

Long-term Corrosion Behavior of Poly-L-lactic Acid Coated Magnesium in Dulbecco's Modified Eagle Medium at Body Temperature

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In this work poly-L-lactic acid (PLLA) is explored as a biocompatible and -degradable coating to slow down corrosion of magnesium. PLLA coatings were obtained with different thicknesses by spin coating technique. The coatings were characterized by FTIR and the adhesion was measured according to the ASTM D3359-09 test. Also, for the first time, long term corrosion behavior (up to 30 days) of uncoated and PLLA coated magnesium was investigated in Dulbecco's modified Eagle medium at body temperature by potentiodynamic polarization scans. The results show that the coating consisted only of PLLA without remnants of the solvent but exhibited low adhesion to the magnesium surface. The corrosion test showed a significant improvement of the corrosion protection for up to 7 days, depending on the coating thickness. Furthermore, the corrosion is altered from a charge controlled to a diffusion controlled dissolution mechanism for up to 30 days, independent of the layer thickness.

Keywords: poly-L-lactic acid, magnesium, DMEM, long term corrosion

1. INTRODUCTION

Magnesium is a promising material for biodegradable implants such as bone fixation screws or cardiovascular stents due to its superb biocompatibility [1]. Magnesium plays a significant role in the metabolism of the human body with an average daily dose of 250 - 500 mg/day for an adult [2, 3]. Additional surplus magnesium is simply discarded by the kidneys [4] and no deadly toxic dose to the human body is known yet [3]. Therefore magnesium is ideal as base material for temporary implants, as the corrosion products are not harmful to the human body and as the risks of second surgery for removal of the implants can be avoided [5]. Also magnesium is a light-weight material that has, compared to most other metals and ceramics, a quite similar Young's modulus as bone [6]. Therefore,

by using Mg as implant material, the “stress-shielding” effect observed for implant materials with a significant higher E-modules than bone can be reduced [6, 7].

The main reason why magnesium is not used as implant material already, is that it is one of the most unstable metal against corrosion [8]. With a practical electrode potential of -1.7 V vs. SHE [8], the corrosion of magnesium as well as the evolution of hydrogen gas is too severe to meet the required stability over time for an implant material. To reduce the corrosion velocity two approaches (or a combination of both) are possible: The first would be decreasing the corrosion by alloying with stabilizing elements such as aluminum or rare earth metals [2]. The second would be the application of a corrosion hindering coating. The main disadvantage of the first approach is the influence of many alloying elements to the human body. Aluminum for example is considered being one possible factor causing Alzheimer’s disease [9] and the influence of rare earth elements is not investigated properly yet. Therefore, the second approach of using a protective coating, in case of for instance pure Mg, does not lead to such challenges in alloying. Of course, the protective coating itself should be biocompatible and biodegradable. Biodegradable polymer coatings therefore are promising approach in this field.

Hornberger et al. [3] recently published a review considering different coating techniques available for corrosion protection of magnesium. Simple dip or spin coating processes can lead to promising results hindering the corrosion of magnesium. Xu et al. [10, 11] showed that poly-L-lactic acid (PLLA) and polycaprolactone (PCL) coated magnesium samples are less exposed to the initial corrosion in simulated body fluid (SBF) and that cell growth on coated magnesium is significantly increased compared to bare magnesium. Li et al. [12], Wong [13] et al. and Yamada et al. [14] came to similar conclusions utilizing PLGA, PCL or a siloxane containing Vaterite/PLLA composite as coating. Chen et al. [15] also investigated PLLA and PCL coatings on high purity magnesium in SBF showing an improved corrosion behavior, but also suggested an interaction between the corroding Mg surface and the polymer interface, leading to an accelerated degradation of the polymer. Alabbasi et al. [16] used electrochemical impedance spectroscopy to investigate the corrosion behavior of PLA coated AZ91 magnesium alloy. This work showed that with increasing coating thickness the corrosion properties are improved but the adhesion gets worse. Degner et al. [17] showed that the corrosion resistance of magnesium in Dulbecco’s Modified Eagle Medium (DMEM) can be significantly improved for up to 15 days by applying a PCL layer. It was also shown that during exposition of the coated samples to DMEM a grey/black layer is forming underneath the PCL coating.

In this study, magnesium (of 99.9% purity) was covered with poly-L-lactic acid by spin coating to achieve a homogenously distributed “model” layer of PLLA, similar to the PCL coating in the work of Degner et al. [17]. The corrosion behavior of this coating in cell culture medium was investigated by electrochemical polarization curves; with a special focus on studying the long-term degradation of the system for up to 30 days; such long-term characterization of PLLA-coated Mg corrosion behavior has not been previously carried out.

