RESEARCH ARTICLE

Corrosion resistance of biodegradable polymeric layer-by-layer coatings on magnesium alloy AZ31

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Biocompatible polyelectrolyte multilayers (PEMs) and polysiloxane hybrid ABSTRACT: coatings were prepared to improve the corrosion resistance of biodegradable Mg alloy AZ31. The PEMs, which contained alternating poly(sodium 4-styrenesulfonate) (PSS) and poly(allylamine hydrochloride) (PAH), were first self-assembled on the surface of the AZ31 alloy substrate via electrostatic interactions, designated as (PAH/PSS)₅/AZ31. Then, the (PAH/PSS)₅/AZ31 samples were dipped into a methyltrimethoxysilane (MTMS) solution to fabricate the PMTMS films, designated as PMTMS/(PAH/PSS)₅/AZ31. The surface morphologies, microstructures and chemical compositions of the films were investigated by FE-SEM, FTIR, XRD and XPS. Potentiodynamic polarization, electrochemical impedance spectroscopy and hydrogen evolution measurements demonstrated that the PMTMS/(PAH/PSS)₅/AZ31 composite film significantly enhanced the corrosion resistance of the AZ31 alloy in Hank's balanced salt solution (HBSS). The PAH and PSS films effectively improved the deposition of Ca-P compounds including $Ca_3(PO_4)_2$ and hydroxyapatite (HA). Moreover, the corrosion mechanism of the composite coating was discussed. These coatings could be an alternative candidate coating for biodegradable Mg alloys.

KEYWORDS: magnesium alloy; polyelectrolyte; polysiloxane; corrosion; layer-by-layer

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Received January 3, 2016; accepted February 18, 2016

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1 Introduction

Magnesium (Mg) alloys are considered to be a candidate for biodegradable implants due to their good biocompatibility and mechanical properties that are close to those of bone [1-5]. However, the clinical applications of biomedical Mg alloys face challenges due to their extremely fast corrosion rates [6-9]. The corrosion resistance of Mg alloys can be improved through surface modifications, including chemical conversion coatings [10-16] (i.e., Ca-P coatings [17]), micro-arc oxidation (MAO) [18] or plasma electrolytic oxidation (PEO) coatings [8,19-21], MgF₂ coatings [22], polymeric coatings [16,23-25] and silane coatings [26–30]. These coatings provide a more favourable microenvironment for cell adhesion, proliferation and tissue compatibility. However, among these surface modifications, several limitations have hindered the application of these technologies. For example, the adhesive bond of chemical conversion coatings to the Mg substrate is not strong enough [31]. The porous MAO coatings only enhance the corrosion resistance of the Mg-Li–Ca–Y alloy in the initial stage, and the polymeric poly (lactic acid) coating leads to acidification of the solution or microenvironment [18].

To date, polymer coatings obtained via the layer-bylayer (LbL) self-assembly technology are popular for preparing polymer coatings on Mg alloys due to the fact that it is lower cost, environmentally-friendly and simplicity in operation. In particular, LbL can impart polymeric coatings with some specific functionalities, i.e., biocompatibility, bioactivity and antibacterial performance. Therefore, a wide variety of materials, including polyelectrolytes [23–24], nanoparticles [32–34], polypeptides, DNA, proteins [35], enzymes [36–37] and dendrimers [38], have been assembled using LbL for biomedical applications.

Moreover, polyelectrolytes, including polycations and polyanions, are polymers whose repeating units bear an ionizable group. Many of these polyelectrolytes are biological molecules, i.e., polypeptides and PEI, and these materials can be exploited in biomedical fields. Thus, they can be utilized for the build-up of polyelectrolyte multilayers (PEMs) [39–40] by alternating the deposition of positively and negatively charged polyelectrolytes onto the charged surfaces via electrostatic interactions. PEMs can be exploited as anticorrosion films on metals due to the physical barrier effect and pH-buffering ability of polyelectrolytes [41–42]. However, few investigations have been conducted on LbL-assembled PEMs on biodegradable Mg alloys [1,23–24,43–44]. The (heparin/CHI)₁₀-(PVP/PAA)₁₀ multilayer film presented an enhanced antibacterial capability [25]. LbL-assembled layers of anionic polymers (PLGA or PCL) and cationic polymers (PEI and PAH) with alkaline surface treatment have been employed to improve the cytocompatibility, cellular adhesion and proliferation on biodegradable Mg alloys [23–24]. The PEI/PSS/8HQ multilayer, fabricated via a spin-assisted LbL technique on AZ91D, exhibited better corrosion resistance and cytocompatibility [45]. Unfortunately, the corrosion resistance of the aforementioned PEM films is not as high as expected and cannot satisfy the requirements for clinical applications.

