



Biodegradation behavior of polymethyl methacrylate–bioactive glass 45S5 composite coated magnesium in simulated body fluid

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Abstract: The biodegradation behavior of Mg, coated by polymethyl methacrylate as well as polymethyl methacrylate (PMMA)–bioactive glass (BG) composite was investigated. Electrophoretic deposition and dip coating techniques were adopted to prepare composite coating using a suspension of different percentages of the above two chemical materials. The deposited coatings were characterized using SEM, EDS, FTIR, and water contact angle measurements. Biodegradation behavior study of the coated Mg was performed using linear polarization, impedance spectroscopy, and immersion tests in simulated body fluid. The compact and homogeneous composite coating was developed as evidenced by electron microscopy results. The water contact angle measurement showed a 44° increase in the contact angle of the composite coated Mg compared to the uncoated one. The composite coating was covered by a bone-like hydroxyapatite layer after 336 h, indicating that the coating has an excellent in vitro bioactivity. The electrochemical testing results confirmed a significant reduction, 96.9%, in the biodegradation rate of Mg coated with the composite prepared from 45 g/L PMMA + 3.5 g/L 45S5 GB suspension compared to that of the uncoated one. Therefore, the composite coated Mg can be proposed as a promising material for biodegradable implant application.

Key words: magnesium alloy; polymethyl methacrylate; bioactive glass; composite coating; electrophoretic deposition; biodegradation

1 Introduction

Mechanical strength and high toughness of metallic implants, compared to those of polymeric and ceramic materials, are the major reasons for their more prevalent usage in orthopedic applications. Stainless steel, titanium, and cobalt–chromium alloys are the major permanent metallic implants, although several problems, like mechanical incompatibility between the implant

and natural bone [1], possible risk of exposure to toxic metal ions due to biodegradation [2], and secondary operation after tissue healing, limit the application of these materials in the human body [3,4]. Such shortcomings encourage researchers to look for biodegradable implants to overcome the problems and fix tissue damage in a specific duration. Mg-based alloys are the most favored highly biocompatible biodegradable metallic materials, due to their unique properties which are close to those of the human bones [5], and simply

resolve the need for second surgery and reduce the possibility of inflammation, stress-shielding, and release of toxic metal ions [6,7].

Mg undergoes an electrochemical reaction in human body to form Mg^{2+} which has some critical physiological roles, comprising bone formation and some numbers of metabolic processes. However, H_2 released during the Mg biodegradation is tolerated only at a low dosage ($0.01 \text{ mL}/(\text{cm}^2 \cdot \text{d})$) by the human body. The release of H_2 and OH^- may have unfavorable influences on cellular functions, decreasing the cytocompatibility of the implant [8]. Moreover, hydroxide, carbonates, and phosphates of Mg or Ca precipitate onto the Mg-based implant surface because of the local alkalization during the implant biodegradation. Cl^- presents in the body fluid and contributes to the Mg biodegradation through pitting corrosion [9].

In order to address the issues considered in Mg-based implant biodegradation, different coatings and deposition methods have been used to reduce the biodegradation rate [10]. Electrophoretic deposition (EPD) has been reported as a feasible and cost-effective coating strategy with simple instrumentation [11,12]. Various coatings, including polymers, ceramics, inorganic or composite materials, and biological entities can be deposited on materials. A number of common polymers, including polylactic acid, poly(lactide-co-glycolic) acid, polycaprolactone, polydopamine, chitosan, and collagen, coated on Mg and its alloys have been investigated [13]. Polymethyl methacrylate (PMMA), a polymer with a lower degradation rate than the aforementioned polymers, has been used in the area of biomedical applications due to its non-toxicity, low cost, good biocompatibility, minimal inflammatory reactions with tissues, and high fracture resistance [14,15], although no investigation has been reported to use PMMA coating on Mg. Different fillers can be incorporated into polymer coatings to increase their protection and biodegradation resistance [16]. Tissue and bone repair capability are two important features in manufacturing of bone implant, which necessitates the presence of some materials to accelerate bone formation. Ceramics coatings such as hydroxyapatite (HA) and bioactive glasses (BG) [17] are used to increase the bone formation rate [18]. HA coatings can be deposited on Mg implants by a wide number of coating techniques such as the EPD,

ion-beam sputter coating, dip coating, and plasma spraying [19]. Poor binding is the main concern of HA deposit on Mg surface. SURMENEVA et al [20] reported the production of highly adhesive, uniform and dense HA coating on Mg alloy using radio frequency magnetron sputtering. HA produces bone-like apatite by releasing ions into the body and enhances implant/bone integration, while BG is a highly bioactive material, possessing both osteoinductive and osteoconductive properties. Moreover, BG particles speed up the rate of new bone deposition and provide a strong chemical bonding between the implant and tissue [21].

The present study was aimed to improve the biodegradation of Mg implant by producing PMMA as well as composite coatings, comprising PMMA and BG, using dip-coating and EPD techniques. The surface morphology, chemical composition, crystalline phases, and water contact angles of the coatings, were characterized. The biodegradation resistance of the PMMA coated and PMMA-BG coated Mg was extensively investigated using electrochemical methods, including linear polarization, impedance spectroscopy, and immersion tests. The biodegradation behaviors of the polymer and composite coatings created on Mg were compared with each other. Appropriate EPD conditions to produce suitable coatings to decrease the biodegradation rate of Mg were proposed.

2 Experimental

2.1 Materials

Commercially high pure Mg ingot (99.95%) was used to prepare coating substrates. PMMA (MW, 996000 g/mol), acetone (99.8%), and ethanol (99.9%) were purchased from Sigma-Aldrich. Bioglass[®] powder (45S5, with the nominal composition of $45\text{SiO}_2-24.5\text{Na}_2\text{O}-24.5\text{CaO}-6\text{P}_2\text{O}_5$ (wt.%), Pardis Pajouhesh Fanavaran Yazd, Iran) with a mean particle size of $37 \mu\text{m}$ was utilized. The following reagents from Sigma-Aldrich were used to prepare simulated body fluid (SBF): NaCl, NaHCO_3 , KCl, $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 , Na_2SO_4 , tris-hydroxymethyl aminomethane, and HCl (1.0 mol/L).