2. EXPERIMENTAL

A magnesium (Mg) rod with a diameter of 25.4 mm and 99.9% purity (Chempur Feinchemikalien und Forschungsbedarf GmbH) was used for preparation of samples. The rod was cut

into approx. 2 mm thick pieces. To ensure a homogenous coating, the Mg samples were polished to gain a mirror like surface finish. Therefore the samples were first ground using a Microcut abrasive paper (Buehler) with Ethanol (Sigma-Aldrich) as lubricant. Subsequently the surface was consecutively polished with diamond paste from 6 μm to 0.25 μm (with 3 and 1 μm as intermediate steps) using an Ethanol/Glycerin (3:1) mixture as lubricant. Between each step the samples were ultrasonically cleaned in Ethanol. After the last polishing and cleaning step the samples were dried under hot air.

Poly-L-lactic acid (PLLA) with an average molecular weight of 100,000 g/mol (Polysciences, Inc.) was dissolved in chloroform (Sigma-Aldrich). To coat the polished samples, a spin coating device (Delta 10, BLE Laboratory Equipment GmbH) was used. A 5 wt% PLLA solution was produced using Chloroform as solvent. The coating procedure was conducted in a grey room at room temperature and 30% humidity. Before coating, the samples were preheated at 120°C to remove remaining water at the surface and then cooled down to room temperature again. 250 μl of the PLLA solution was applied to the surface using a micropipette. Afterwards three different coating thicknesses were achieved by varying the rotation speed at 5000 rpm, 2500 rpm and 1250 rpm for 30 s. The coating thickness was calculated using the mass difference between coated and uncoated samples, assuming that the layer had a homogeneous distribution over the whole sample surface.

The adhesion of PLLA to the Magnesium was measured using the standard test method ASTM D3359-09 [18]. The samples were first provided with a rectangular grid of scratches on top and then a pressure-sensitive tape was applied and removed of the surface. The adhesion strength was then determined by comparing the remaining percentage of polymer residues on the surface to the standard's categories.

The chemical composition of the PLLA coating was investigated using Fourier transform infrared spectroscopy (FTIR, Nicolet 6700, Thermo Scientific) over the PLLA/Mg coated samples with different coating thicknesses and then compared to the literature.

As corrosive medium Dulbecco's Modified Eagle Medium (DMEM) (Biochrom) was used, to simulate human body like corrosion conditions. The composition of DMEM is shown in Table 1. Prior to electrochemical testing the samples were stored in 80 ml DMEM at 37°C for 15 min, 60 min, 24 h, 7, 15 and 30 days to study the long-term corrosion behavior of the PLLA coated Mg samples in simulated body conditions.

Table 1. Composition of Dulbecco's modified eagle medium

Substance	Concentration (mg/l)	Substance	Concentration (mg/l)
NaCl	6400	L-Lysine·HCl	146
KCl	400	L-Methionine	30
CaCl ₂	200	L-Phenylalanine	66
MgSO ₄ ·7H ₂ O	200	L-Threonine	95
NaH ₂ PO ₄	124	L-Tryptophan	16
D-Glucose	1000	L-Tyrosine	72

Fe(NO ₃) ₃ ·9H ₂ O	0.1	L-Valine	94
Na-Pyruvate	110	Glycine	30
Phenol red	15	L-Serine	42
NaHCO ₃	3700	Cholinchloride	4
L-Arginine·HCl	84	Folic acid	4
L-Cysteine	48	Myo-Inositol	7.2
L-Glutamine	580	Nicotinamide	4
L-Histidin·HCl	42	Da-Ca-Pantothenate	4
H ₂ O		Pyridoxal·HCl	4
L-Isoleucine	106	Riboflavin	0.4
L-Leucine	106	Thiamine·HCl	4

Bare, polished Mg samples were also investigated under the same condition as a reference. Potentiodynamic polarization curves were measured in a standard 3-electrode set-up to characterize the corrosion behavior of bare and PLLA coated Mg samples. An Ag/AgCl electrode served as reference and a Pt sheet with 1 cm² surface area as counter electrode. A surface area of 0.78 cm² was exposed to the electrolyte. Each experiment was conducted three times and a representative curve is shown. All electrochemical experiments were performed in a Faradaic cage using an IM 6 potentiostat (Zahner Elektrik GmbH). The polarization was carried out from -300 mV relative to OCP up to 0 V with a scan rate of 3 mV/s. The measurements were stopped when the current exceeded 10 mA/cm². To determine the corrosion current density (i_{corr}) Tafel extrapolation was used. Therefore, Tafel lines were applied 50 mV from the corrosion potential (E_{corr}) over several decades of current density. After the corrosion tests a picture of the surface was taken with a microscope (M420, WILD).