Note that Mg alloys are susceptible to corrosion in chloride-containing solutions [43]. The high alkalinity of the surface of the alloys resulting from the dissolution of Mg leads to a decrease in blood biocompatibility and cell viability [1]. As is known, PAH/PSS PEMs [46] are readily available and well-studied candidates for constructing nanomaterials with good biocompatibility and low/non-toxicity [32,47]. Thus, it is necessary to develop a biocompatible and corrosion-resistant coating that contains PEMs on biomedical Mg alloys.

On the other hand, polysiloxanes have widespread applications in industrial areas, resulting from the unique alternating silicon–oxygen (Si–O) units, which impart the materials with good flexibility, high or low temperature stability, environmental durability and film formability [48]. Moreover, PMTMS can easily be functionalized with sulfonic, amine, carboxyl and carbonyl groups via the copolycondensation or ring-opening polymerization of functional monomers or direct hydrosilylation between olefins and poly(methylhydrosiloxane) [49]; thus, it is likely to crosslink to the polyelectrolyte via LbL technology.

In this study, nanostructured PEMs were deposited onto AZ31 substrates to obtain excellent corrosion resistance based on the biocompatible and biodegradable synthetic polymers PSS and PAH using the LbL method. PMTMS, based on methyltrimethoxysilane (MTMS), was incorporated into the PEMs, after optimization of the process to enhance the corrosion resistance of the system. The film was characterized through morphological, physicochemical and electrochemical analyses to evaluate the modification and the corrosion resistance.

2 Materials and methods

2.1 Materials and chemicals

The employed material is an as-extruded Mg alloy AZ31 with a nominal chemical composition (wt.%) of Al 2.5–3.0, Zn 0.7–1.3, Mn > 0.20, Si \leq 0.3, Cu \leq 0.05, Ni \leq 0.005, Fe \leq 0.005 and balanced Mg, supplied by the Beijing Guangling Jinghua Science & Technology Co., Ltd., China. PAH (Mw = 15000), PSS (Mw = 70000), PEI (Mw = 600, 99.0%), and MTMS (Mw = 136.22, 99%) were purchased from the Qingdao Jingke Chemical Reagent Co., Ltd., China. Figure 1 shows the chemical structures of the PEI, PAH, PSS and MTMS used in this work. All measurements were performed at room temperature.

2.2 Alkaline treatment of the substrate

The substrates were cut into squares with dimensions of 20 mm \times 20 mm \times 3 mm and were ground with sand papers up to 2500 grit, and then they were washed with a deionized (DI) water and alcohol solution and dried by warm air. The polished substrates were soaked in a 1 mol/L NaOH solution for 20 min, followed by thoroughly cleaning with DI water and drying with warm air.

2.3 Preparation of coatings

The PEMs were prepared using a dip-coating method; for each film, the substrates were dipped into the polyelectrolyte solution. Layers were generated in the following sequence: "ABCBCBCBCBC". Solutions A and C contained the cationic polyelectrolytes PEI (pH 9.0) at a concentration of $1.25 \text{ g} \cdot \text{L}^{-1}$ in DI water and PAH (pH 4.0) at a concentration of 2 g \cdot L⁻¹ in DI water, respectively. Solution B consisted of the anionic polyelectrolyte PSS (pH 5.2) at a concentration of 4 g \cdot L⁻¹ in DI water. The substrate was dipped into solution A for 30 min, and it was dipped into solutions B and C for 5 min. Five cycles selected by the deposition experiment were performed in this study to obtain (PAH/PSS)₅/AZ31 samples. Then, the obtained samples were dipped in the MTMS solution (*V*(MTMS):*V*(ethanol):*V*(DI water) = 3:10:20) at 40°C for 2 h. After heat treatment at 120°C for 2 h, the PMTMS/ (PAH/PSS)₅/AZ31 samples were obtained. The preparation process is schematically illustrated in Fig. 1.