2.2 Sample preparation and coating procedure

Mg samples with dimensions of $1.7 \text{ cm} \times 1.0 \text{ cm} \times 0.1 \text{ cm}$ were cut from Mg ingot and their

surfaces were ground using SiC sandpapers successively up to 1200 grit followed by ultrasonic cleaning in ethanol, rinsing with deionized water for 5 min, and finally drying in air. PMMA was dissolved in a mixture of acetone and ethanol (50:50, volume ratio) at concentration levels of 30 and 45 g/L. The solutions were magnetically stirred for 5 h to achieve complete dissolution of the polymer. The highest concentration of PMMA, to be completely dissolved, was found to be 45 g/L since higher concentrations resulted in a very viscous and unstable solution. For dip coating technique, Mg substrates were immersed in the polymer solution for 8 min. For composite suspensions, the Bioglass[®] powder was added to the PMMA solution at concentrations of 0.5, 2, and 3.5 g/L, respectively. The latter was the highest concentration to be mixed with 45 g/L PMMA to provide a stable suspension for the coating process. EPD was performed at an electric field of 120 V/cm for a duration time of 8 min at room temperature using Mg and stainless steel substrates as the cathode and anode electrodes, respectively.

2.3 Coatings characterization

The surface morphologies of the coated samples were studied by scanning electron microscopy (SEM; VEGA TESCANA-LMU) after sputter coating of samples with a thin layer of gold to avoid sample charging. Energy-dispersive X-ray spectrometry (EDS, INCA, Oxford Instruments) mounted on the SEM instrument was used for qualitative elemental analysis of the coatings. Fourier transform infrared spectroscopy (FTIR, ABB Bomem, MB100) in transmission mode was used in the wavelength range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} to chemically investigate the interaction between the coating components as well as the nature of the coatings. To prepare the samples, coatings were removed from the substrates, mixed, and ground with potassium bromide (KBr) at a mass ratio of 1:100 and pressed into pellets. X-ray diffraction (XRD, PANalytical diffractometer, equipped with X'Pert PRO MPD software) was utilized to determine the crystalline state of the coatings. Wetting properties of uncoated, polymer-coated, and composite-coated samples were studied by observing the shape of a distilled water droplet during 2000 ms and the angles were measured by a contact angle meter. The

measurement was carried out for at least 8 times for each sample to achieve reliable results and the average values were reported.

2.4 Biodegradation experiments

To investigate the biodegradation behavior of the samples before and after applying the coating, electrochemical measurements were performed using a commercial potentiostat (Autolab PGSTAT 302, Metrohm) equipped with NOVA 2.1 software. A conventional three-electrode cell consisting of coated and uncoated samples with an approximate area of 1.0 cm^2 as the working electrode, a platinum rod with a length of 2 cm, as the counter electrode, and saturated Ag/AgCl, as the reference electrode was employed. The biodegradation test was carried out in simulated body fluid (SBF) prepared based on the Kokubo formula [22]. The changes in the open-circuit potential (OCP) were first monitored as a function of time for about 120 s, and then the linear polarization tests were performed at a scan rate of 0.5 mV/s in the potential range from –250 to 250 mV (vs OCP). The low current valley in the graph is the position where the anodic and cathodic half-reactions are in equilibrium. The electrochemical impedance spectroscopy (EIS, IM6, ZAHNER Elektrik) measurement was performed in the frequency range from 100 kHz to 100 MHz at an AC amplitude of 10 mV against the OCP. Based on the approximate linear polarization data, polarization resistance (R_p) values were calculated by the Stern–Geary equation, according to the method of ASTM G59–97.

2.5 Immersion test

In order to complement the study of biodegradation behavior of the specimens, immersion test was used to evaluate the mass loss of the samples, the biodegradation rate, and to characterize the biodegradation products formed on the surface. PMMA and PMMA-BG coated Mg, and uncoated Mg with an exposed area of 1 cm^2 (1 cm × 1 cm) were immersed in a closed polypropylene beaker containing 20 mL of SBF and maintained for 24, 48, 72, 144, 216, 288, and 336 h at (37±1) °C, respectively. Afterward, the samples were taken out and gently washed with deionized water and chromic acid (to remove the biodegradation products from the surface of the samples), respectively, and then dried. The masses

of the samples, before and after immersion, were measured using a precise balance (Sartorius, 0.1 mg). The biodegradation rate (η_{BR}) of the samples was calculated as follows according to ASTM G31:

$$\eta_{BR} = \frac{8.76 \times 10^4 \Delta m}{\rho A t} \quad (1)$$

where η_{BR} is the biodegradation rate (mm/a, 1 a=1 year), Δm is the mass loss (g), A is the surface area (cm²), t is the time of exposure (h), and ρ is the density of Mg (g/cm³).

3 Results and discussion

3.1 Coatings characterization

EPD procedure was carried out for the precipitation of charged particles on the surface of the Mg substrate. The function of the EPD method is based on the motion of charged particles. Due to the fact that the PMMA is almost an electrically neutral polymer, imparting a surface charge to PMMA particles is very difficult [15]. In this study, no significant change in PMMA coating was observed compared with dip-coating and EPD techniques. Therefore, it is assumed that during EPD, PMMA is coated on Mg substrate via dip-coating. However, the BG particles are positively charged inside the suspension, and cathodic deposition occurs accordingly [23]. In other words, the BG particles are deposited on the cathode electrode (Mg) onto the PMMA background. The surface morphologies of uncoated Mg and PMMA and PMMA-BG coatings are shown by SEM images given in Figs. 1(a–c), respectively. As can be seen from Fig. 1(a), the surface of Mg is nearly rough and has scratches originating from surface preparation. Figure 1(b) shows a uniform and smooth surface obtained after dip coating in 45 g/L PMMA solution. Figure 1(c) exhibits the image from the surface obtained after EPD in 45 g/L PMMA + 3.5 g/L BG suspension and demonstrates the presence of several particles with an average diameter of 10 μ m dispersed on the surface. The higher magnified SEM image of particle mounted on Fig. 1(c) reveals a good interface between the matrix and particle (Point A in the inset of Fig. 1(c)).