3. RESULTS AND DISCUSSION

3.1. Characterization of the coatings

Figure 1 illustrates the layer thicknesses obtained at different rotation velocities. The different velocities were 1250, 2500 and 5000 rounds per minute (rpm, the different thicknesses are afterwards referred to as 1250, 2500 and 5000 rpm). For 5000 rpm the layer thickness was $3.5 \mu\text{m} \pm 1.1 \mu\text{m}$, for 2500 rpm $5 \mu\text{m} \pm 1 \mu\text{m}$ and for 1250 rpm $7.5 \mu\text{m} \pm 1.2 \mu\text{m}$. Degner et al. [17] controlled the layer thickness in spin-coated PCL/Mg samples by varying the concentration of the PCL/Chloroform solution, therefore changing the viscosity of the solution. In the present work the layer thickness is controlled by applying different rotation velocities. Despite the different approach of controlling the thickness, it was possible to achieve similar layer thicknesses with the 5000 and 2500 rpm coating velocities compared to the 5.0 wt% and 7.5 wt% PCL coatings of the previous study. Also the deviation is similar to Degner et al. [17] and Xu et al. [10]. The deviation might be due to slightly differing temperature and humidity in the grey room, due to the spin coating itself [19], or due to the

possibly slightly varying amount of PLLA/Chloroform solution that is applied to surface prior to the spin coating.

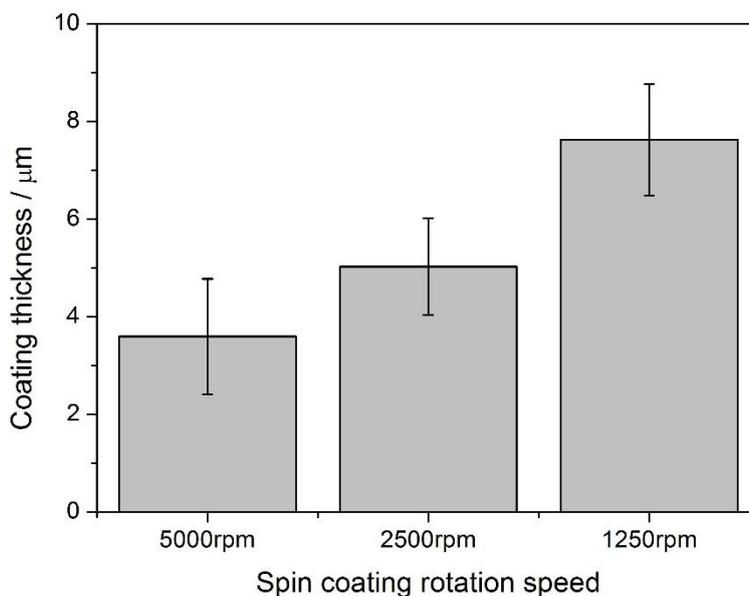


Figure 1. Film thicknesses for PLLA coatings on Mg prepared by spin-coating with different rotation velocities from 5 wt% PLLA dissolved in chloroform

The adhesion was tested as described above following ASTM D3359-09. The adhesion strength of the PLLA-film to the magnesium surface was categorized in class 0(B) [18]. This means more than 65% of the film inside of the grit was removed by detaching the adhesive tape. This implies a low adhesive strength of the film to the surface. Despite reports claiming that an increased ratio of oxygen in PLLA should lead to an improved adhesion compared to e.g. PCL, significant differences in adhesion could not be observed [10, 20].