2.4 Surface analysis

The surface morphologies of the films were studied using field-emission scanning electron microscopy (FE-SEM, Nova NanoSEM 450, USA). The possible chemical bonding formed in the coatings was confirmed using a Fourier transform infrared (FTIR) spectrophotometer (Nicolet380, Thermo Electron Corporation, USA) and an X-ray photoelectron spectrometer (ESCALAB250, Thermo VG Corporation, USA). The crystal structures of the samples were determined using an X-ray diffractometer (XRD, Rigaku D/MAX2500PC, Japan).

2.5 Corrosion characterization

The potentiodynamic polarization curves and electrochemical impedance spectra (EIS) were obtained using an electrochemical analyser (PAR Model 2273, Princeton, USA). A three-electrode cell set-up was used in which the prepared samples were the working electrode and a



Fig. 1 Schematic representation of the preparation of the PMTMS/(PAH/PSS)₅/AZ31 films and corresponding chemical structures of PEI, PAH, PSS and MTMS.

saturated calomel electrode and a platinum sheet were used as the reference and counter electrodes, respectively. The polarization started from approximately -2000 to -1000mV at a scan rate of 1 mV \cdot s⁻¹. EIS studies were performed at open-circuit potential for a 10-mV sinusoidal amplitude over a frequency range of 100 kHz to 0.01 Hz. A stable open-circuit potential was established prior to testing. The experiment was performed in a corrosive environment of HBSS (8 $g \cdot L^{-1}$ NaCl, 0.4 $g \cdot L^{-1}$ KCl, 0.14 $g \cdot L^{-1}$ CaCl₂, 0.35 $g \cdot L^{-1}$ NaHCO₃, 1 $g \cdot L^{-1}$ glucose, 0.1 $g \cdot L^{-1}$ $MgCl_2 \cdot 6H_2O, \ 0.1 \ g \cdot L^{-1} \ MgSO_4 \cdot 7H_2O, \ 0.06 \ g \cdot L^{-1}$ KH₂PO₄, and 0.126 g·L⁻¹ Na₂HPO₄·12H₂O) [50–51]. The hydrogen evolution set-up design was tested by placing the substrates in HBSS at 37°C under an inverted funnel connected to a graduated burette and measuring the water level in the burette intermittently for 150 h with full surface exposure. Three samples were placed under each condition to account for the low hydrogen evolution anticipated from the coated samples.

3 Results

3.1 Surface morphology

Figure 2 presents the macro- and SEM morphologies of the bare AZ31 substrate (Figs. 2(a) and 2(d)), the (PAH/PSS)₅/ AZ31 film (Figs. 2(b) and 2(e)), and the PMTMS/(PAH/ PSS)₅/AZ31 film (Figs. 2(c) and 2(f)). No obvious changes appeared on the surfaces of any of the substrates in the light of the macro-photographs. The as-prepared AZ31 substrate showed abrasive scratches resulting from the mechanical polishing. In contrast, the (PAH/PSS)₅/AZ31 films exhibited a smoother surface with shallow scratches, which can be attributed to the interaction of the substrate with the coating solutions. After the MTMS modification, the films exhibited uniform morphologies without any obvious scratches or pits, which can be attributed to the formation of PMTMS. It is believed that the PMTMS coatings can completely cover the surface and seal the PEM network, which might be the reason for the PMTMS/(PAH/PSS)₅/ AZ31 film possessing the best corrosion resistance compared with (PAH/PSS)₅/AZ31 and will be confirmed later.

Moreover, the cross-sectional images of the PMTMS/ (PAH/PSS)₅/AZ31 films are presented in Fig. 3. The PMTMS film was tightly combined with the AZ31 substrate, and the thickness of PMTMS film was 0.75 ± 0.08 µm, which can be confirmed from the EDS



Fig. 2 Macro-photographs and FE-SEM images of **(a)(d)** the bare AZ31 substrate, **(b)(e)** the (PAH/PSS)₅/AZ31 film and **(c)(f)** the PMTMS/(PAH/PSS)₅/AZ31 film.

mapping of the Si_{2p} signal (Fig. 3(b)) and the EDS spectra of three points with obvious Si peaks (Fig. 3(c) and Table 1). As the comparison, the EDS spectra of the substrate was shown in Fig. 3(d), the content elements of Mg and O in Table 1 demonstrated that the Si element was introduced from the PMTMS film. And a linear scanning to show the change of element from the coating to the substrate was shown in Figs. 3(e)–3(i), revealing the thickness of the composite coating. 5% Mg in the composite coating may be contributed to the possible corrosion product Mg(OH)₂ during the preparation of the coating, the polymer coating acted as a sealing treatment for the Mg(OH)₂ plates.