Figure 2 shows EDS analysis corresponding to Point A in the inset of Fig. 1(c), revealing the

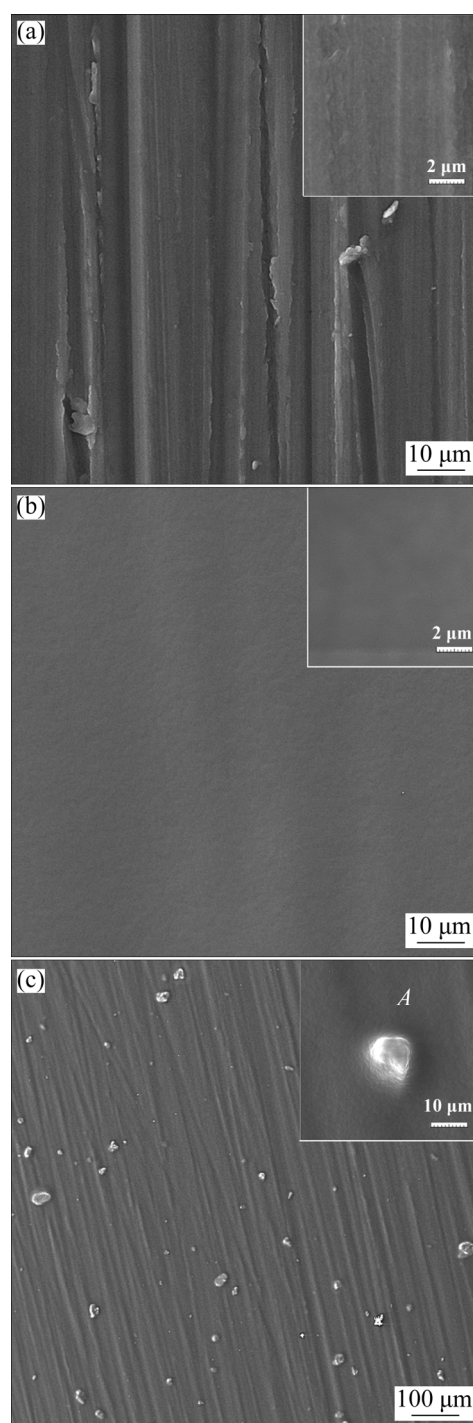


Fig. 1 SEM images from surfaces of Mg (a), coating deposited from 45 g/L PMMA solution (b), and composite coating deposited from 45 g/L PMMA + 3.5 g/L BG suspension (c) (Point A in inset is the higher magnification of BG particle in (c))

presence of the main elements of Ca, Si, P, and Na, and confirming the successful embedding of BG onto the coating. The presence of the Mg peak originates from the Mg substrate, while the Au peak is seen owing to the sputtering of the Au thin layer during the preparation of the sample.

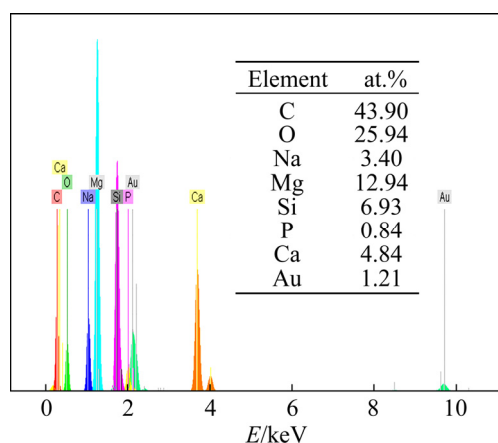


Fig. 2 EDS spectrum corresponding to Point A in inset of Fig. 1(c)

The FTIR spectra provided in Fig. 3, corresponding to the surfaces shown in Figs. 1(b, c), prove that the PMMA coating and PMMA-BG composite coating are deposited on the Mg substrate. The FTIR spectrum corresponding to PMMA coating shows that the vibrations at 2951 and 1732 cm^{-1} are attributed to the C—H stretching and C=O containing groups, respectively. The peak at 1448 cm^{-1} corresponds to C—H bending, while the other band at 1254 cm^{-1} can be assigned to the C—O stretching vibration of the ester group [24]. The characteristic peaks corresponding to the BG in the composition of composite PMMA-

BG coating can also be observed; the phosphate group stretching vibration appears at 501 cm^{-1} while the other two bands at 751 and 1148 cm^{-1} correspond to Si—O—Si vibration modes of silicate groups [25]. The spectrum corresponding to the PMMA-BG composite shows both characteristic peaks of PMMA and BG. Some shifts in band location indicate the occurrence of interaction between components within the composite coating. From this result, it can be noticed that the PMMA and BG components are combined with each other in the composite coating layer.

Figure 4 shows the elemental mapping images of PMMA-BG coating, indicating that constitutive elements are homogeneously distributed within the

