Enhancement of corrosion resistance and mechanical properties of Mg–1.2Ca–2Bi via a hybrid silicon-biopolymer coating system

H.R. Bakhsheshi-Rad a,b,⁎, E. Hamzah a, M. Daroonparvar a, M.R. Abdul Kadir b, M. Kasiri-Asgarani c, Mark P. Staiger d

a Department of Materials, Manufacturing and Industrial Engineering, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia
b Medical Devices & Technology Group (MEDITEG), Faculty of Biosciences and Medical Engineering, Universiti Teknologi Malaysia (UTM), 81310, Skudai, Johor Bahru, Johor, Malaysia
c Advanced Materials Research Center, Faculty of Materials Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Isfahan, Iran
d MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Mechanical Engineering, University of Canterbury, Private Bag 4800, Christchurch 8140, New Zealand

⁎ Corresponding author at: Department of Materials, Manufacturing and Industrial Engineering, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia.
E-mail addresses: rezbakhsheshi@gmail.com, bhamadrea20@live.utm.my

Article info
Article history:
Received 20 June 2015
Revised 20 September 2015
Accepted in revised form 21 September 2015
Available online 25 September 2015
Keywords:
Magnesium
Biomaterial
Polycaprolactone
Microstructure
Corrosion resistance
Mechanical properties

Abstract
In this work, a hybrid dual layer surface coating consisting of a silicon (Si) underlayer and poly(ε-caprolactone) (PCL) overlayer was investigated that was designed to reduce the corrosion rates of magnesium-based biomaterials. The Si underlayer was 1.2 μm thick and composed of spherical nanoparticles. The overlayer of PCL was 75.2 μm thick and comprised network of pores. Corrosion-induced reduction of the compressive strength of a Si/PCL-coated Mg–Ca–Bi alloy was lower than that of the uncoated or Si layer-coated alloys. However, the bonding strength of the Si coating (24.6 MPa) was significantly higher than that of the Si/PCL-coated samples (6.8 MPa). The Si/PCL coating dramatically enhances the charge transfer resistance of the Mg alloy (2.11 kΩ·cm²) in simulated body fluid when compared with a Si-coated sample (2265.12 kΩ·cm²). Si/PCL coatings are considered a promising route to control the corrosion rate and mechanical properties of Mg-based biomaterials.

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1. Introduction

Recently, magnesium-based alloys applied as biodegradable materials for implant applications have attracted great attention [1]. Mg-based alloys are bioactive, enhancing bone growth and have mechanical properties close to bone [2]. The major drawback of Mg-based alloys as biodegradable implants is their high degradation rate that results in production of hydrogen gas and serious local alkalization that may hinder the clinical application of Mg alloys [1,3–5]. Numerous attempts to control the rapid corrosion rate of Mg alloys have been carried out [1,6–9] through surface modification. For example, coating AZ31B with silicon (Si) results in reduced corrosion rates and an improved biological response [1]. As an essential trace element in skeletal development, Si was shown to increase the proliferation of osteoblast-like cells [1]. Additionally, the release of Si has been associated with angiogenesis during bone regeneration [1]. Si-hydroxyapatite coatings have also been used to increase the corrosion resistance of Mg alloys [6,10].

Organic coatings are known to reduce the corrosion rate of Mg. For example, AZ91 can be coated with a polymer to reduce the corrosion rate of the alloy and maintain the mechanical properties [11]. In addition, polymer-coated alloys appear to assist in retaining the mechanical strength of the Mg-based implant during immersion testing when compared with that of uncoated alloys [11,12]. For example, poly(ε-caprolactone)(PCL) is a semi-crystalline biopolymer widely used in biomedical applications due to its mechanical strength, flexibility, hydrophobicity, biocompatibility and biodegradability [13]. PCL may also improve cell adhesion, cell function, maintenance of differentiated cells, and assist in the function of the extracellular matrix [11,12].

