarrow$ $(R_1COO)2Mg + 2H_2O$	Reaction of polymeric acid and $Mg(OH)_2$ [13]

In the course of corrosion, Mg and the polymer interact, which has the potential to accelerate both materials' corrosion processes. Here, the combination of surface treatments and different coatings might be the key to reducing or preventing this interaction. With this in mind, within this study the influence of an intermediate layer of MgF_2, which was used to circumvent the direct contact of Mg and PLA, was analysed regarding its potential to further delay the corrosion of the base material.

Materials and Methods

The magnesium alloy LANd442 (Mg 90 wt.%, Li 4 wt.%, Al 4 wt.%, Nd 2 wt.%) was chosen as base material due to its rapid and sudden corrosion properties [11].

LANd442, whose designations correspond to B275-05 guidelines of the "American Society for Testing and Materials" [16], was initially manufactured by gravity die-casting. Here, the base material and the additional alloying elements were obtained from Magnesium Elektron UK, magnesium, Treibacher Industrie AG (neodymium), Chemetall GmbH (lithium); and Hydro Aluminium Deutschland GmbH (aluminum). To produce the quaternary alloy, the magnesium and the corresponding alloying elements were melted at a temperature of 750 °C in a steel crucible and subsequently stirred for 30 min. Owing to the material's elevated reactivity with air, melting and casting was carried out in a dynamic argon atmosphere.

In order to obtain a fine-grained alloy with advanced mechanical and corrosive properties, hot extrusion was carried out after casting. Here, a direct extrusion operation was arranged in a 10 MN extruder. The extrusion die, which had an orifice diameter of 30 mm, was heated, along with its recipient, to a temperature of 380 °C. Subsequently, the respective cast billets could be inserted into the extruder and pressed through the extrusion die with a profile velocity of 1.9 $\mathrm{m \cdot min^{-1}}$. The deformation was carried out at an extrusion ratio of 16.

In order to ensure sufficient specimen geometry, sample dimensions used in prior studies [11, 17, 18] and adequate for a three-point-bending test were chosen. Here, rods with a diameter of 2.5 mm and a length of 25 mm (exhibiting a surface area of 206 $\mathrm{mm^2}$) were manufactured by machining.

To delay the corrosion of LANd442, two coating systems were combined and attached to the specimens. For the intermediate layer, a magnesium fluoride coating was chosen. In order to obtain a sufficient coating, the specimens were boiled in NaOH (200 $\mathrm{g \cdot L^{-1}}$) for 120 min. Subsequently, the specimens were placed in hydrofluoric acid (40 %) for 96 h to achieve the MgF_2 coating. To remove the remains of the chemicals, the specimens were rinsed with distilled water and ethanol after the hydrofluoric acid treatment. The procedure was adapted from Seitz *et al.* [11, 12].

A PLA/DCM solution was prepared using PLA-3051D and dichloromethane to form the top sealing layer. Both agents (6.675 g PLA and 100 ml dichloromethane) were mixed together and stirred at room temperature for 60 minutes until the PLA dissolved completely. Subsequently, the solution was refilled to 100 ml by adding dichloromethane. The Mg samples were then lowered into the PLA/DCM solution for 15 seconds. The sample lowering process was repeated 2 times. Afterwards, the samples were dried at room temperature for 72 hours.

The experimentation involved *in vitro* corrosion of LANd442 in the PLA-coated state as well as in the combined MgF2 and PLA coated state, via immersion in smoothly flowing simulated body fluid (SBF) to acquire information about the coating systems' influence on degradation. Specimens of each coating state were removed from the experimental set-up after 15 and 30 days. For the total test duration, measurements were performed on separate samples (three for each measurement point), which were not immersed again after extraction. Single specimens were put into sample containers that were then filled with 25 mL of SBF (achieving a "fluid-volume:sample-surface" ratio of 0.12 $\mathrm{mL \cdot mm^{-2}}$). The samples' containers were then submerged in a water–filled, sealable, insulated container that was heated to a constant temperature of 36.5 °C (±0.4 °C) by means of an appropriate regulating circuit to imitate human body temperature during the process of corrosion. Here, an immersion heater (Titanium Heizer 50 W) was connected to a universal thermostat (Universal-Thermostat "UT 200"). In order to establish a certain flow of the corrosive medium, the entire experimental set-up was placed on an orbital shaker (GFL3015) that was set to 60 $\mathrm{L \cdot min^{-1}}$.