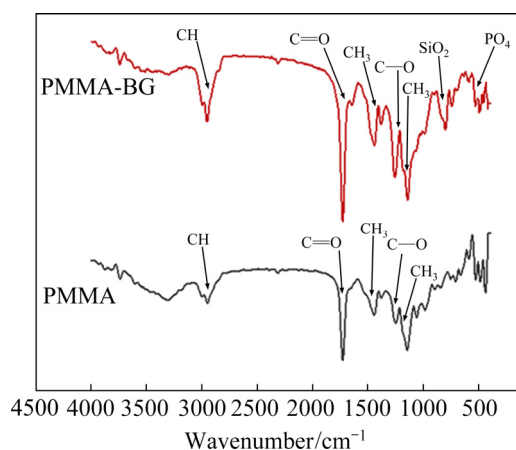


Fig. 3 FTIR spectra of PMMA and PMMA-BG coatings

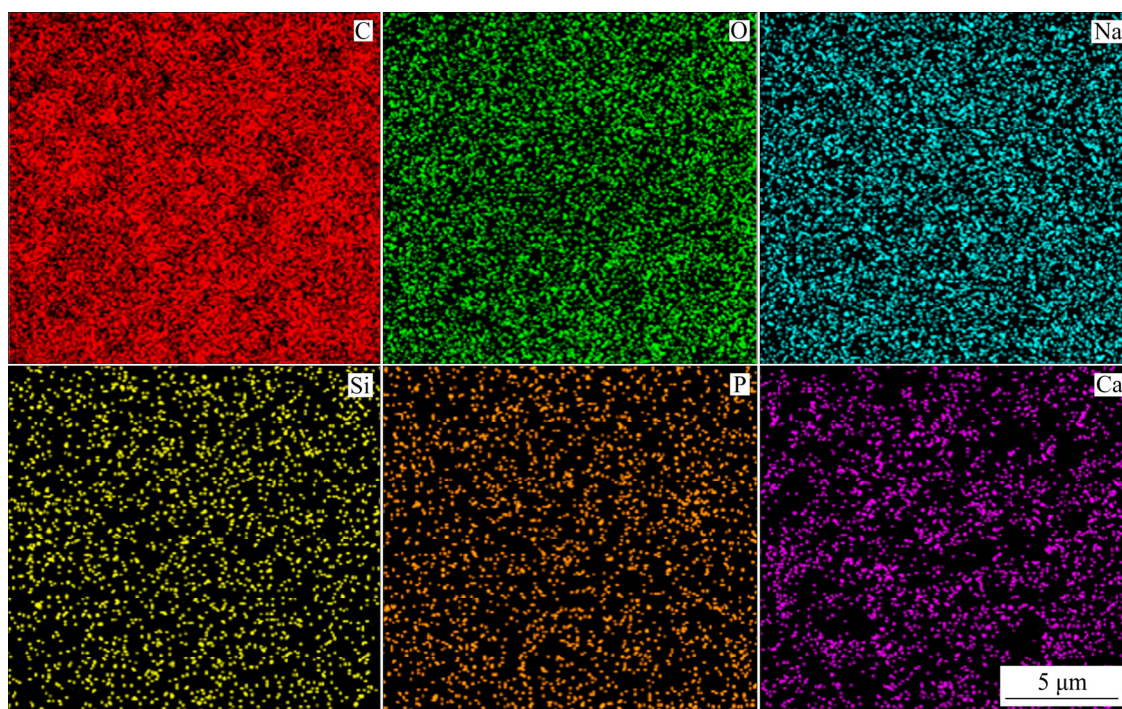


Fig. 4 Elemental mapping images of PMMA-BG coating

prepared coating film, demonstrating the suitability of the EPD technique for the coating process.

Figure 5 exhibits the photographs of the measured water contact angles of Mg PMMA-coated and PMMA-BG-coated samples. The surface wettability, which defines the capability of

water molecules to spread on solid substrates, is a critical parameter for the estimation of water permeation characteristics. Wetting characteristics of uncoated and coated samples are discovered via contact angle measurements. The water contact angle on the uncoated Mg is $(23.46 \pm 1.12)^\circ$, while it is $(61.99 \pm 0.14)^\circ$ and $(67.46 \pm 0.22)^\circ$ on the PMMA-coated and PMMA-BG-coated samples, calculating 164% and 187% increments, respectively. The Mg surface is hydrophilic, which is shown obviously by the spreading of the water droplet on its surface, meaning that pre-treatment of Mg could produce a hydrophilic surface. However, the coated Mg samples show higher contact angles ascribed to their increased hydrophobicity after the deposition of the coatings. The higher contact angle of the PMMA-BG composite coating in comparison to that of the PMMA coating is more probably due to its rougher surface. Furthermore, increasing the water contact angle shows that the composite coating limits the interaction between the surface and corrosive species, like water and ions. In other words, composite coating acts as a physical barrier against water penetration to significantly increase the hydrophobicity of the coated Mg, enhancing the biodegradation resistance of the composite-coated Mg compared to the uncoated and PMMA-coated Mg samples [26]. Therefore, wettability or water contact angle is an important assessing factor for biomaterials.

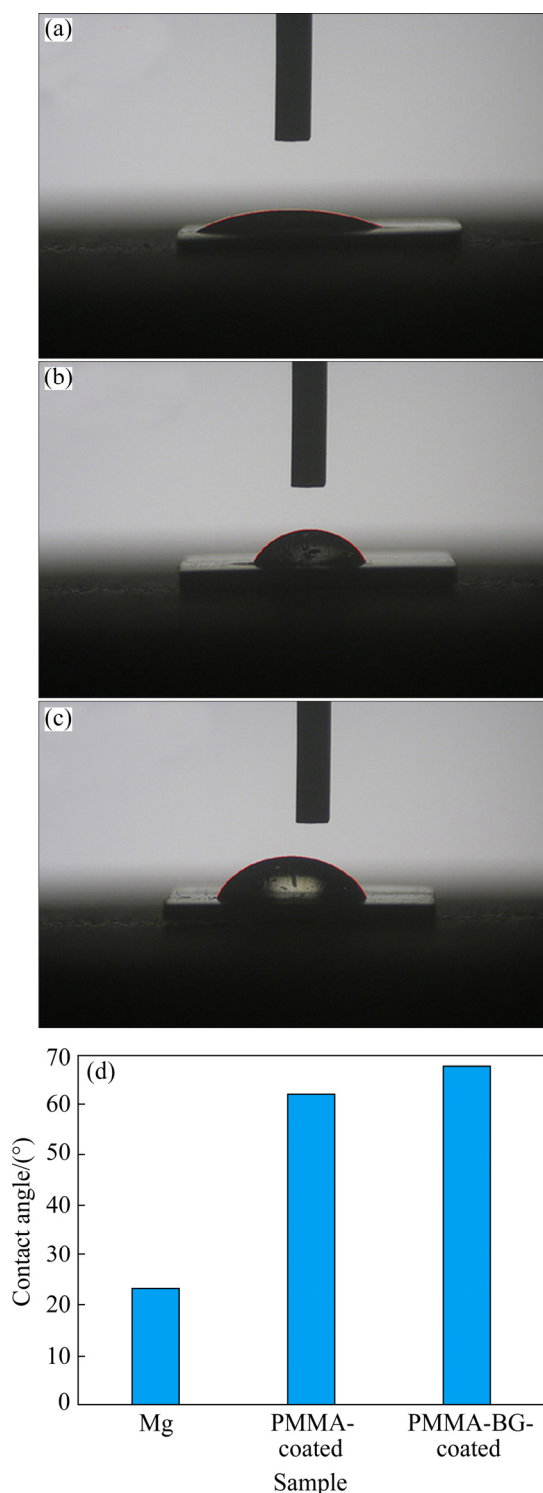


Fig. 5 Water contact angle on uncoated (a), PMMA-coated (b), and PMMA-BG-coated (c) samples, and comparison of contact angles (d)