Although there are investigations of both Si and PCL for the protection of Mg substrates, there are no studies on the use of hybrid Si-PCL coating systems aimed at further improving the degradation and biological characteristics of Mg-based alloys. The main purpose of the present study was to investigate the synergistic effect of using a hybrid Si/PCL dual layer coating system to control the loss of mechanical properties during the in vitro degradation of Mg–1.2Ca–2Bi alloy in a simulated body fluid. The dual layer Si/PCL coating was produced by a combination of physical vapour deposition (PVD) and dip coating.
Mg alloys were prepared by melting 99.9% pure magnesium ingots, and Mg–32 wt.% Ca and pure bismuth (99.99% Bi) in an electrical resistance furnace under protective gas atmosphere (60% Ar–40% CO₂). The crucible was held at a temperature of 760 °C for 30 min to melt the materials and further 15 min to allow for homogenisation of the melt. Melts were cast in a 300 °C preheated stainless steel mould. Subsequently, several Mg–1.2Ca–2Bi specimens, with actual composition of 0.012 wt.% Fe, 2.12 wt.% Bi, 1.21 wt.% Ca, 0.004 wt.% Cu, 0.003 wt.% Ni, and 96.651 wt.% Mg were fabricated. The actual composition was determined by inductively coupled plasma (ICP). The ingots were then cut to provide specimens with dimensions of 15 × 10 × 10 mm. The specimens were then wet ground down to 2000 grit SiC paper to remove all visible scratches.

2.2. Preparation of Si underlayer and PCL overlayer.

A hybrid ion beam deposition system (HVC Penta Vacuum), consisting of a linear ion source and magnetron sputtering source with a Si (99.99%) target, was selected to deposit the coatings on the substrates. The Mg alloys were ultrasonically washed in pure alcohol for 5 min before placement inside the vacuum chamber. An ion source with Ar gas was used to clean the surface of the Mg alloys for 40 min. This pre-treatment was performed when the base pressure of the chamber was below 2.55 × 10⁻³ Pa. Physical vapour deposition (PVD) was performed at room temperature with argon gas as the sputtering gas. The process used a sputtering pressure of 0.24 Pa, RF sputtering current of 200 W, deposition time of 90 min, and bias voltage of −150 V.

The Si-coated alloys were then dipped into a 2.5 wt.% PCL (pellets; Mₘ = 80,000 g/mol, Sigma-Aldrich, UK) dichloromethane solution (DCM; CH₂Cl₂, Sigma-Aldrich, UK) by stirring for 6 h at room temperature. The Si-coated samples were dipped for 3 times and withdrawn at a constant speed of 40 mm/min to form a uniform coating and then dried at room temperature.

2.3. Corrosion testing and analysis.

Rectangular specimens with a surface area of 1 cm² were mounted in epoxy resin for electrochemical testing. Electrochemical tests were conducted at 37 °C in an open-air glass cell containing 350 ml Kokubo solution with a pH of 7.44, using a PARSTAT 2263 potentiostat/galvanostat (Princeton Applied Research). The chemical composition of the Kokubo solution is listed in Table 1 [14]. A three-electrode cell was used for potentiodynamic polarisation testing. The reference electrode was a saturated calomel electrode (SCE), the counter electrode was a graphite rod, and the specimen was the working electrode. All experiments were carried out at a constant scan rate of 0.5 mV/s, initiated at −250 mV relative to the open-circuit potential. The polarisation resistance (Rp) and corrosion rate (Rcorr) were calculated according to [10]. The electrochemical impedance spectra (EIS) were measured over a frequency range of 0.01 Hz to 100 kHz using a VersaSTAT 3 machine. Each electrochemical test was repeated to confirm reproducibility of the results.

Immersion testing was carried out according to ASTM G1-03 [15]. Alloy specimens with a diameter of 10 mm and height of 20 mm were immersed in a beaker containing 200 ml of Kokubo SBF [14] for 10 days. The SBF was not replenished during the testing period. The average pH value of the SBF from three measurements was recorded during the soaking experiment after an interval of 24 h. The immersion tests were repeated at least once to check the reproducibility of the results. The hydrogen evolution rate of the specimens was also measured throughout a 10 day immersion period during which the SBF was replenished daily. Specimens were immersed in a beaker containing 250 ml of SBF. The beaker was covered with a glass and burette (50 ml) so as to collect the evolved hydrogen. At least two specimens were tested to confirm reproducibility of the results. Following immersion, the samples were cleaned in a boiling solution of chromium trioxide (CrO₃) to remove surface corrosion products and then dried in warm air prior to further testing.