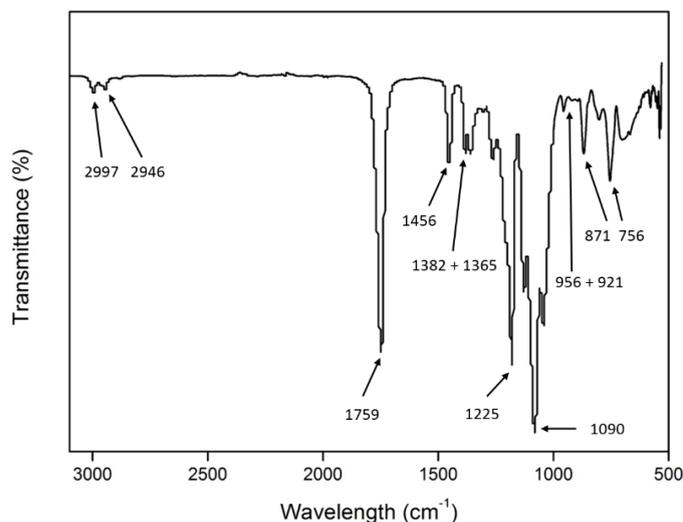


Figure 2. Representative FTIR spectra of PLLA coated magnesium

Figure 2 shows the FTIR results for PLLA coated magnesium. Only one spectrum is shown, as the different layer thicknesses exhibited the same spectral features. The spectra are in good agreement with the literature. The IR bands at 2997 cm^{-1} and 2946 cm^{-1} are assigned to the CH stretching region. At 1759 cm^{-1} the C=O stretching region appears. CH_3 is responsible for the broad IR band at 1456 cm^{-1} and the double peak at 1382 and 1365 cm^{-1} is related to the CH deformation. At 1225 cm^{-1} the stretching of the ester groups appear and the C-O-C asymmetric mode is visible at 1090 cm^{-1} . The IR bands at 957 and 921 cm^{-1} correspond to the characteristic helical backbone vibrations with the CH_3 rocking modes. The IR bands at 871 and 756 cm^{-1} could be attributed to the crystalline and amorphous phases of PLLA [21-26]. The FTIR spectra shows that PLLA is present on the surface. Furthermore, these results indicate that the chloroform used as solvent evaporates completely after coating the magnesium, as no bands related specifically to chloroform are present (at least to a minimum accuracy limit of 5% for FTIR). This is important as chloroform is known as a potential cancerogenic substance and therefore its remnants in the coating would raise questions on the suitability of PLLA coated magnesium as implant material [27].

3.2. Corrosion behavior

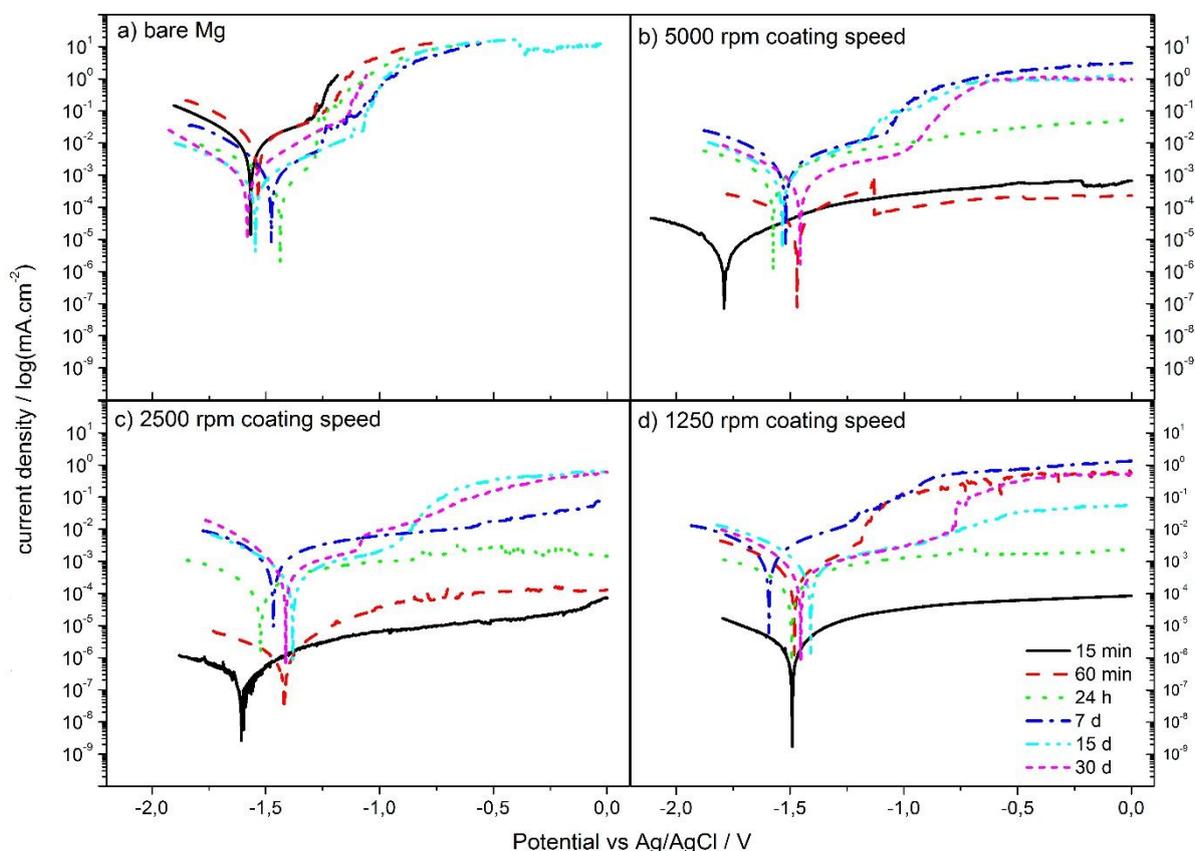


Figure 3. Polarization curves for (a) bare magnesium, (b) 5000 rpm, (c) 2500 rpm and (d) 1250 rpm PLLA coated magnesium samples in DMEM at 37°C for immersion times up to 30 days

Polarization curves were recorded for uncoated and PLLA coated magnesium in DMEM at 37°C after different immersion times. The aim was to investigate the corrosion protection properties of the coating and to test the long term stability of the different coating thicknesses compared to bare magnesium. Figure 3 shows the measured polarization curves for bare magnesium (a) as well as for 5000 (b), 2500 (c) and 1250 rpm (d) PLLA covered magnesium in DMEM for up to 30 days at 37°C. Tables 2 and 3 show the obtained corrosion potential (E_{corr}) and corrosion current density (i_{corr}). Figure 4 shows the logarithmic i_{corr} over the immersion time. After testing the coated and uncoated samples at different immersion times a macroscopic picture is taken and shown in figure 5.

