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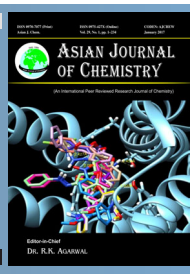

Corrosion resistance of D,L-Polylactic Acid Coated- AZ31 and Porous AZ31

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D,L-Polylactic acid (PDLLA) coatings were prepared on the surface of AZ31 and porous AZ31, respectively. Before PDLLA coating, MgO coating or a zinc phosphate conversion coating (ZnP) formed on magnesium alloy AZ31. The electrochemical and dynamic degradation tests were used to investigate the degradation behaviours of the PDLLA coated samples. The weight loss and pH over the tests were recorded to characterize the corrosion performance. The surface topography of all specimens after the dynamic degradation was tested, which undermined the corrosion resistance of the PDLLA-AZ31. The results indicated that the uniform and smooth polymer films with thicknesses of about 3 μm were successfully prepared on the compact and porous AZ31. The results showed that PDLLA-AZ31 had higher free corrosion potentials (E_{corr}) and lower corrosion currents (I_{corr}) in the simulated body fluid at 37 °C. In addition, the pore of porous AZ31 had important effects on the corrosion of magnesium alloys. A model was proposed to illustrate the interaction between the PDLLA coating and AZ31 substrate. The results also suggested that this reciprocity may also exist on the implanted magnesium stents coated with biodegradation, which is a potential obstacle for the further development of bone repair.

Keywords: Corrosion resistance, PDLLA-AZ31, Compact AZ31, Porous AZ31.

INTRODUCTION

Magnesium and its alloys have been considered to be a potential material for bone repair with similar mechanical properties to natural bone, biocompatibility and biodegradation properties [1,2]. In addition, porous magnesium alloy may be promising for bone tissue engineering application, especially at the load bearing area compared with the polymer or ceramic scaffold, due to their good mechanical properties and porous structure similar to natural bone [3]. As is well-known, porous structure is beneficial to regulate the modulus for fitting the bone. In addition, the porous structure is beneficial to the invasion of cells, formation of the blood vessel, which is easier for matching to the bone growth. In previous study, many methods have been used to prepare porous magnesium or its alloys, such as infiltration process, powder metallurgy and negative salt-pattern molding process [4].

Magnesium and its alloys all have higher degradation rate and release much H_2, which have limited the development of magnesium or its alloys and its application in bone repair operation [5,6]. Hardwick *et al.* [7] indicated that the magnesium absorption had important interaction relationship with absorption of vitamin D, calcium and phosphate. What did lead to the high corrosion rate of magnesium alloy? Undoubtedly, it is the high reactivity of magnesium with the active hydrogen. Therefore, preventing the contact of magnesium alloy substrate surface with active hydrogen will play an important role in increasing the corrosion resistance of magnesium and its alloys. Purifying and alloying can improve the corrosion resistance [8]. Surface modification has been investigated in a great number of reports recently such as microarc oxidation [9], conversion coating [10,11] and polymer coating [5] *etc*. Biodegradable polymer coating is considered to be a promising technique for stent applications. In addition, coated biodegradable polymers can be modified by reactive factors for better cytocompatibility [12]. In addition, the compounding of porous magnesium alloy with biodegradable polymers maybe regulate the mechanical properties of materials to adapt to natural bone and decrease the possible of failure because of sudden break. However, research on biodegradable polymer-coated porous magnesium alloy has rarely been reported until now.

In this paper, the conversion coating (MgO or ZnP) and polymer coating (PDLLA) were prepared for improving the corrosion resistance of AZ31 and then investigated the dynamic degradation behaviour and electrochemical corrosion of PDLLA-porous AZ31 in simulated body fluid. D,L-Polylactic acid (PDLLA) was chosen to use as the coating polymer, because it is biodegradable and biocompatible and have been approved to apply in clinical operations by FDA. Furthermore, the low hydrophily of PDLLA is beneficial to prevent contact of magnesium from water solution. The results of present study showed that there was the obvious corrosion resistance of PDLLA coating and pore played important role in the corrosion of porous compounding.

EXPERIMENTAL

Preparation of ZnP coating and MgO coating: AZ31 was made to round plate with diameter, thickness is 12 and 2.5 mm, respectively. AZ31 plates were ground with sic paper progressing up to 1200 grit and then were electropolished and dried at room temperature. The porous AZ31 was prepared by laser boring method and then was electro polished and dried at room temperature. The pore size of porous AZ31-1 and porous AZ31-2 is 1 mm; while the pore depth is 1 and 2.5 mm (equal to the thickness of round plate), respectively.