The FTIR spectrum (Fig. 4) of the PMTMS/(PAH/ PSS)₅/AZ31 films presents absorption peaks at 1277 and 775 cm⁻¹, corresponding to the Si–CH₃, and an asymmetric stretching vibration of CH₃ was observed at 2975 cm⁻¹. The absorption at 1135 cm⁻¹ is attributed to an asymmetric Si–O–C stretching band, and the peak at 1029 cm⁻¹ is assigned to the Si–O–Si [52–53]. Thus, we infer that the PMTMS film was formed during the MTMS treatment process. The FTIR results will be confirmed by the XPS results presented in Fig. 5.

The aminolysis and MTMS treatments on the AZ31 substrate surfaces were monitored using XPS, revealing the presence of N, S and Si elements (Fig. 5). The XPS spectra showed an N_{1s} peak at 397.57 eV and a S_{2p} peak at 166.35



Fig. 3 Cross-sectional SEM images of (a) the PMTMS/(PAH/PSS)₅/AZ31 films and its corresponding (b) EDS mapping of elemental Si, (c)(d) the EDS spectra of points 1 and 4 and (e)(f)(g)(h)(i) the linear scanning images.

Table 1 The mass contents of C, O, Mg, Si and S elements for different EDS spectra

EDS spectrum	Mass content /wt.%							
	С	0	Mg	Si	S			
Spectrum 1	69.28	19.98	5.34	4.79	0.61			
Spectrum 2	68.89	19.21	5.30	5.06	0.55			
Spectrum 3	69.28	21.06	4.74	4.46	0.46			
Spectrum 4	-	15.89	84.11	—	-			



Fig. 4 FTIR spectrum of the PMTMS/(PAH/PSS)₅/AZ31 films.

eV, indicating that PAH and PSS were successfully introduced (Fig. 5(a)) [42]. Furthermore, Fig. 5(a) also reveals the existence of Si_{2p} peak at 103.2 eV and Si_{2s} peak 152.2 eV, demonstrating that MTMS was successfully fabricated on the (PAH/PSS)₅/AZ31 films. Additionally,

the presence of two potential Si_{2p} peaks were contributed to the Si–C (102.8 eV) and Si–O (103.9 eV) [54], indicating the formation of the PMTMS film, which can be confirmed by the C_{1s} peaks in Fig. 5(c).

3.2 Corrosion behaviour

The corrosion resistance of the bare and modified substrates were characterized through potentiodynamic polarization in HBSS (Fig. 6). The bare AZ31 has a corrosion potential (E_{corr}) of about -1.492 V. After coated by the PEMs and polysiloxane, the corrosion potentials of about -1.432 and -1.358 V were obtained. And the corrosion current density (i_{corr}) was decreased from 2.65×10^{-5} to 8.45×10^{-7} and 6.65×10^{-8} A·cm⁻², respectively (Table 2). These results clearly prove that the ability of corrosion resistance of AZ31 alloy substrate is improved prominently by the composite coating.

The corrosion resistance of the films in HBSS was also



Fig. 5 XPS survey scan of (a) the $(PAH/PSS)_5/AZ31$ and the PMTMS/(PAH/PSS)_5/AZ31 films, and high resolutions of (b) the Si_{2p} peak and (c) the C_{1s} peak of the PMTMS/(PAH/PSS)₅/AZ31 films.

evaluated using EIS (Fig. 7(a)). After modification of PEMs, the semicircle diameter of Nyquist plots became larger than that of bare AZ31. When further modification of polysiloxane, the semicircle diameter of the Nyquist plots also increased, suggesting that the composite coating exhibited optimal corrosion resistance, which are in agreement with the polarization measurement results. Moreover, the low-frequency impedance modulus |Z| is one of the parameters used to evaluate the corrosion resistance of different samples in Bode plots (Fig. 7(b)). A larger |Z| indicates a better corrosion protection performance [55–56]. It can be observed that the |Z| increases with surface modification on the AZ31 substrate, indicating



Fig. 6 Polarization curves of the bare AZ31 substrate (a), (PAH/ PSS)₅/AZ31 film (b) and PMTMS/(PAH/PSS)₅/AZ31 film (c) in HBSS.