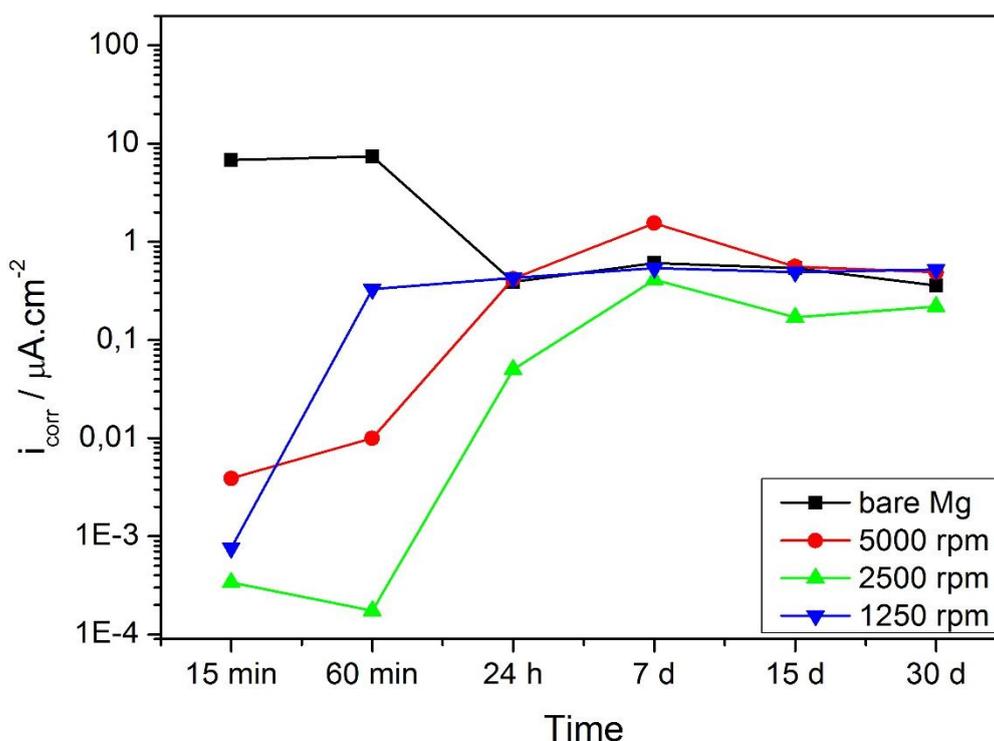


Figure 4. Logarithmic illustration of i_{corr} of the uncoated and PLLA coated magnesium samples after different immersion times in DMEM at 37°C

For bare magnesium the cathodic as well as the anodic current density is lowered with increasing immersion time. E_{corr} increases for 7 days but after 15 days of immersion it decreases again. The corrosion current density (i_{corr}) for bare Mg therefore decreases in the first 24 h of immersion, and then remains ca. constant (see Fig. 4). This initial decrease of the corrosion rate can be due to the formation of a corrosion product layer: as can be seen in Fig. 5, a grey to black layer is forming on the surface. The formation of such a relatively well protecting corrosion product layer on Mg exposed to DMEM has been previously discussed [1,17]. It should be mentioned that these experiments were carried out in a static electrolyte which can strongly influence the corrosion product layer formation (as well as the surface pH increase due to Mg dissolution).

The 5000 rpm (the thinnest) PLLA coating shows a different corrosion behavior than bare magnesium. Until 24 h the cathodic as well as the anodic current density are significantly lower as for bare magnesium (Fig. 3b), leading to ca. 100 times lower i_{corr} values than those measured for uncoated Mg (Table 2). Thereafter the cathodic current density increases to a similar level as uncoated magnesium and remains constant for immersion times up to 30 days, the anodic current density however shows a different behavior.