MgO coating was formed on AZ31 by oxidized of H_2O_2. AZ31plates were immersed in the wt. 30 % H_2O_2. The thickness of MgO coating can be regulated by changing soak time. In present work, the soak time was confirmed to be 320s, which can gain the uniform MgO coating. The oxydic AZ31 was named AZ31-MgO.

ZnP coating is formed on AZ31 by zinc phosphating in phosphating bath. The optimal contents of chemical compositions of the zinc phosphating and experimental conditions are listed in Table-1. The phosphating treatments were carried out at 45 °C for 10 min. A water bath was used to keep the temperature of treatment baths constant [11]. The zinc phosphating AZ31 was named AZ31-ZnP. Therefore, the porous AZ31-1-ZnP and porous AZ31-2-ZnP were recorded porous-1 and porous-2, respectively.

Preparation of PDLLA coating: PDLLA [-(-$CHCH_3COO)_n$-] with an average molecular weight of 50, 000 was bought from Shandong Province. The PDLLA was dissolved in dichloromethane as the concentration 3 wt %. PDLLA coating was prepared by soaking AZ31 and porous AZ31 into PDLLA solution at room temperature. And then, all samples were dried at 40 °C for 72 h. Surface morphologies of AZ31, AZ31-MgO, AZ31-ZnP and PDLLA-AZ31-ZnP were observed with SEM.

Electrochemical test: Electrochemical test was performed to evaluate the corrosion resistance of AZ31, PDLLA-AZ31-MgO, PDLLA-AZ31-ZnP, PDLLA-porous-1. The electrochemical test was conducted with a three-electrode system in 150 mL 3.5 wt % NaCl at 25 °C. A saturated calomel electrode and platinum mesh were used as the reference and counter electrode, respectively. The polarization curves were measured at a scan rate of 1 mV s^{-1}. The free corrosion potential (E_{corr}) and current (I_{corr}) for each specimen were also tested.

Dynamic degradation test: In the dynamic degradation test, simulated body fluid was chosen as a pseudo-physiological solution. The pH of simulated body fluid was adjusted to 7.4 at 37 °C. All the experiments were performed in a shaking incubator (37 ± 0.5 °C, 50 rpm). At 0, 1, 2, 3, 4, 5, 6, 7, 14, 21, 28 days, specimens were removed from the test platform and their pH measured. At 7, 14, 21 and 28 days, their weights and Mg^{2+} were measured after drying. After the test, the morphologies and compositions, structures were studied using SEM and EDS.

RESULTS AND DISCUSSION

Fig. 1 shows the surface morphologies of AZ31 (a), AZ31-MgO (b), AZ31-ZnP (c) and PDLLA-AZ31-ZnP (d). It can be observed that MgO coating presented nets structure; zinc phosphate was crystal structure, however, there was a net layer under crystal structure; PDLLA coating was smooth and no pores. Fig. 2 showed the morphology of PDLLA-porous-1. It was found that surface of PDLLA-porous-1 was smooth, however, the in-hole was rough and the contact wall between PDLLA and pore is not tight.

The results of polarization curves of the AZ31, PDLLA-AZ31, PDLLA-AZ31-MgO, PDLLA-AZ31-ZnP and PDLLA-porous are summarized in Fig. 3 and Table-2. E_{corr} with the control uncoated-magnesium alloy was increased by 220 mV, 221.8 mV for the PDLLA- AZ31-MgO, 368.6 mV for the PDLLA-AZ31-ZnP and 203.2 mV for the PDLLA-porous-1. On the other hand, I_{corr} of AZ31, PDLLA-AZ31, PDLLA-AZ31-MgO, PDLLA-AZ31-ZnP and PDLLA-porous-1 was 9.954e-004, 8.695e-008, 2.296e-009, 8.651e-009, 1.565e-008, respectively, which results showed that the I_{corr} of PDLLA-AZ31 and PDLLA-porous-1 were inferior to that of the control samples. However, the curves of PDLLA-AZ31 and PDLLA-AZ31-MgO showed wide peak at open potential place, which may be attributed to the stability of contact between coating and AZ31 substrate. Compared with PDLLA-AZ31, PDLLA-

TABLE-1
COMPOSITIONS OF THE PHOSPHATING BATH AND EXPERIMENTAL CONDITIONS

	Degreasing	Ultrasonic derusting	Surface conditioning	Phosphating/L	
Compositions	NaOH 1.5wt %	H_3PO_4:HNO_3 = 300:1	200-250 mL/L HF	H_3PO_4 (85wt. %)	30 mL
				ZnO	6.8 g
				NaF	1.8
				$NaNO_3$	2.8
				$NaNO_2$	1.2
				Citric acid	2.8
				MEA	1.2
				SDS	0.15
Conditions	1 min 50-60 °C	3-5 s 25 °C	15 min 25 °C	10 min 45 °C	