Table 2 Electrochemical parameters of the polarization curves

Sample	$E_{\rm corr}$ /(mV, SCE)	$i_{\rm corr}$ /(A · cm ⁻²)	$E_{\rm b}$ /(mV, SCE)
AZ31 substrate	-1492	2.65×10^{-5}	_
(PAH/PSS)5/AZ31 film	-1432	8.45×10^{-7}	-1336
PMTMS/(PAH/ PSS) ₅ /AZ31 film	-1358	6.65×10^{-8}	-1328

the beneficial effect of the PEMs in improving the corrosion resistance of the AZ31 alloy. The sample modified by MTMS had the highest value of |Z|, demonstrating that the PMTMS/(PAH/PSS)5/AZ31 films greatly improved the corrosion resistance of the alloy. Moreover, two time constants for the AZ31 substrate and (PAH/PSS)₅/AZ31 film, and three time constants for PMTMS/(PAH/PSS)₅/AZ31 films can be determined from the Bode plots of phase angle vs. frequency (Fig. 7 (c)), which is in accord with the feature of the Nyquist plots in Fig. 7(a). The additional time constant of PMTMS/ (PAH/PSS)₅/AZ31 films indicate the existence of the PMTMS coating, which leads to new interfacial reaction on the surface of the composite coating. Additionally, the hydrogen evolution rate (HER) provided supporting evidence for the corrosion protection effectiveness of the PEMs, particularly the PMTMS/(PAH/PSS)₅/AZ31 films.

4 Discussion

4.1 Characteristics after immersion

The HER as a function of time curves consist of two distinct stages for the bare and modified substrates (Fig. 8). For the Mg and the (PAH/PSS)₅/AZ31, in the first 30 h of



Fig. 7 (a) Nyquist plots and fitting curves, (b) Bode plots and (c) Bode plots of phase angle vs. frequency for the bare AZ31 substrate (i), the (PAH/PSS)₅/AZ31 film (ii) and the PMTMS/ (PAH/PSS)₅/AZ31 film (iii) in HBSS.

immersion in HBSS, the continuous decrease in HER indicates the formation of a dense corrosion product layer and a period of incubation of corrosion pits. In the subsequent immersion period, continuous acceleration in the HER indicates the breakdown of the oxide film and the exposure of fresher surface to the solution. After 70 h, the curve of the HER becomes smooth, indicating that there may be new precipitates deposited on the surfaces of the alloy substrates and the (PAH/PSS)₅/AZ31 films.

Note that the $(PAH/PSS)_5/AZ31$ substrate had a lower HER than the bare AZ31 substrate, particularly after 30 h of immersion. This result can be ascribed to the fact that the



Fig. 8 HER as a function of immersion time for the bare AZ31 substrate (a), (PAH/PSS)₅/AZ31 film (b) and PMTMS/(PAH/PSS)₅/AZ31 film (c) in HBSS for 150 h.

thick PEMs may accelerate the formation of phosphates, which was subsequently observed. However, for the PMTMS/(PAH/PSS)₅/AZ31 films, the HER was the lowest and smooth during the initial 40 h of immersion. Consequently, the slight increase in HER may be due to the localized attack from the HBSS for the PMTMS/(PAH/ PSS)₅/AZ31 films. After 80 h, the curve stabilized, demonstrating that the Mg(OH)₂ and phosphates precipitates were formed on the surface and jammed the corrosion pits. These results will be discussed in following sections. As for the change in solution pH, the measurements will be performed in our future study.

Figure 9 presents the EIS spectra of the $(PAH/PSS)_5/AZ31$ and $PMTMS/(PAH/PSS)_5/AZ31$ films in HBSS at 37°C for immersions of various intervals over a period of 48 h. The Nyquist plots (Fig. 9(a)) of the $(PAH/PSS)_5/AZ31$ films exhibited well-defined capacitance loops with diameters that increased as the immersion times increased from 1 min, 1 h, 12 h, 24 h to 36 h. However, the diameter decreased after an immersion of 48 h, implying initial rupture of the $(PAH/PSS)_5/AZ31$ films.

Moreover, the |Z| of the Bode plots of the (PAH/PSS)₅/AZ31 films (Fig. 9(b)) shows that the magnitude of the impedance monotonously increases as a function of immersion time. Note that a decrease in |Z| occurred after an immersion of 48 h, also implying damage of the (PAH/PSS)₅/AZ31 films. This result is in good agreement with the HER results (Fig. 8).