3.2 Biodegradation behavior

3.2.1 Electrochemical polarization response

The potentiodynamic polarization curves corresponding to the uncoated Mg and PMMA-coated and PMMA-BG-coated Mg in SBF are shown in Fig. 6. The differences between the biodegradation potentials (ϕ_{corr}) and biodegradation current density (J_{corr}) of the uncoated Mg and the coated ones are good indicators to find the appropriate coating conditions. In addition to ϕ_{corr} and J_{corr} , the values of polarization resistance (R_p), biodegradation rate (η_{BR}), anodic Tafel slope (β_a), and cathodic Tafel slope (β_c) are extracted from the polarization curves and summarized in Table 1. ϕ_{corr} and J_{corr} , as the critical parameters of the electrochemical polarization test, are obtained by extrapolation of electrochemical polarization curves from the linear parts of the cathodic and anodic branches of the polarization curves at the joint

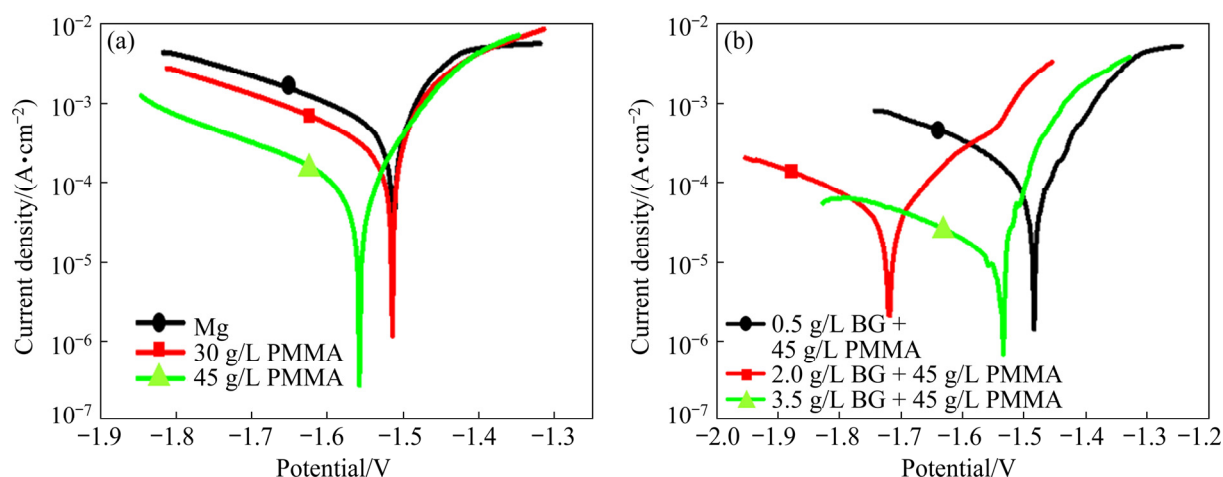


Fig. 6 Potentiodynamic polarization curves of uncoated and PMMA-coated (a), and PMMA-BG-coated (b) samples

Table 1 Electrochemical parameters extracted from potentiodynamic polarization curves

Sample	$R_p/$ ($\Omega \cdot \text{cm}^2$)	$\varphi_{\text{corr}}/$ V	$J_{\text{corr}}/$ ($\mu\text{A} \cdot \text{cm}^{-2}$)	$\eta_{\text{BR}}/$ ($\text{mm} \cdot \text{a}^{-1}$)	$\beta_a/$ ($\text{V} \cdot \text{dec}^{-1}$)	$\beta_c/$ ($\text{V} \cdot \text{dec}^{-1}$)
Mg	65.89	−1.513	563	25.762	0.12	−0.28
PMMA-coated Mg (30 g/L PMMA)	101.73	−1.514	335	15.347	0.10	−0.29
PMMA-coated Mg (45 g/L PMMA)	295.5	−1.558	126	5.788	0.12	−0.28
PMMA-BG-coated Mg (45 g/L PMMA + 0.5 g/L BG)	286.17	−1.484	102	4.688	0.09	−0.24
PMMA-BG-coated Mg (45 g/L PMMA + 2 g/L BG)	1060.3	−1.720	45.6	2.401	0.17	−0.30
PMMA-BG-coated Mg (45 g/L PMMA + 3.5 g/L BG)	1382.8	−1.534	18.6	0.855	0.06	−0.43

point of the anodic and cathodic branches. In the electrochemical polarization assessment, the biodegradation potential of Mg describes the relationship between the cathodic and anodic reactions during the test, where the anodic reaction addresses the Mg dissolution and the cathodic reaction shows the hydrogen (H_2) evolution.

Figure 6(a) exhibits that the uncoated Mg displays the most positive and highest φ_{corr} and J_{corr} . Even though the φ_{corr} values of various PMMA-coated Mg are gently more negative than that of the uncoated one, the lower J_{corr} values of both samples dedicate a better biodegradation resistance compared to the uncoated Mg sample. These results are in good agreement with previous studies [27,28]. Based on the results given in Table 1, the φ_{corr} and J_{corr} of the PMMA coating, produced from 45 g/L PMMA solution, are −1.558 V and 126 $\mu\text{A}/\text{cm}^2$, respectively, revealing an η_{BR} of 5.788 mm/a. As Fig. 6(b) and the electrochemical parameters tabulated in Table 1 display, the PMMA-BG-coated Mg provides better biodegradation resistance. The J_{corr} values decrease from 102 $\mu\text{A}/\text{cm}^2$ to