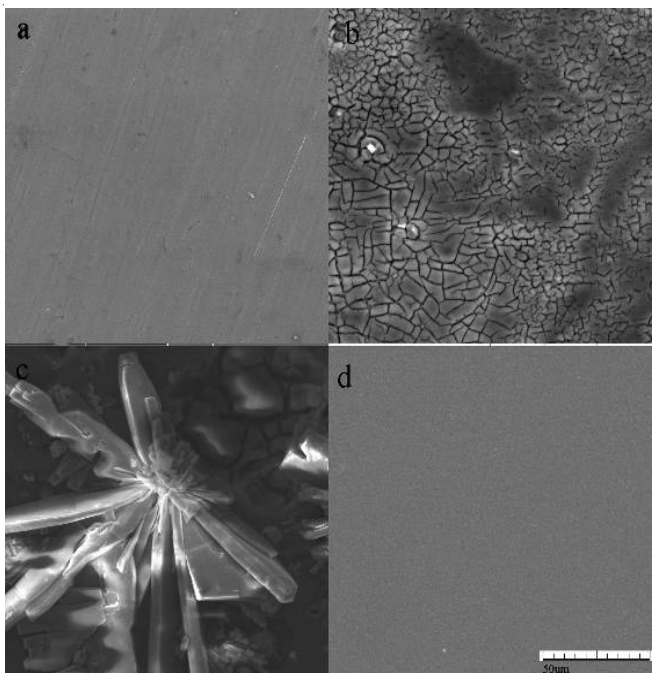

Fig. 1. SEM images of AZ31(a), AZ31-MgO (b), AZ31-ZnP (c) and PDLLA-AZ31-ZnP (d) (×1000)

porous-1 showed the lower corrosion resistance in SBF. In brief, the results of E_{corr} and I_{corr} both demonstrated that PDLLA played an important role in the corrosion resistance of magnesium alloy and zinc phosphating was beneficial to improve bond between PDLLA and AZ31 substrate. In addition, we can find that the pore depth has obvious effect on the corrosion resis-tance of magnesium alloy substrate and has the influence of rate of coating, by which we can regulate the matching rate of degradation of substrate and coating.

TABLE-2
E_{corr} AND I_{corr} OF UNCOATED AZ31 AND COATED AZ31

Samples	E_{corr} (mV)	I_{corr} (A)
AZ31	1792.5	9.954e-004
PDLLA-AZ31	1572.5	8.695e-008
PDLLA-AZ31-MgO	1570.7	2.296e-009
PDLLA-AZ31-ZnP	1423.9	8.651e-009
PDLLA-porous-1	1589.0	1.565e-008

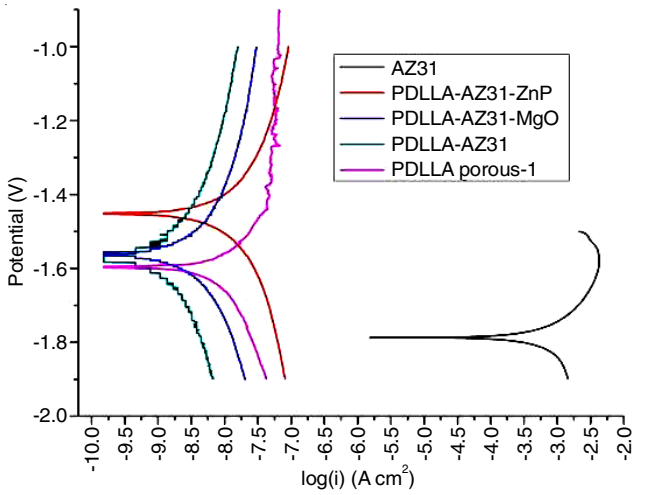

Fig. 3. Polarization curves of AZ31, PDLLA-AZ31-MgO/ZnP and PDLLA-porous-1

Fig. 4 showed the picture of AZ31 and coated specimens after degradation 3 months. From the pictures, we can find that AZ31 did not have complete structure, so cannot take the SEM detection. PDLLA-AZ31-ZnP and PDLLA-porous have intact structure. Fig. 5 showed that the surfaces have many protuberances, when we observed at ten fold and fifty fold of SEM. However, when the multiple was 2000, we can find nice crystal structure. The compositions were listed in Fig. 5d, from which we can find C, O, P, Mg and Ca (4 sites of in-hole and 3 sites of surface of PDLLA-porous-2). Comparing of the compositions of in-hole and surface of PDLLA-porous-1 further, we can find that the deposition of Ca and P is better on the in-hole than on the surface of PDLLA-porous-2. In addition, comparing of the surface morphologies of PDLLA-porous-1 and PDLLA-porous-2, we can find the corrosion extent of porous-1 is higher than porous-2 and there was not the obvious crystal structure at porous-1, while there was the crystal structure at porous-2. Especially, we can find pyknomophic crystal structure at the pore of porous-2 and the crystal structure grows from external to internal along the pore wall to pore center.