In order to prepare a SBF that contained ions corresponding to the concentration of real body fluid, 700 mL of distilled water were heated to 36.5 °C, and the substances shown in **Table 2** were subsequently added, according to the table's sequence. Using the method of titration, the mixture was set to a pH of 7.4 by adding sodium hydroxide (1.0 mol) at 36.5 °C. A 1 000 mL Pyrex-Glas (to obtain an inert temperature) was then used to cool the mixture to 20 °C while it was filled to 1000 mL by adding distilled water. Owing to the verified high stability and similarity to blood plasma in ion concentrations, the preparation of the SBF was carried out according to Oyane *et al.* [19].

Table 2: Sequence of substances for the SBF

Substance	Mass	Purity[%]
NaCl	5.403 g	>99.5
$NaHCO_3$	0.504 g	>99.5
Na_2CO_3	0.426 g	>99.5
KCl	0.225 g	>99.5
$K_2HPO_4 * 3H_2O$	0.230 g	>99.0
$MgCl_2 * 6H_2O$	0.311 g	>98.0
0.2 M – NaOH/HEPES	100 ml / 17.892 g	- / >99.9
$CaCl_2$	0.293 g	>95.0
Na_2SO_4	0.072 g	>99.0

The coated and uncoated specimens were weighed before and after the *in vitro* corrosion procedure using a precision balance (Analytical Balance A204). In order to acquire information about the corrosive medium's pH during the course of the experiments, a measurement was taken each time the coated specimens were removed from the experimental set-up. For each pH measurement, the specimen was removed from the sample container, during which a separate pH-measuring vessel was filled with the corrosive medium. The Winlab Data Line pH Meter was calibrated and rinsed with distilled water thoroughly before each measurement. A SEM 1455 VP with an EDAX Genesis unit and an Axioplan 2 reflecting-light microscope, which incorporates a ProgRes2008 CCD camera, were used to obtain information about the coatings' thickness. To determine the performance of the coatings after deformation, a 3-point bending test was carried out in which the coated samples were bent to 50 % of their prior determined ultimate bending punch displacement via Universal Testing Machine Z250. Subsequently these samples were immersed into SBF and analysed according to the non-bend sample protocol.

Results and Discussion

With and without the intermediate MgF_2 layer, a compact PLA layer could be established on top of the samples. ESEM cross-sectional analyses revealed a PLA layer thickness of 93 µm after dipping the samples into the PLA/DCM solution 2 times. Here, the coating appeared dense and homogeneous. Furthermore, the PLA coating exhibited a porous segment on its top (**Figure 1** (left)). This porous segment showed a thickness of 6.5 µm, and the pores revealed a top opening with diameters of 1 µm to 1.5 µm (**Figure 1** (right)).

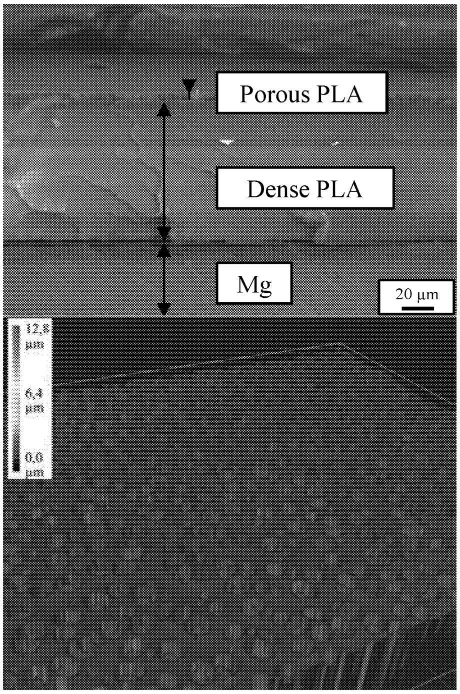

Figure 1: (Top) Cross-sectional SEM image of the PLA coated specimen; (Bottom) 3D-microscopical image of the top PLA layer

As displayed in **Table 3**, SBF immersion testing resulted in an insignificant loss in mass after an overall duration of 30 days for both of the differently prepared sample groups. Compared with the results of Seitz *et al.* [11] the corrosion properties could be significantly optimized by means of an additional PLA layer. In the prior study, samples with a MgF_2 coating demonstrated a mass loss of 80 % after 20 days of immersion in SBF. Within this study, mass loss could be clearly reduced to 7 % after 30 days by attaching an additional PLA layer. Furthermore, the PLA-only coating resulted in a loss in mass of 7 % after 30 days as well. The pH, however, remained stable within the 30 days of immersion and was not being heavily influenced by the release of corrosion products as in Seitz *et al.* [11], which investigated pure and MgF_2 coated LANd442.