45.6 $\mu\text{A}/\text{cm}^2$ and 18.6 $\mu\text{A}/\text{cm}^2$ with increasing the BG concentration in the suspension from 0.5 to 2 and 3.5 g/L, respectively, revealing the improved protective effect of the coatings with the presence of BG. In addition, the sample coated from the suspension having 45 g/L PMMA + 3.5 g/L BG shows the highest biodegradation resistance. In other words, the composite-coated Mg samples provide more negative φ_{corr} than the uncoated ones and have lower J_{corr} . The electrochemical parameters indicate that J_{corr} of Mg is 563 $\mu\text{A}/\text{cm}^2$, which is higher than those of the coated samples, while the composite-coated sample (from the suspension 45 g/L PMMA + 3.5 g/L BG) has the lowest J_{corr} (18.6 $\mu\text{A}/\text{cm}^2$). The decrease in biodegradation rate, from 25.762 mm/a for the uncoated one to 5.788 mm/a and 0.855 mm/a for those coated by 45 g/L of PMMA solution and 45 g/L PMMA + 3.5 g/L BG suspension, respectively. This indicates about 77% and 97% reduction in biodegradation rate for coatings obtained from 45 g/L of PMMA and 45 g/L PMMA + 3.5 g/L BG suspensions, respectively, and reveals a

more efficient modification of the Mg substrate by the contribution of both PMMA and BG components in the coating. In the case of the cathodic reaction, Fig. 6 and Table 1 specify that a higher Tafel slope is obtained for the composite coating, meaning that the coating not only limits anodic dissolution of Mg but also decreases the rate of hydrogen evolution by decreasing the diffusion coefficient of electrolyte ions, which is necessary for both anodic and cathodic reactions to establish the electroneutrality [29]. The improved biodegradation resistance approached by depositing the coatings can be attributed to their kinetic barrier, hydrophobic nature, as well as shielding effect [30]. Therefore, there is less tendency for electrolyte ions, especially Cl^- ion and water molecules, to diffuse through the coating layer, reaching the surface of Mg.

3.2.2 Electrochemical impedance spectroscopic response

EIS was utilized to achieve more information on the biodegradation behavior of uncoated and coated Mg in SBF and to study the biodegradation mechanism. Figure 7(a) shows the Nyquist plot of Mg exposed to SBF. It represents a capacitive loop in a high-frequency range corresponding to the charge transfer resistance. A RC (resistor-capacitor) circuit, serially linked to equivalent series resistance, can be used to deconvolute the resistance behavior of the uncoated sample. The joint point intersection in very high-frequency regions with a real resistance axis reflects the solution resistance of the media along with contact resistances and also internal resistance of the samples. However, the second intersection with the real axis at low frequencies is the sum of the solution resistance and charge transfer resistance since the double-layer capacitor of the sample is an open circuit at such low frequencies, which does not allow charge transportation through it [31]. Hence, the diameter of the arc is a good estimation of the biodegradation resistance. In low-frequency range, uncoated Mg discloses an inductive loop, indicating that pitting corrosion happens on Mg, which is a rate-determining step in these frequency domains [32].

However, the PMMA-coated (Fig. 7(b)) and PMMA-BG-coated (Fig. 7(c)) samples show a larger capacitive loop in comparison to the uncoated Mg, specifying higher resistance of these samples against the transportation of charges

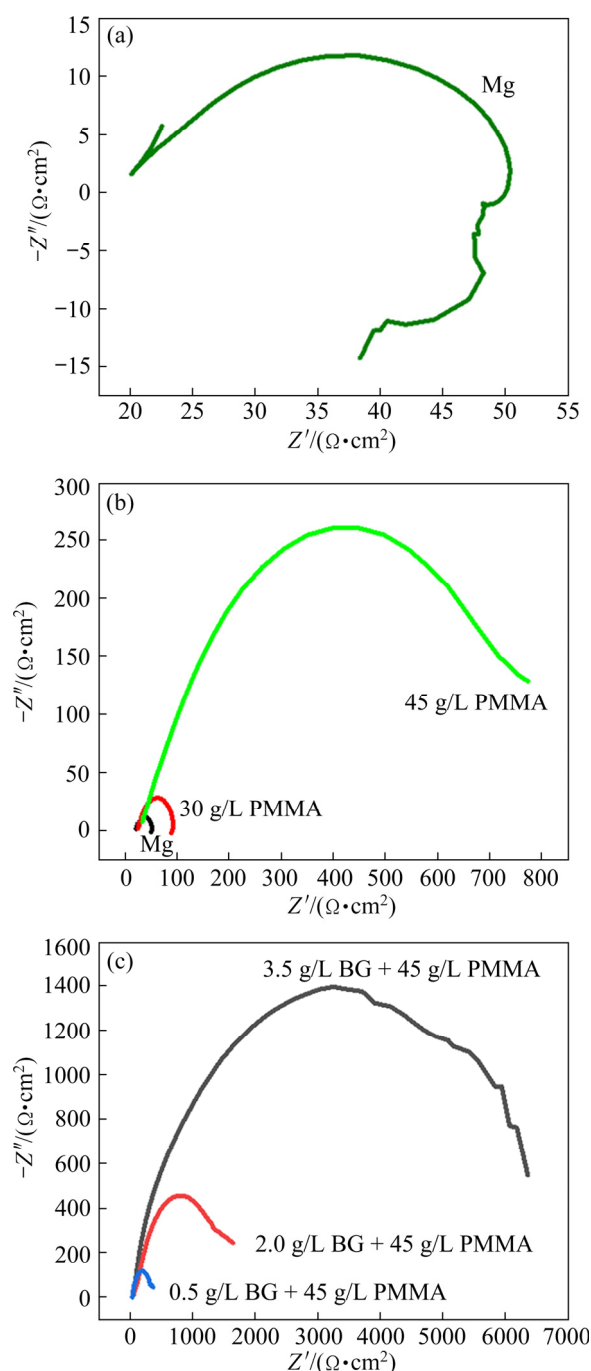


Fig. 7 Nyquist plots of uncoated (a), PMMA-coated (b), and PMMA-BG-coated (c) samples

through the interfacial area of electrolyte/electrode. Moreover, it can be clearly seen from Fig. 7 that increasing concentration of PMMA and BG raises the radius of curvature, indicating higher biodegradation resistance, which is in a good agreement with the electrochemical polarization response in this work.

Interestingly, there is no sign of an inductive loop for the PMMA-coated and PMMA-BG-coated

samples, approving that PMMA coating and PMMA-BG composite coating protect Mg from pitting corrosion [33]. Hence, it can be suggested that both coatings prevent the permeation of chloride ions into the coating to reach the substrate [2]. Furthermore, the lack of bulging of the coating suggests that the electrolyte permeation through both coatings is minimal.

Figure 8 suggests equivalent circuits for modeling EIS results of the uncoated and coated Mg. In the circuits, R_s and R_{ct} stand for solution resistance and charge transfer resistance, respectively, CPE_1 is the constant phase element, L is the inductance, and R_L is the inductance resistance.