The weight loss of specimens and the pH of simulated body fluid as function of corrosion time are showed in Figs. 6 and 7. The weight of AZ31 decreased from 1361.2 to 1201.5 mg after 1w and the pH increased from 7.4 to 10.2. The PDLLA-

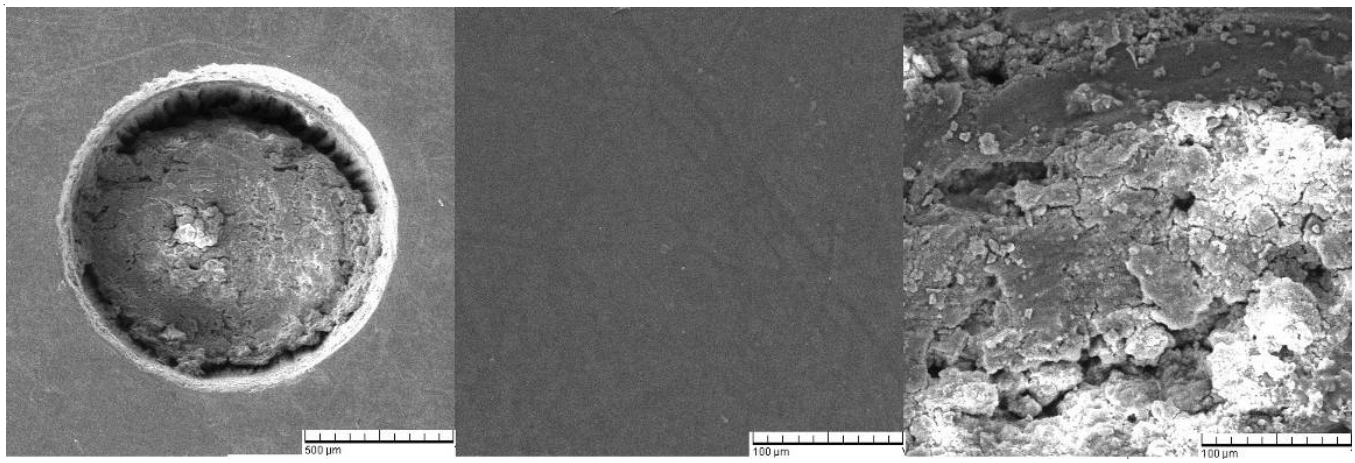

Fig. 2. SEM images of PDLLA-porous-2

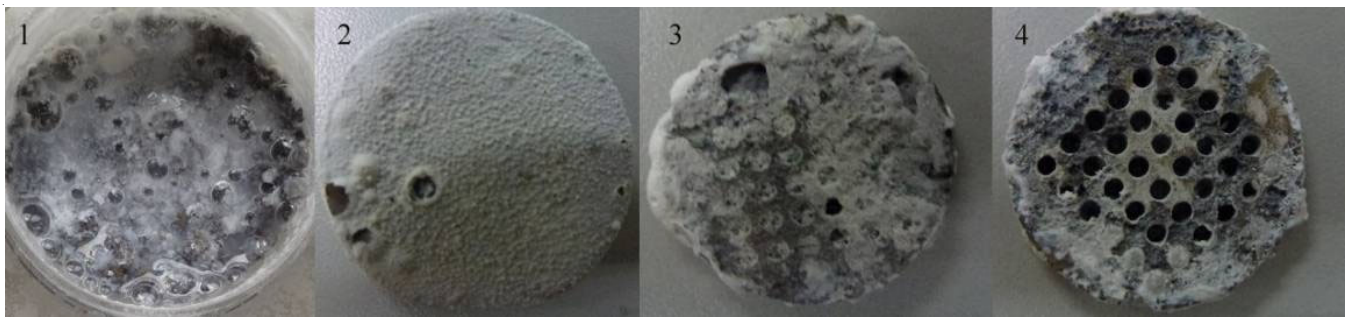

Fig. 4. Optical pictures of samples: 1. AZ31; 2. PDLLA-AZ31-ZnP; 3. PDLLA-porous-1; 4. PDLLA-porous-2 after 3 months