![Fig. 1. Scanning electron micrographs of the surface of (a) uncoated Mg–1.2Ca–2Bi, (b) Si-coated Mg–1.2Ca–2Bi, and (c) Si/PCL-coated Mg–1.2Ca–2Bi, and (d) EDS analysis of Points A and B in (b) and (c), respectively. Scanning electron micrographs of the cross-section of (e) Si-coated and (f) Si/PCL-coated Mg–1.2Ca–2Bi. Insets show higher magnification images.](image_url)
2.4. Materials characterisation.

An X-ray diffractometer (Siemens D5000) was used to evaluate phase transformations using Cu-Kα radiation (λ = 1.5405 Å) generated at 35 kV and 25 mA, over the 2θ range of 10–70° with increment steps of 0.04. Microstructures were analysed with scanning electron microscopy (JEOL JSM-6380LA equipped with EDS system, JEOL Inc., Tokyo, Japan) and transmission electron microscopy (HT7700 Hitachi). The surface topography and roughness of the coated samples was evaluated using atomic-force microscopy (AFM, NanoScope IV, Digital Instruments). AFM imaging was performed in the tapping mode at room temperature using a standard silicon nitride probe with a spring constant of 0.58 N/m and a typical radius of 10 nm. The scanning area selected was 10 × 10 μm. Compression testing (Instron 5569, Norwood, MA, USA) of specimens immersed in SBF was performed at ambient temperature using 2 replicates and a crosshead speed of 0.5 mm/min. The Instron load frame was also used to measure the coating-substrate bond strength according to ASTM F1044 [16], using a crosshead speed of 1 mm/min and 10 kN load cell. Two rectangular specimens (30 × 10 mm) were tested for each type of sample to obtain an average value of the bond strength.

3. Results and discussion

3.1. Alloy and coating microstructures

The Mg–1.2Ca–2Bi (wt.%) alloy substrate consisted of primary α-Mg phase, and Mg6Bi2 and Mg2Ca secondary phases (Fig. 1a). The secondary phases form a eutectic phase that consists of α-Mg, Mg6Ca and Mg6Bi2 located along the grain boundaries. The eutectic phase has a significant effect on the corrosion behaviour of the Mg alloy due to the formation of micro-galvanic cells between the matrix and secondary phases. Kirkland et al. [17] showed that the microstructure of Mg alloys has an appreciable effect on corrosion performance. The Si coatings exhibit dimple-like microstructures where the dimples consist of a dense arrangement of nanocrystalline columns (Fig. 1b). Some microscopic pores and flaws were observed in the Si coating that presumably reduce the corrosion resistance and associated mechanical properties of the alloy. It was reported that the type of resulting phases and their morphology depend on the coating method and the operating conditions [18]. The surface of the Si-coated Mg–1.2Ca–2Bi is composed of Mg, Ca, O and Si, where Mg, Bi and Ca were detected due to the presence of high degree of porosity of the Si layer. This porosity allowed penetration of corrosive materials toward the substrate which led to pit corrosion (Fig. 1d). The surface microstructure of the PCL overlayer was comprised of pore networks (Fig. 1c). While the PCL layer was found to be highly porous, the Si underlayer was a denser coating that could act as a barrier to corrosive electrolytes. There was also a significant amount of C present (64.45 at.%) that originates from the PCL (Fig. 1d). The cross-sectional SEM image of the Si-coated Mg–1.2Ca–2Bi was composed of a thin and compact coating with columnar structure. The Si coating was found to cover the Mg–1.2Ca–2Bi substrate homogeneously (Fig. 1e). Si/PCL coatings formed relatively thick layers homogeneously over the surface of Mg–1.2Ca–2Bi (Fig. 1f). Si/PCL coatings were composed of distinct PCL and Si layers that were 70–80 μm and 0.9–1.2 μm in thickness, respectively. Gu et al. showed that the thickness of the coating layer has a significant effect on the corrosion behaviour of the Mg substrate where the thicker coating layer prohibited further corrosion in Mg during tests in chloride containing solutions [19].

The microstructure of the Si coating was composed of very fine nanocrystallites with size of ~30–40 nm. After coating with a PCL layer as the top layer, dark spherical particles can be observed that are assumed to be PCL (Fig. 2a). The microstructure of Mg–1.2Ca–2Bi was determined to consist of α-Mg, Mg6Bi2 and Mg2Ca (Fig. 2b). X-ray diffraction peaks detected at 2θ values of 27.5°, 47.6°, 56.3° and 69.3° with orientation along (111), (200), (311) and (400) planes also confirmed the formation of a Si coating on Mg alloy substrate [20]. The PCL background spectrum mainly consists of two intense peaks for 

Fig. 2. (a) Transmission electron micrograph of Si/PCL-coated Mg–1.2Ca–2Bi, and (b) X-ray diffractograms of uncoated, Si-coated and Si/PCL-coated Mg–1.2Ca–2Bi.