Table 3: Mass loss and SBF pH value of the corroded samples (n=3)

Group	Mass loss 15 days	p	Mass loss 30 days	p
LANd442 + PLA	0 %	7.6	7 %	7.8
LANd442 + MgF_2 + PLA	7 %	7.7	7 %	7.7

Optical analyses of the corroded samples revealed an induced blister formation under the PLA top layer in the case of the PLA-only coated samples (**Figure 2**). These blisters resulted most likely from the Mg corrosion process in which hydrogen gas is formed (**Table 1** eq. 1). Since blistering appears significantly stronger in the PLA-only coated state, the intermediate MgF_2 layer seems to potentially block the interaction of the PLA and the base material and therefore improves the system's corrosion properties. The risk of a delaminating of the PLA due to induced blistering is clearly lowered. Nonetheless, the corrosion rate seems not to be affected by the existence of the intermediate MgF_2 layer, at least in the first 30 days of corrosion.

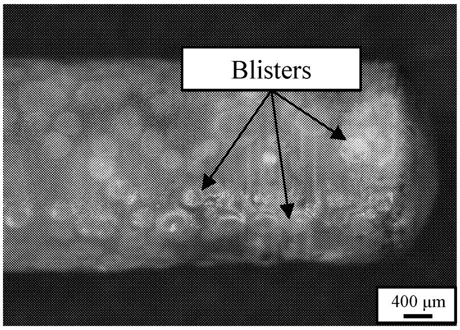

Figure 2: PLA only coated sample after 30 days of corrosion in SBF (sample diameter = 2.5 mm)

To validate the coating toughness and its corrosion protection abilities after plastic deformation, coated and bent samples were immersed into SBF as well. Bending was carried out until the outer PLA layer clearly showed damaging (50 % of the alloy's ultimate bending punch displacement). The pH and mass loss were determined for both coating systems after 15 and 30 days of immersion (**Table 4**). After bending and cracking the coatings at the same time, the PLA only coated samples show an increased mass loss when compared to the MgF_2 and PLA coated samples while corroding. Due to corrosion, the pH is initially slightly increased before the SBF's buffer takes effect.

Table 4: Mass loss and SBF pH value of the bend and corroded samples (n=3)

Group	Mass loss 15 days	p	Mass loss 30 days	p
LANd442 + PLA	5 %	8.0	13 %	7.7
LANd442 + MgF_2 + PLA	2.5 %	7.7	7 %	7.7

The damaged PLA surface of a bent sample is displayed in **Figure 3**. Here, it becomes obvious that the pure or MgF_2 coated base material, in either case, are directly exposed to the corrosive environment. Due to the crackled surface structure of the Mg, the formation of $Mg(OH)_2$ and MgO is expected. Here, damaging of the PLA layer was determined after high plastic deformation only. An MgF_2 layer is known to be brittle; it loses its integrity after low deformation ratios as shown by Seitz *et al.* [12]. In its combinations, the PLA appeared to prevent the MgF_2 from flaking off the sample's surface, thereby, in case of the PLA's fracturing; the MgF_2 layer could actively act as a second corrosion barrier.

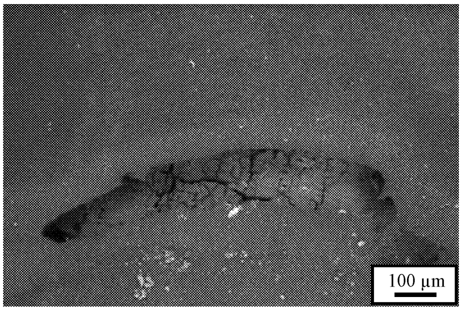

Figure 3: Damaged PLA layer (due to bending) of a MgF_2 and PLA coated sample after 30 days of corrosion in SBF

Conclusions

The results made within this study prove that the combination of MgF_2 and PLA form a good coating system to prevent magnesium from rapidly corroding. While both coatings reduce the Mg's corrosion speed, their combination added advantages regarding longevity and toughness. MgF_2 as an intermediate layer prevented the PLA and the Mg from catalyzing each other's corrosion processes. Only at high plastic deformation ratios did the PLA break open, and in this case the intermediate MgF_2 layer became an active corrosion barrier.

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