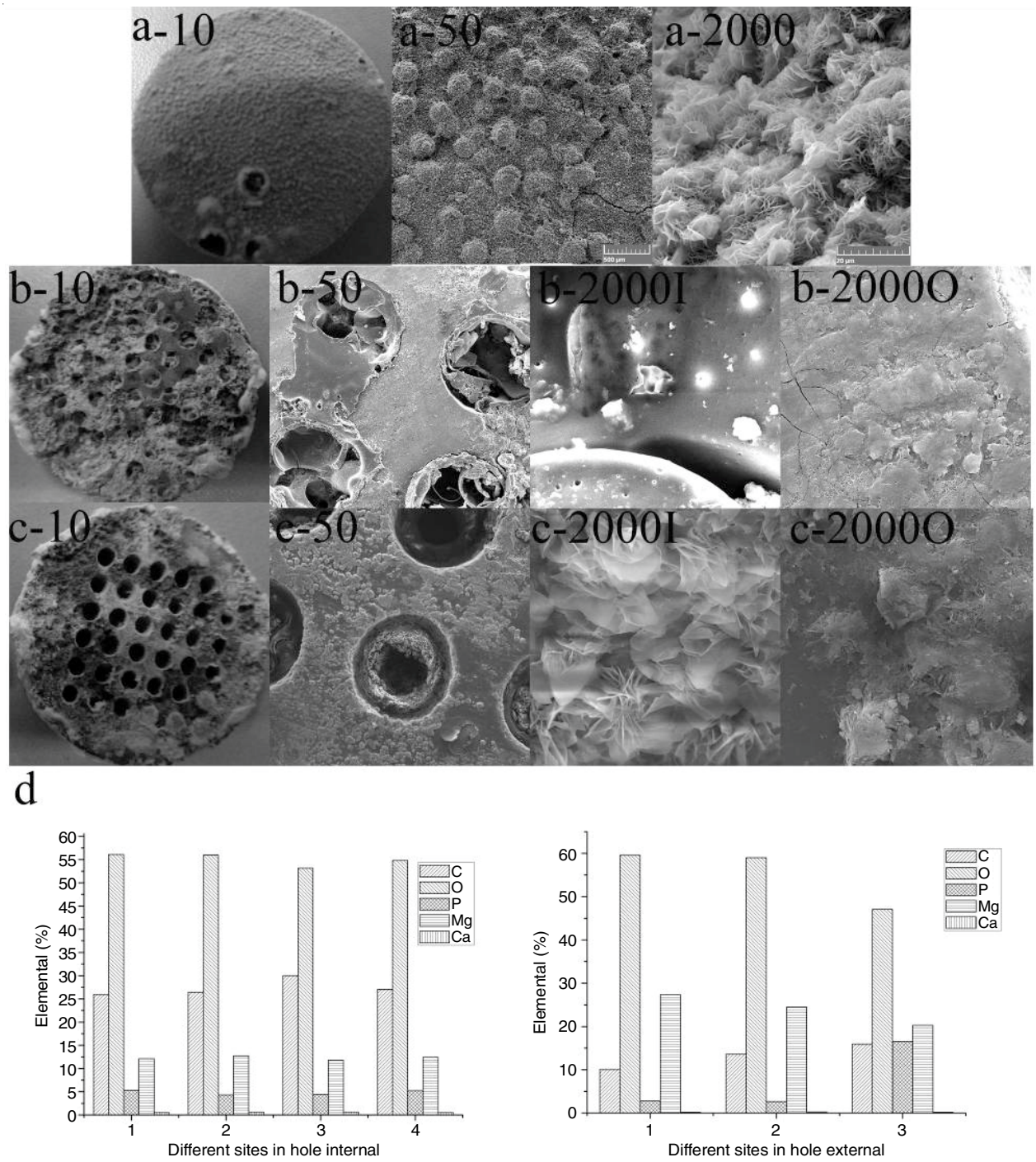

Fig. 5. Surface morphologies after degradation tests of (a) PDLLA-AZ31-ZnP; (b)PDLLA-porous-1; (c) PDLLA-porous-2; (d) Compositions of crystal structure (c-2000I, C-2000O). I and O in Fig. 5b, 5c and 5d show in-hole and surface of PDLLA-porous

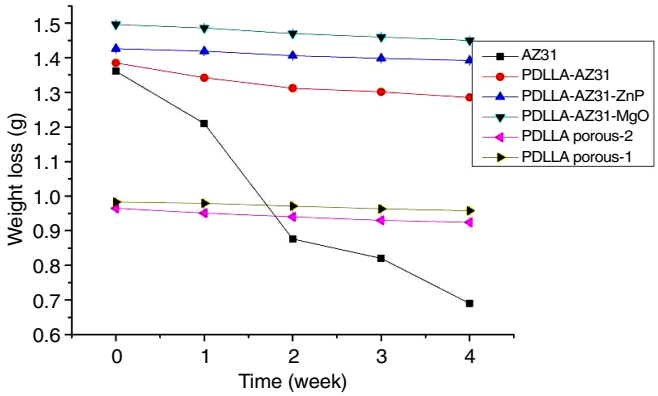

Fig. 6. Weight of specimens plotted as functions of corrosion time in dynamic degradation test