The EIS results of the PMTMS/(PAH/PSS)₅/AZ31 films as a function of immersion time are presented in Figs. 9(c) and 9(d). As shown in Fig. 9(c), the well-defined capacitance loops decreased as a function of immersion time, and a new loop appeared after an immersion of 12 h.



Fig. 9 Nyquist plots and Bode plots of **(a)(b)** the (PAH/PSS)₅/AZ31 and **(c)(d)** the PMTMS/(PAH/PSS)₅/AZ31 films in HBSS after immersions of 1 min, 1 h, 12 h, 24 h, 36 h and 48 h, its corresponding equivalent circuits for fitting the impedance data for **(e)** the bare AZ31, the $(PAH/PSS)_5/AZ31$ and $(PAH/PSS)_5/AZ31$ in HBSS at the initial 1 h of immersion, **(f)** the $(PAH/PSS)_5/AZ31$ after 1 h of immersion and the PMTMS/(PAH/PSS)₅/AZ31 during 48 h of immersion.

The |Z| (Fig. 9(d)) also gradually decreased due to the permeation of electrolyte into the film, and localized corrosion occurred during this immersion time.

The simplified equivalent circuits are also illustrated in Fig. 9. In this model, R_{ct} is the charge-transfer resistance, R_s is the electrolyte resistance, R_f is a coating resistance (virtual pore resistance) paralleled with a constant phase element (CPE). A CPE was used instead of a capacitive element and the formula ($Y_{CPE}(\omega) = 1/Z_{CPE} = Q_a(j\omega)^n$) proposed by Zoltowski was used for the admittance, Y, of the CPE element [57]. Based on the proposed equivalent circuit model, EIS curves were best fitted, and the corresponding values of the equivalent circuit parameters were listed in Table 3. The R_{ct} of the AZ31 samples increased from 451.8 to 2142 and 78500 $\Omega \cdot cm^2$ for (PAH/PSS)₅/AZ31 and PMTMS/(PAH/PSS)₅/AZ31 samples, the improvement in the corrosion resistance by MTMS treatment could still be seen clearly [58–60].

The Nyquist plots of the (PAH/PSS)₅/Mg films in HBSS at 37°C for immersions of various intervals over a period of 48 h were best fitted in Figs. 9(e) and 9(f), the variation tendency of $R_{\rm f}$ confirmed the formation of phosphates and the damage of the PEMs. Meanwhile, the Nyquist plots of the PMTMS/(PAH/PSS)₅/AZ31 films in HBSS over a period of 48 h were best fitted in Fig. 9(f), the changeable of $R_{\rm f1}$ and $R_{\rm f2}$ revealed the damage of the PMTMS and the formation of the corrosion product, but the high value of the $R_{\rm f}$ demonstrated the good corrosion resistance during the immersion time.

Figure 10 presents the SEM images of the surfaces of the samples after immersion in HBSS for 150 h without removal of the corrosion products. A dry riverbed corrosion morphology can be observed on the surfaces of the bare AZ31 substrate (Fig. 10(a)) and the $(PAH/PSS)_5/AZ31$ film (Fig. 10(b)). However, the PMTMS/(PAH/PSS)_5/AZ31 film exhibited a well-pre-

Table 3 Electrochemical data obtained by equivalent circuit fitting of EIS curves