Table 2. E_{corr} obtained from Tafel plot extrapolation

	Bare Mg		5000 rpm		2500 rpm		1250 rpm	
	Aver. [V]	Dev.						
15 min	-1.58	± 0.05	-1.56	± 0.06	-1.61	± 0.03	-1.50	± 0.03
60 min	-1.56	± 0.05	-1.46	± 0.02	-1.44	± 0.03	-1.48	± 0.01
24 h	-1.42	± 0.06	-1.46	± 0.09	-1.47	± 0.03	-1.46	± 0.08
7 d	-1.50	± 0.02	-1.57	± 0.06	-1.45	± 0.09	-1.56	± 0.02
15 d	-1.57	± 0.04	-1.54	± 0.04	-1.42	± 0.03	-1.50	± 0.07
30 d	-1.51	± 0.05	-1.50	± 0.06	-1.42	± 0.03	-1.48	± 0.08

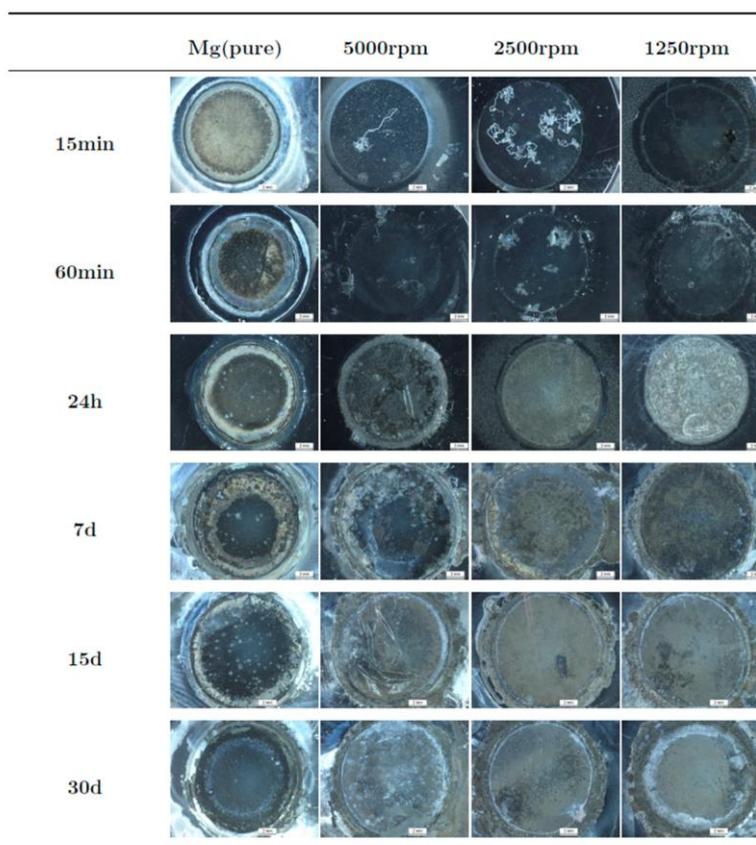


Figure 5. Macroscopic pictures of uncoated and PLLA coated Mg samples after different immersion times in DMEM at 37°C

It first increases to a similar level as for bare magnesium and then remains constant for 15 days. After 30 days a slight decrease of the anodic current densities can be seen. For 15, 60 min and 24 h the anodic current density shows similar behavior as the previously studied PCL coated magnesium samples [17]. The very low current densities up to 0 V imply a very efficient corrosion protection of the Mg substrate, similar to the results of Degner et al. [17]. After 24 hours immersion, the anodic current density however shows a similar behavior as bare magnesium. The onset of increased dissolution rates is shifted to more positive potentials, and the current densities are slightly lower than for uncoated Mg, indicating that the PLLA layer may still be hindering ion transport. The electrochemical results indicate that the 5000 rpm coating is penetrated quite fast by the electrolyte and the protecting effect of the PLLA is reduced. This is verified by visual observations of the sample surfaces after different immersion times. The pictures in figure 5 show filiform corrosion already for immersion time of 15 min, and with increasing immersion time a similar layer of corrosion products is observed on the surface as for bare magnesium. Therefore it is assumed that the PLLA layer is penetrated by water and/or ions during the first 15 min of immersion, leading to onset of corrosion. The loss of corrosion protection of the PLLA layer might also result from the degradation of the coating itself due to the contact with water [28, 29]. The results indicate that the protection of the PLLA layer fails within the first 7 days but still shows a small influence on the corrosion rate due to the hindering of ion movement.

Table 3. i_{corr} obtained from Tafel plot extrapolation

	Bare Mg		5000 rpm		2500 rpm		1250 rpm	
	Aver. [$\mu\text{A}/\text{cm}^2$]	Dev.	Aver. [$\mu\text{A}/\text{cm}^2$]	Dev.	Aver. [$\mu\text{A}/\text{cm}^2$]	Dev.	Aver. [$\mu\text{A}/\text{cm}^2$]	Dev.
15 min	6.81	± 2.45	$3.89 \cdot 10^{-3}$	$\pm 0.87 \cdot 10^{-3}$	$0.34 \cdot 10^{-3}$	$\pm 0.19 \cdot 10^{-3}$	$0.76 \cdot 10^{-3}$	$\pm 0.17 \cdot 10^{-3}$
60 min	7.42	± 1.53	0.01	$\pm 7.43 \cdot 10^{-3}$	$1.75 \cdot 10^{-3}$	$\pm 1.77 \cdot 10^{-3}$	0.33	± 0.15
24 h	0.39	± 0.16	0.42	± 0.20	0.05	± 0.02	0.43	± 0.25
7 d	0.61	± 0.20	1.55	± 0.54	0.41	± 0.17	0.54	± 0.24
15 d	0.54	± 0.17	0.56	± 0.13	0.17	± 0.05	0.49	± 0.20
30 d	0.36	± 0.08	0.49	± 0.21	0.22	± 0.07	0.52	± 0.19