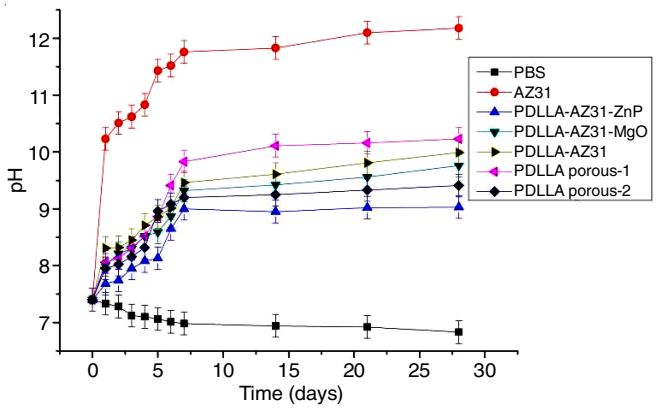

Fig. 7. pH of specimens plotted as functions of corrosion time in dynamic degradation test

AZ31, PDLLA-AZ31-MgO, PDLLA-AZ31-ZnP have not obvious weight loss, the weight of it decreased much less than AZ31 after one week. The weight of PDLLA-porous-1 decreased from 986.3 to 948.2 mg and that of PDLLA-porous-2 decreased from 986.3 to 979.6 mg after 1 week and decreased to 924.2 and 957.9 mg, respectively, after 30 days. The pH of PDLLA-AZ31, PDLLA-AZ31-MgO, PDLLA-AZ31-ZnP and PELLA-porous-1 and PDLLA-porous-2 increased from 7.4 to 9.99, 9.76, 9.03, 10.23 and 9.41, respectively, after 30 days.

The concentration of Mg^{2+} in simulated body fluid is listed in Fig. 8. From the results of Fig. 8, we can find that the concentration of Mg^{2+} of PDLLA-AZ31–increased from 57 to 102 mg/L, while that of AZ31 increased to 328 mg/L after 30 days. The difference between uncoated specimens and coated specimens is very large.

For PDLLA-AZ31 and PDLLA-porous AZ31, the weight change during 30 days seemed to have a moderate, but there was much more weight loss of AZ31 after 1 w, especially after 4w. Similarly, the pH of all the samples has three stages as showed in Fig. 7. The pH of AZ31 sharply increased to 10.2 at first day and increased to 11.8 at 1 week and then kept slowly change between 1 week and 30 days. While the pH of PDLLA-AZ31, PDLLA-AZ31-MgO, PDLLA-AZ31-ZnP and PDLLA-porous-1/2 increased to 8.31, 8.01, 7.68, 8.06 and 7.95 after 1 day, respectively and increased to 9.46, 9.32, 8.86, 9.83 and 9.2 after 1 week, respectively and then kept moderate between 1 and 4 week. It was reported that the high pH value was able contribute to the high corrosion rate of AZ31. From the corrosion

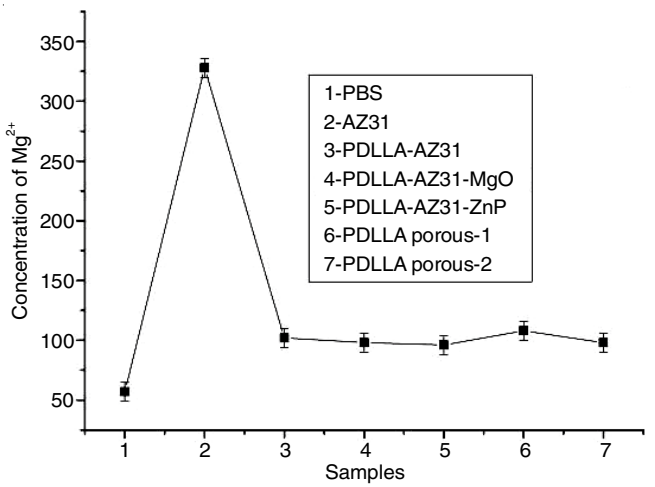

Fig. 8. Concentration of Mg^{2+} (mg/L) in simulated body fluid after 30 days

pictures (Fig. 4), we can confirm this conclusion. From the results of Fig. 3, we can find that the AZ31 had higher corrosion rate to uncompleted structure, while the PDLLA-AZ31-ZnP kept the complete shape. According to weight loss and pH change, corrosion pictures shown in Fig. 4, it is obvious that PDLLA coating played an important role in corrosion resistance of AZ31. In this study, we chose the AZ31, which is apt to degrade in simulated body fluid or NaCl, however, all specimens showed that the PDLLA thin film can protect AZ31 from corrosion. In addition, we can find that the pore depth of porous AZ31 is key factor for its corrosion, which can be contributed to the boundary effect when we made the PDLLA thin film on the surface and in the pore.