Sample	$R_{\rm S}/(\Omega \cdot {\rm cm}^2)$	$R_{\rm fl}/(\Omega \cdot {\rm cm}^2)$	$\frac{\text{CPE}_1}{(\Omega^{-1} \cdot \text{s}^n \cdot \text{cm}^{-2})}$	n_1	C/ $(\Omega^{-1} \cdot s^n \cdot cm^{-2})$	$R_{f2}/(\Omega \cdot cm^2)$	C/ $(\Omega^{-1} \cdot s^n \cdot cm^{-2})$	$R_{\rm ct}/$ ($\Omega \cdot \rm cm^2$)
AZ31 substrate	77.73	1179	1.923E-5	0.8654		_	1.479E-3	451.8
(PAH/PSS) ₅ /AZ31 film	82.31	4332	9.994E-6	0.799	_	_	1.752E-3	2142
PMTMS/(PAH/PSS) ₅ /AZ31 film	60.01	1.923E4	1.197E-6	0.6473	$2.984 \mathrm{E} - 7$	3.709E5	2.668E-6	7.854E4
(PAH/PSS) ₅ /AZ31 film, 1 min	67.05	2360	1.094E-5	0.7674	—	-	1.627E - 4	3661
(PAH/PSS) ₅ /AZ31 film, 1 h	59.16	4157	1.545E-5	0.6315	_	—	1.91E-6	7988
(PAH/PSS) ₅ /AZ31 film, 12 h	56.21	1736	1.001E-5	0.6797	7.613E - 7	1.291E4	1.09E - 9	1.776E4
(PAH/PSS) ₅ /AZ31 film, 24 h	68.39	2828	7.581E-6	0.6841	2.372E-6	1.563E4	3.123E-6	1.015E4
(PAH/PSS) ₅ /AZ31 film, 36 h	64.73	2979	9.628E-6	0.728	3.991E-7	1.775E4	4.695E-6	1.147E5
(PAH/PSS) ₅ /AZ31 film, 48 h	61.08	1832	1.06E-5	0.7199	6.434E - 7	1.094E4	9.132E-5	1.095E4
PMTMS/(PAH/PSS) ₅ /AZ31 film, 1 min	53.28	1.008E4	3.449E-6	0.6708	3.243E-7	2.661E4	1.538E-6	6.397E4
PMTMS/(PAH/PSS) ₅ /AZ31 film, 1 h	66.75	6167	3.552E-6	0.738	8.588E-7	1.65E4	8.022E-4	5.162E4
PMTMS/(PAH/PSS) ₅ /AZ31 film, 12 h	63.84	1.525E4	1.052E-6	0.7559	2.766E-6	1.593E4	7.763E-6	3.245E4
PMTMS/(PAH/PSS) ₅ /AZ31 film, 24 h	58	9220	7.166E-6	0.6863	1.299E-6	5.298E4	4.929E-4	1.118E4
PMTMS/(PAH/PSS) ₅ /AZ31 film, 36 h	49.92	6714	5.563E-6	0.6411	2.762E-7	2.377E4	2.413E-6	2.43E4
PMTMS/(PAH/PSS) ₅ /AZ31 film, 48 h	50.81	3739	5.402E-6	0.6311	4.593E-8	1.925E4	5.711E-8	3.883E4



Fig. 10 FE-SEM images and the corresponding EDS spectra of (a)(d) the bare AZ31 substrate, (b)(e) the (PAH/PSS)₅/AZ31 film and (c)(f) the PMTMS/(PAH/PSS)₅/AZ31 film in HBSS after a 150-h immersion.

served surface appearance, except for the presence of several localized corrosion pits (shown by the white tiny area in Fig. 10(c)). The presence of the peaks of Mg, C, O, P, Al, Ca and Zn elements (Figs. 10(d) and 10(e)) in the EDS spectra confirmed the possible corrosion products, such as $Mg(OH)_2$ and Ca–P precipitates, whereas the presence of the Mg and Si elements and relatively weaker peaks of C, O, Al, Zn and P elements in Fig. 10(f) indicated that no severe attack

occurred on the PMTMS/(PAH/PSS) $_5$ /AZ31 films after a 150-h immersion.

Figure 11 presents the XRD patterns of the samples after the hydrogen evolution tests in HBSS. For the AZ31 substrates, peaks corresponding to $Ca_3(PO_4)_2$ and HA $(Ca_{10}(PO_4)_6(OH)_2)$ compounds clearly appeared. However, it can be observed that the HA peak of the (PAH/ PSS)₅/AZ31 was stronger than that of AZ31 substrate, which indicated that the selected polyelectrolyte effectively improved the formation of HA. But the peaks of the $Ca_3(PO_4)_2$ and HA compounds on the PMTMS/(PAH/ PSS)₅/AZ31 were not obvious after an immersion test of 150 h, that is, the PMTMS presented good corrosion resistance which can be considered as a barrier of the solution. These results coincided with the EDS results presented in Fig. 10.



Fig. 11 XRD patterns of the bare AZ31 substrate, the (PAH/ PSS) $_5$ /AZ31 film and the PMTMS/(PAH/PSS) $_5$ /AZ31 film in HBSS after 150 h.