The medium-thick coating, prepared with 2500 rpm, shows the best corrosion protection (see Figs. 3c, 4, 5); in this case corrosion protection is provided for up to 7 days. The corrosion rates in the first 24 h or immersion are lower than for the thinner coating. The polarization curves in Figure 3c indicate that the protective effect is due to blocking of both the cathodic and anodic reactions. During the first 7 day of immersion, the coating seems to be penetrated, detached or dissolved, resulting in a gradual increase of both the anodic and cathodic current densities, and hence an increased dissolution rate. However, even after the (partial) degradation of the coating, the dissolution rate remains lower than that of bare magnesium. Also the anodic current density is remarkably low up to 0V, compared to

bare Magnesium, what indicates the ion movement hindering of the PLLA layer again. The pictures in figure 5 indicate filiform corrosion during the first 60 min of immersion and afterwards the growth of a corrosion product layer underneath the PLLA coating. Compared to the 5000 rpm coating and bare magnesium, the corrosion product layer is less dark, indicating less dissolution on the 2500 rpm coated samples during 30 days of immersion.

The thickest PLLA coating studied here (prepared with 1250) shows a significantly different behavior compared to the thinner coatings (see figures 3d, 4 and Tables 2,3). After 15 min immersion the corrosion behavior is similar to that of 2500 rpm PLLA covered magnesium. The macroscopic picture after 15 min shows less filiform corrosion for this coating thickness. However, the corrosion protection decreases significantly faster than for the other coatings thicknesses. Already after 60 min of immersion the corrosion current density is on the same level as for the thinnest coating and bare magnesium after 24 h. As can be seen in figure 3 and 4 as well as in table 2 and 3, the corrosion rates stay on a similar (high) level for up to 30 days. The macroscopic pictures in figure 5 also show that after 60 min of immersion a layer of corrosion products seems to form underneath the coating. After 24h of immersion it is obvious that the PLLA layer is detached from the magnesium surface and the surface is strongly corroding. Despite the early detachment, the layer still seems to hinder the diffusion of ions, as the anodic current density stays below the break off criteria of 10 mA/cm^2 for up to 0 V even after 30 days of immersion. The earlier detachment of the PLLA layer, compared to the thinner layers, may be due to water uptake (which is higher for the thicker coating), and thus a change in the internal stresses or a volume expansion of the layer. This can lead to cracking of the coating.

It should be mentioned that factors influencing the here observed behavior - that are not representative of a biological system - are the static electrolyte and resulting pH shifts in the alkaline region due to Mg dissolution. In contrast to a dynamic system, corrosion products formed in a static electrolyte as well as remnants of the degraded PLLA could form a corrosion hindering layer on the surface by precipitation. This layer could slow down dissolution, in spite of not being well attached to the substrate. The pictures in figure 5 indicate that such a layer is formed on magnesium in DMEM at 37°C . Another factor influencing the corrosion properties measured is a pH increase due to the static electrolyte and the dissolution of magnesium. This could lead to a partial passivation of the Mg surface therefore hindering the dissolution. The pH increase at the Mg surface (or at the Mg/PLLA interface) could also influence degradation of the PLLA coating itself [30]. On the other hand, PLLA degradation leads to release of lactic acid, which could partially neutralize the Mg dissolution induced pH increase [31].

In summary, PLLA coatings prepared by a simple spin-coating technique on pure Mg substrate can offer significant corrosion protection in DMEM, 37°C . For an optimum coating thickness in this study ($5 \mu\text{m}$), good barrier properties of the coating could be observed for up to 7 days of immersion. Both thinner and thicker coatings showed a faster degradation of the protection effect. Filiform corrosion was observed in early stages of immersion, for longer immersion times partial detachment of the coatings seems to take place and a formation of a corrosion product layer at the Mg substrate/coating interface could be observed. In spite of limited adhesion of the coatings on the Mg surface, some corrosion protection effects could be observed even after coating degradation; i.e. up to 30 days of immersion.