Interaction between AZ31 substrate and PDLLA coating: The use of magnesium as a medical material can be dated back to 1878 [6,11], however, the extensive application of magnesium and its alloys was limited by their high corrosion rate. There are many different methods for modification of magnesium or its alloys for increasing its corrosion resistance, such as alloying, micro arc oxidation and organic conversion film [12]. In general, polymer coating has been used, because of its nice biocompatibility and lower degradation *in vitro* and *in vivo* by hydrolysis of its ester, in addition, the polymer can be chose the modified polymer with higher bioactivity, such as bioactive PDLLA, which is modified by growth factor (RGDS), collagen, MGF-Ct24E [13,14], which can further increase the adhesion of osteoblasts or increase the mechanical stimulus in bone repair. Therefore, the PDLLA can be use to be an ideal material surface modification material to increase the corrosion resistance of magnesium or its alloys *in vitro* and *in vivo*. Chen *et al.* [5] indicated that PDLLA coating can reduce the corrosion rate of magnesium.

In present work, we used PDLLA as the surface coating to prepare PDLLA-AZ31 and PDLLA-porous AZ31 and investigated the function of PDLLA coating on the corrosion resistance and the influence of pore size and pore depth on the corrosion resistance of porous magnesium alloy. The electrochemical tests and the dynamic degradation all showed that PDLLA coating an obvious role in corrosion resistance. From the experimental phenomenon and the surface morphologies, we can find following results:

There is obvious bubble on the surface of uncoated specimens; there is not macroscopic bubble on the surface of PDLLA-AZ31-ZnP, including PDLLA-porous AZ31-ZnP and not macroscopic defect, however, there still has the increasing of Mg^{2+} in the simulated body fluid. Therefore, the release of hydrogen and the Mg^{2+} maybe peel off from the PDLLA coating (Fig. 9), which is correspond with the pitting corrosion theory [15].

The corrosion of AZ31 and the degradation of PDLLA have important interaction relationship. In present work, we confirmed that the pH variation are obvious at 1w and then stable, which can be contributed to the coating on AZ31 and the degradation mechanism of AZ31 substrate and PDLLA. R-COOH from degradation of PDLLA can bound Mg^{2+} from AZ31 substrate and remitted the concentration of Mg^{2+} in simulated body fluid. The generation of PDLLA has four stages [16]: (1) swelling and hydration of the polymer; (2) breakage of the ester bonds; (3) diffusion of the soluble degradation products and (4) disappearance of the polymer scaffold chips.

The interaction between PDLLA coating and AZ31 substrate can be divided into three steps: First, hydrophilic group of PDLLA and H_2O formed hydrogen bond and depredated as polymer degradation mechanism [16] and then H_2O entered into AZ31 substrate by the pores on PDLLA as the reported by Lei *et al*. [17]. Second, H_2O reacted with Mg to gain $Mg(OH)_2$ and H_2; with $Mg(OH)_2$ accumulating and H_2 releasing, the stability of PDLLA was affected, so the bond force played an important role in stability. Third, $Mg(OH)_2$ reacted with R-COOH from PDLLA, which can release of $Mg(OH)_2$ to surrounding.

Effects of the pretreatment coating: MgO or ZnP: In this work, we prepared the pretreatment coating (MgO/ZnP coating) on AZ31 for improving the bond between AZ31 substrate and PDLLA coating and improving corrosion resistance of AZ31. From the electrochemical test and dynamic degradation experiment, we can find the PDLLA-AZ31-ZnP, PDLLA-AZ31-MgO has higher corrosion resistance than PDLLA-AZ31, expecially the PDLLA-AZ31-ZnP had best corrosion resistance.

Lei *et al.* [17] reported that in the past several decades, the coating from micro-arc oxidation and other treatment can provide protection to magnesium alloys [18]. Lei *et al.* [17] prepared a novel MgO coating on AZ31 by anodic eletrodeposition in 6 M KOH solution for improving the corrosion resistance of magnesium alloy compared to bare metallic magnesium and then showed that the MgO coating film could protect substrate from corrosion attack by acting as a physical shield between metal and medium and thus the corrosion process shows down. In this study, we prepared the MgO not only can be used as another protect coating but also can improve the bond, because of the rough surface morphology (Fig. 1). However, the curve of PDLLA-AZ31-MgO electro-chemical test (Fig. 3) showed the wide peak, which was similar with the curve of PDLLA-AZ31, but was different with the curve of PDLLA-AZ31-ZnP.