A comparison of the corrosion current densities of a variety of LbL-assembled PEM films is presented in Fig. 12. It is clear that the current density of the (PAH/PSS)₅/AZ31 film in this study was close to that of the PLGA/AZ31, and the PMTMS/(PAH/PSS)₅/AZ31 film had the lowest corrosion rate among these films, indicating its outstanding corrosion resistance.

4.2 Corrosion mechanism

The corrosion mechanism model of the PMTMS/(PAH/ PSS)₅/AZ31 film is shown in Fig. 13. First, PMTMS sealed



Fig. 12 A comparison of the corrosion resistances of various PEM films on Mg alloys [20,23,45].

the surface of the substrate, effectively blocking the penetration of aggressive ions in HBSS.

The hydrogen phosphate (HPO₄^{2–}) and dihydrogen phosphate (H₂PO₄[–]) ions in the weak alkaline HBSS were transformed into phosphate (PO₄^{3–}) ions through the following ionic reactions:

$$\mathrm{H}_{2}\mathrm{PO}_{4}^{-} + \mathrm{OH}^{-} \to \mathrm{HPO}_{4}^{2-} + \mathrm{H}_{2}\mathrm{O} \tag{1}$$

$$HPO_4^{2-} + OH^- \to PO_4^{3-} + H_2O$$
 (2)

Subsequently, Ca^{2+} and PO_4^{3-} ions led to the formation of $Ca_3(PO_4)_2$ precipitates through the following reaction (3) on the surface:

$$3Ca^{2+} + 2PO_4^{3-} \rightarrow Ca_3(PO_4)_2$$
 (3)

If the PMTMS were penetrated by H₂O molecules and



Fig. 13 Schematic representation of the corrosion mechanism of the PMTMS/(PAH/PSS)₅/AZ31 films on the AZ31 substrate in HBSS.

aggressive Cl⁻ ions, the polyelectrolytes easily led to calcification (presented as HA) [61]. Additionally, HA precipitates formed and deposited in the HBSS under the effect of the PSS and PAH to protect the substrates over immersion time, seen as following:

$$10Ca^{2+} + 6PO_4^{3-} + 2OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2$$
 (4)

Thus it can be seen that, thanks to the synergistic effect of polysiloxane film acting as the physical barrier and PEMs which could promote the HA deposition from HBSS, the high corrosion resistance is produced.

After a longer immersion of 50 h, as shown in Fig. 8, some localized areas of the protective films started to blister or peel off after a swelling stage due to the penetration of water molecules into the polymeric films on the film/Mg substrate interface. Thus, a fresher surface of the substrate was exposed to the solution with increasing immersion time. Generally, intermetallic compounds of AlMn phases in the AZ31 alloy are the initiators of pitting corrosion [11,62]. The corrosion reactions that occurred on the AZ31 substrate in HBSS are given as Eqs. (5)–(7):

$$Mg \to Mg^{2+} + 2e^{-} \tag{5}$$

$$2\mathrm{H}_{2}\mathrm{O} + 2\mathrm{e}^{-} \rightarrow 2\mathrm{OH}^{-} + \mathrm{H}_{2} \uparrow \tag{6}$$

$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2 \uparrow$$
 (7)

5 Conclusions

1) A PMTMS/(PAH/PSS)₅ composite film, consisting of PEMs and PMTMS, has been successfully prepared via layer-by-layer assembly on the AZ31 alloy.

2) The PMTMS/(PAH/PSS)₅ film on the alloy results in a marked decrease in the HER and current density from 2.65×10^{-5} to 6.65×10^{-8} A·cm⁻², indicating that the film possesses excellent corrosion resistance.

3) The PEMs and PMTMS play different roles in the composite coating for the protection of AZ31 Mg alloy. PMTMS as a corrosion barrier increase the corrosion resistance of the coating. While the PEMs would accelerate the precipitation of HA compound on the surface of the sample, which plays a key role in enhancing the corrosion resistance.

4) The results imply that the PMTMS/(PAH/PSS)₅ film may be an ideal candidate for biomedical applications for Mg alloys.

Acknowledgments This work was supported by the National Natural Science Foundation of China (Grant No. 51571134), Scientific Research Foundation of Shandong University of Science and Technology (SDUST) for Recruited Talents (2013RCJJ006), SDUST Research Fund (2014TDJH 104) and Science and Technology Innovation Fund of SDUST for graduate students (YC150358).

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