4. CONCLUSION AND OUTLOOK

PLLA was successfully deposited as biodegradable layer with different thicknesses on 99.9% bare magnesium by spin coating method. FTIR confirmed the presence of PLLA on the surface and showed that no solvent remains in the layer. The adhesive strength of the layer was found to be very low. The corrosion properties of bare magnesium and PLLA coated magnesium were investigated in DMEM at body temperature by potentiodynamic polarization for up to 30 days of immersion. The results show that the corrosion mechanism of magnesium is altered from charge-controlled to diffusion controlled due to the PLLA layer for up to 30 days. The duration of attachment of the layer depends on the layer thickness. If the PLLA layer is too thick, it detaches within the first 60 min and the corrosion protection is significantly lowered. If the layer is too thin, the electrolyte penetrates it already after 60 min. Both effects may be due to water uptake of the layer and lead to a loss of corrosion protection. A medium thick PLLA layer can offer good corrosion protection for up to 7 days of immersion. Further investigations will include the increasing of adhesion to the surface, as well as corrosion tests in a dynamic electrolyte.

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References

1. S. Virtanen, *Mater Sci Eng B-Adv*, 176 (2011) 1600
2. G.L. Song and S.Z. Song, *Adv Eng Mater*, 9 (2007) 298
3. H. Hornberger, S. Virtanen and A.R. Boccaccini, *Acta Biomaterialia*, 8 (2012) 2442
4. W. Jahnen-Dechent and M. Ketteler, *CKJ: Clinical Kidney Journal*, 5 (2012) i3
5. L. Claes and A. Ignatius, *Biodegradierbare Implantate Und Materialien*, Springer, 1997.
6. M.P. Staiger, A.M. Pietak, J. Huadmai and G. Dias, *Biomaterials*, 27 (2006) 1728
7. J. Nagels, M. Stokdijk and P.M. Rozing, *J Shoulder Elb Surg*, 12 (2003) 35
8. G.L. Song and A. Atrens, *Adv Eng Mater*, 1 (1999) 11
9. D.P. Perl and A.R. Brody, *Science*, 208 (1980) 297
10. L. Xu and A. Yamamoto, *Colloids and Surfaces B: Biointerfaces*, 93 (2012) 67
11. L.P. Xu and A. Yamamoto, *Appl Surf Sci*, 258 (2012) 6353
12. J.N. Li, P. Cao, X.N. Zhang, S.X. Zhang and Y.H. He, *J Mater Sci*, 45 (2010) 6038
13. H.M. Wong, K.W.K. Yeung, K.O. Lam, V. Tam, P.K. Chu, K.D.K. Luk and K.M.C. Cheung, *Biomaterials*, 31 (2010) 2084
14. S. Yamada, H. Maeda, A. Obata, U. Lohbauer, A. Yamamoto and T. Kasuga, *Materials*, 6 (2013) 5857
15. Y. Chen, Y. Song, S.X. Zhang, J.N. Li, C.L. Zhao and X.N. Zhang, *Biomed Mater*, 6 (2011)
16. A. Alabbasi, S. Liyanaarachchi and M.B. Kannan, *Thin Solid Films*, 520 (2012) 6841
17. J. Degner, F. Singer, L. Cordero, A.R. Boccaccini and S. Virtanen, *Appl Surf Sci*, 282 (2013) 264
18. A.S.f.T.a. Materials, in, 2011.
19. C.J. Lawrence, *Physics of Fluids*, 31 (1988) 2786
20. J.J. Huang, Y.B. Ren, B.C. Zhang and K. Yang, *Zhongguo Youse Jinshu Xuebao/Chinese Journal of Nonferrous Metals*, 17 (2007) 1465

21. C.M.B. Gonçalves, J.o.A.P. Coutinho and I.M. Marrucho, Optical Properties, in: Poly(Lactic Acid), John Wiley & Sons, Inc., 2010, pp. 97.
22. R. Auras, B. Harte and S. Selke, *Macromol Biosci*, 4 (2004) 835
23. D. Garlotta, *J Polym Environ*, 9 (2001) 63
24. C.M.B. Goncalves, L.C. Tome, J.A.P. Coutinho and I.M. Marrucho, *J Appl Polym Sci*, 119 (2011) 2468
25. G. Kister, G. Cassanas and M. Vert, *Polymer*, 39 (1998) 267
26. G. Kister, G. Cassanas, M. Vert, B. Pauvert and A. Terol, *J Raman Spectrosc*, 26 (1995) 307
27. X. Xu and C.P. Weisel, *J Expo Anal Env Epid*, 15 (2005) 6
28. R.K. Kulkarni, E.G. Moore, A.F. Hegyeli and F. Leonard, *Journal of Biomedical Materials Research*, 5 (1971) 169
29. G.L. Siparsky, K.J. Voorhees, J.R. Dorgan and K. Schilling, *J Environ Polym Degr*, 5 (1997) 125
30. L.B. Xu, K. Crawford and C.B. Gorman, *Macromolecules*, 44 (2011) 4777
31. Y. He, W.R. Wang and J.D. Ding, *Chinese Sci Bull*, 58 (2013) 2404

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