The form of wide peak showed the unstability of current during 2 s. The differences among different PDLLA-AZ31s can be attributed to the bond between AZ31 and PDLLA coating, which can be affected by the surface under PDLLA coating. Comparing with AZ31, AZ31-ZnP has nice affinity with PDLLA and higher toughness, which is beneficial to the bond between AZ31 and PDLLA; comparing with MgO coating has higher toughness and compactness (Fig. 1). Qing Li [12] reported that the structure and electrochemical behaviour had important role in the magnesium alloy AZ91. The results of Qing Li [12] showed that the phosphate conversion coatings formed a duplex structure, a crystal outer layer and an amorphous inner layer; the inner layer was flat with non-penetrating microcracks to the substrate and the outer layer was made up by crystal clusters hopeite. From the Fig. 1, we can find the same result with Qing Li [12]. The structure of ZnP is more beneficial to the bond between AZ31 substrate and PDLLA coating and shows more nice protection as a physical shield.

Effect of pore on the corrosion of compound specimens: Figs. 4-8 showed that the PDLLA-porous-2, with open-cell structure had the nicer corrosion resistance than porous-1, with closed-cell structure. We already referred to that the PDLLA surface morphologies of PDLLA played an important role in the corrosion of magnesium alloy substrate, the H_2O and Cl^- can pass the PDLLA into the AZ31 substrate and released easily with the Mg^{2+}. From the results of SEM (Fig. 5), we can find that there is distinct boundary effect, which produced the gap between substrate and coating. Therefore, the H_2O and Cl^- can easily pass into the substrate. However, the PDLLA-porous-2 did not have the obvious gap because it is open-cell structure.

In present work, we designed the compound of porous AZ31 and PDLLA for another purpose, regulating the mechanical property for being appropriate for the nature bone and regulating the elasticity modulus. As is well known, magnesium alloy has mechanical anisotropy, which is adverse to the

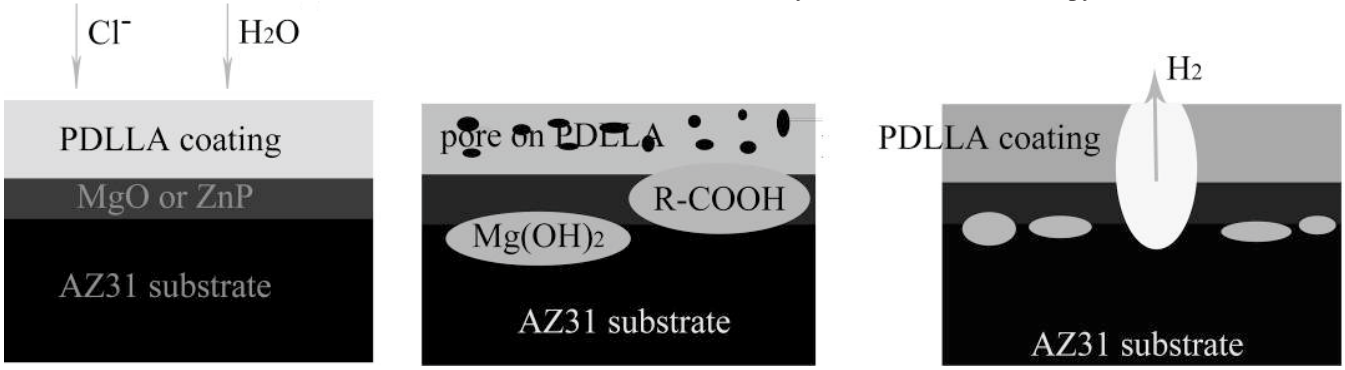

Fig. 9. Scheme of interaction between PDLLA and AZ31 substrate

bone repair, because it maybe bring into the abrupt failure bone repair. However, porous or foam structure may decrease or eliminate the mechanical anisotropy. In addition the porous or foam structure is beneficial to integrally compound with PDLLA, which can increase the ductility of composite.

Conclusion

In summary, PDLLA-AZ31 and PDLLA-porous AZ31 were successfully prepared and PDLLA coating can improve the corrosion resistance of AZ31 substrate in NaCl or in simulated body fluid at 37 °C. In addition, we can find that interaction relationship between substrate and coating and the complexing relationship between Mg^{2+} and R-COO^{-}. In this work, I prepared pretreatment coating MgO and ZnP, from the results of electrochemical tests and dynamic degradation experiments, we can find that pretreatment coating, expecially ZnP coating, can improve the bond between AZ31 substrate and PDLLA coating. The results also showed that the boundary effect of PDLLA-porous AZ31 can affect the interaction relationship of substrate and coatings. Therefore, it is important to design an open-cell porous magnesium alloy in future porous magnesium alloy.

In future study, we will study the complexing relation between Mg^{2+} from magnesium alloy and the R-COO- from PDLLA. In addition, we will design the foam magnesium alloy and study the corrosion and mechanical properties PDLLA foam AZ31.

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