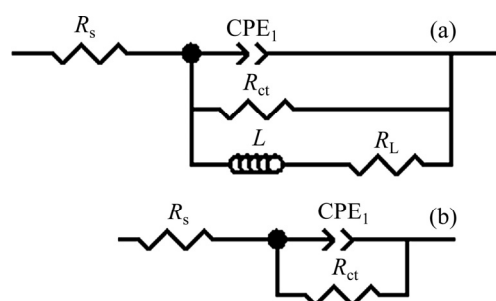


Fig. 8 Equivalent circuits used for modeling EIS spectra of uncoated (a) and coated (b) samples

CPE_1 is the equivalent electrical circuit component that reflects the non-ideal characteristics of the electrochemical process instead of a pure double-layer capacitance. The resistance of a CPE_1 is calculated by Eq. (2):

$$Z_{CPE} = |Q(j\omega)^n|^{-1} \quad (2)$$

where ω is the angular frequency; j is the imaginary number; Q is the capacitance, which is directly corresponding to the surface area; n is the exponent factor, which could take quantities between 0 and 1 and could be associated with the roughness of the electrode surface and takes various quantities

following the treatment or deposition of the coating layer. R_{ct} values can be used to calculate the J_{corr} and η_{BR} , and the larger the R_{ct} , the better the biodegradation resistance. The electrochemical parameters which are extracted from the Nyquist plots are given in Table 2. It can be seen that the R_{ct} value found for the sample coated with PMMA-BG, developed from 45 g/L PMMA + 3.5 g/L BG suspension, is $5.62 \text{ k}\Omega \cdot \text{cm}^2$, which is remarkably larger than those for the other coatings and also the uncoated Mg, revealing the most effective performance against biodegradation. The R_{ct} value for the samples coated with PMMA, developed from 30 and 45 g/L, is 0.059 and $0.897 \text{ k}\Omega \cdot \text{cm}^2$, respectively, emphasizing that increasing PMMA concentration has a positive effect on barrier characteristics of the coating. Although there is a consistent result in terms of η_{BR} in both linear polarization and EIS experiments, the considerable differences in the values may be ascribed to the destructive nature of the linear polarization method while the EIS method was done by small perturbations around the open circuit potential.

3.2.3 Immersion test results

In parallel with the electrochemical tests, the long-term immersion test was utilized to evaluate the mass loss and biodegradation rate of the samples and to characterize the biodegradation products formed on the surface. Figure 9 provides the biodegradation rates of uncoated, PMMA-coated and PMMA-BG-coated Mg samples in SBF, calculated using Eq. (1). It is worth noting that the mass loss for Mg only addresses its biodegradation reaction, while in the coated samples, the dissolution of the coating layer occurs in addition to the biodegradation of Mg [34]. As shown in Fig. 9, the biodegradation rate of the samples increases in the first 72 h (although it is very sharp for uncoated Mg), calculated as 31.27, 7.33, and 3.79 mm/a for

Table 2 Electrochemical parameters extracted from Nyquist plots

Sample	R_s/Ω	$R_{ct}/(\text{k}\Omega \cdot \text{cm}^2)$	$J_{corr}/(\mu\text{A} \cdot \text{cm}^{-2})$	$\eta_{BR}/(\text{mm} \cdot \text{a}^{-1})$	$Q/(F_n^{n-1} \cdot \text{cm}^{-2})$	n
Mg	20.5	0.027	0.817	18.55	97.6	0.847
PMMA-coated Mg (30 g/L PMMA)	24.4	0.059	0.369	8.37	43.6	0.903
PMMA-coated Mg (45 g/L PMMA)	29.1	0.897	0.024	0.545	38	0.671
PMMA-BG-coated Mg (45 g/L PMMA + 2 g/L BG)	28.69	1.23	0.017	0.386	58.5	0.608
PMMA-BG-coated Mg (45 g/L PMMA + 3.5 g/L BG)	33.06	5.62	0.003	0.068	6.52	0.603

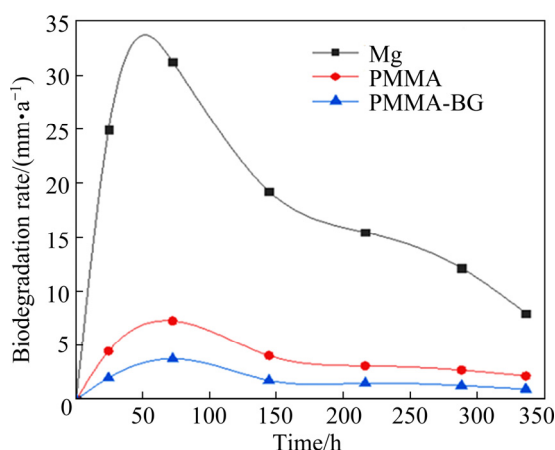


Fig. 9 Biodegradation rates of uncoated, PMMA-coated and PMMA-BG-coated samples after soaking in SBF for different periods of time

uncoated, PMMA-coated, and PMMA-BG-coated samples, respectively, due to chemical dissolution of Mg. The biodegradation rates, however, decrease in the following 72 h, reaching 19.23, 4.09, and 1.77 mm/a, respectively, due to the formation of biodegradation product, $\text{Mg}(\text{OH})_2$, which then reacts with Cl^- ions in SBF to create the soluble MgCl_2 [35]. The decrease in the biodegradation rate of the uncoated Mg happens sharply, whereas those of the coated ones experience a more moderate reduction. Afterward, as the experiment progresses, the biodegradation rate continues almost sharply, which can be attributed to the formation of hydroxyapatite (HA) crystals in a cauliflower morphology.

In contrast, the coated samples follow a nearly even rate, showing very good protection of PMMA and PMMA-BG coatings. ZHANG et al [36] reported that the presence of $\text{Mg}(\text{OH})_2$ inhibits the absorption of Ca and P by the surface. Therefore, the formation of HA on the surface of uncoated Mg is approximately impossible, while HA can be formed on the coated samples and decrease the biodegradation rate [37]. Considering the results of electrochemical experiments (Tables 1 and 2), the presence of BG reduces the biodegradation rate of the coated Mg significantly. The presence of BG is a factor to intensify the formation of HA on the surface, which is why it is effective in reducing the biodegradation rate [21]. At the end of the immersion test, the biodegradation rates of the mentioned specimens after 336 h are calculated as 8.04, 2.18, and 0.96 mm/a, for Mg, PMMA-coated,

and PMMA-BG-coated samples, respectively. The results confirmed a significant reduction in degradation rate (72.88% and 88.06%), for the PMMA-coated and PMMA-BG-coated samples, respectively, as compared to bare Mg substrate. The overall findings from the immersion tests are consistent with the electrochemical test results. The coating produced using 45g/L PMMA + 3.5 g/L BG suspension evidently demonstrates longer-term protection to the Mg surface and provides a more desirable biodegradation resistance performance compared with other coated samples.

Figure 10 represents the SEM image from the surface of the coating deposited from the 45 g/L PMMA + 3.5 g/L BG suspension soaked in SBF for 336 h. It is seen that the coating morphology shows a uniform cauliflower structure on the surface. The formation of this HA layer is a qualitative indication of the bioactivity of the coating [38].

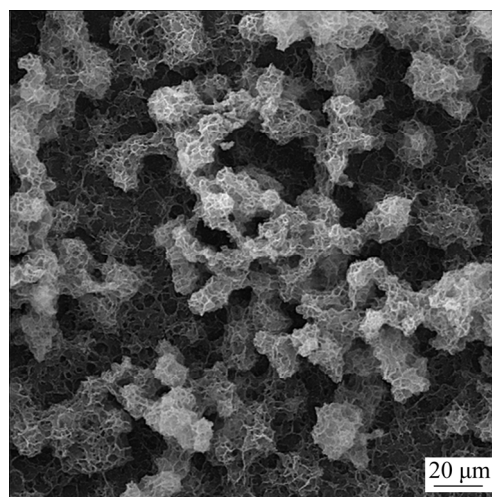


Fig. 10 SEM image of HA formed on surface of 45 g/L PMMA + 3.5 g/L BG coated sample after immersion in SBF for 336 h

The result of the XRD analysis performed on the coating, given in Fig. 11, confirms the formation of HA on the surface of the composite coating encouraged by BG within the coating. HA and $\text{Mg}(\text{OH})_2$ crystals are detected on the coating. The peaks of HA at 2θ values of 32.3° , 34.54° , 48.08° , 51.04° , and 72.39° (ICDD card No. 09-432) in the pattern suggest that the PMMA-BG coating is able to induce the successful formation of HA on the surface of Mg [33]. However, other characteristic peaks which were observed in XRD pattern were associated to Mg (ICDD card No. 35-0821), and $\text{Mg}(\text{OH})_2$ (ICDD card No. 7-239), respectively [39].

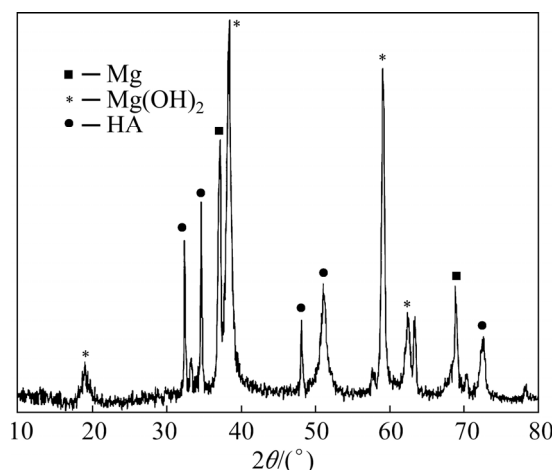


Fig. 11 XRD pattern of 45 g/L PMMA + 3.5 g/L BG coated sample after immersion in SBF for 336 h

4 Conclusions

(1) Microstructural studies show that uniform and compact PMMA and PMMA-BG coatings formed on the surface of Mg by the coating techniques. The nature of the PMMA is almost neutral. The dip-coating and EPD techniques were used to develop the PMMA coating and PMMA-BG composite coating, respectively.

(2) Contact angles of samples containing PMMA and PMMA-BG coatings are increased by 164% and 187% compared to that of the uncoated Mg, respectively, indicating deposition of the hydrophobic coatings on the Mg, which provide better performances.

(3) Embedding BG in PMMA coating significantly improves the biodegradation resistance of the coating on Mg. 45 g/L PMMA + 3.5 g/L BG as the medium for EPD is able to produce an appropriate coating on Mg having over 85% biodegradation resistance compared to the PMMA-coated Mg.

(4) Bioglass further induces the formation of the hydroxyapatite layer on the surface of the coated Mg.

(5) Considering the non-toxic and biocompatible characteristics of the components, PMMA and BG, due to the appropriate microstructural features as well as the improved biodegradation behavior, PMMA-BG composite is proposed as a potent candidate coating to be applied on Mg in biodegradable biomedical applications.

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具有甲基丙烯酸甲酯-45S5 生物活性玻璃复合涂层的镁在模拟体液中的生物降解行为

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摘 要：研究甲基丙烯酸甲酯(PMMA)和甲基丙烯酸甲酯-生物活性玻璃(BG)复合材料对镁生物降解行为的影响。通过电泳沉积和浸涂技术，利用含有不同比例两种涂层材料的悬浮液制备复合涂层。用 SEM、EDS、FTIR 和水接触角测量对涂层进行表征。通过线偏振、阻抗谱和模拟体液浸泡实验研究镁的生物降解行为。电镜结果表明，复合涂层致密且均匀。水接触角测量显示，与没有复合涂层的镁相比，具有复合涂层的镁接触角增加 44°。复合涂层在模拟体液中浸泡 336 h 后其表面被类骨羟基磷灰石层覆盖，表明涂层具有良好的体外生物活性。电化学测试结果证实，与未涂覆复合材料涂层的镁相比，涂覆了由 45 g/L PMMA 和 3.5 g/L 45S5 BG 组成的悬浮液所制复合涂层的镁，其生物降解率显著降低了 96.9%。因此，具有复合涂层的镁可作为一种有前景的生物降解植入材料。

关键词：镁合金；聚甲基丙烯酸甲酯；生物活性玻璃；复合涂层；电泳沉积；生物降解

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