Fig. 3. AFM topography of (b) Si-coated; (c) Si/PCL-coated Mg–1.2Ca–2Bi.

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PCL at $2\theta = 21.6$ and $23.8^\circ$ that can be attributed to (1 1 0) and (2 0 0) planes, respectively. PCL has a crystalline structure with a polyethylene-like orthorhombic unit cell and lattice parameters of $a = 0.748 \text{ nm}$, $b = 0.498 \text{ nm}$ and $c = 1.727 \text{ nm}$ [21].

The topography of the Si and Si/PCL coatings was observed using atomic force microscopy. The Si-coated Mg–1.2Ca–2Bi was mainly composed of granular structures beside small voids which allowed easier interaction between the solution and matrix, accelerating the corrosion of the matrix. The average surface roughness ($R_a$) of the Si coating (16.4 nm) is considerably lower than that of the Si/PCL coatings (385.2 nm) (Fig. 3b). The higher roughness of the PCL overlayer was due to the existence of numerous pores within the PCL layer. Such a rough coating may be beneficial for bioactivity and mechanical bonding with bone [7].

### 3.2. Corrosion behaviour of Si and Si/PCL coatings on Mg–1.2Ca–2Bi

The electrochemical polarisation curves of uncoated, Si-coated, and Si/PCL-coated Mg–1.2Ca–2Bi are shown in Fig. 4a. The corrosion potential ($E_{corr}$) of both Si and Si/PCL coatings shifted to more positive values, indicating the protective nature of the coatings. $E_{corr}$ of Si-coated and Si/PCL-coated Mg–1.2Ca–2Bi increased to $-1501.2$ and $-1352.8 \text{ mV}_{\text{SCE}}$, respectively, relative to uncoated Mg–1.2Ca–2Bi, indicating that a PCL layer enhances the corrosion resistance of a Si-coated substrate. The electrochemical parameters of uncoated and coated Mg alloys in Kokubo solution are listed in Table 2. The more negative $E_{corr}$ of uncoated Mg–1.2Ca–2Bi compared to the coated specimens is due to the formation of micro-galvanic cells that exist between the primary $\alpha$-Mg phase and secondary phases. The corrosion current density ($i_{corr}$) of the uncoated, Si-coated and Si/PCL-coated Mg–1.2Ca–2Bi was 389.7, 32.7 and 0.43 $\mu\text{A/cm}^2$, respectively. Clearly, the Si/PCL-coated specimens exhibited a significantly lower $i_{corr}$ compared with the other samples. The presence of the PCL film as a top layer and Si as an inner layer caused significant reduction of the corrosion rate although the precise reason for this is unclear. The samples coated with single-layered Si suffered from a high level of attack by water molecules. Water diffusion through tiny micro- or nano-defects on the coating layer deteriorated the coatings and destroyed the adhesion of the organic layer on the substrate [10,19]. PCL as top layer also over the Si surface could hinder the hydrogen evolution reaction, and in turn the current densities decreased significantly compared to the uncoated sample. There was a corresponding increase in corrosion resistance ($R_p$) from 0.32 k$\Omega$ cm$^2$ for uncoated Mg–1.2Ca–2Bi to 7.58 and 639.01 k$\Omega$ cm$^2$ for the Si-coated and Si/PCL-coated specimens, respectively. The large increase in $R_p$ values observed for the Si/PCL-coated alloy is due to the additional coverage of the Si-coated Mg by the thick PCL layer. The dependence of the corrosion resistance on the thickness of the PCL coating suggests that the corrosion rate of dual-layered coated Mg can be adjusted by controlling its thickness [19,22,23]. The corrosion rate of the Si/PCL-coated alloy (0.09 mm/year) was significantly lower compared to the Si-coated (0.74 mm/year) or uncoated (8.90 mm/year) alloy. Nyquist plots of the uncoated and coated samples showed the typical single-capacitive semi-circle that represents an electrochemical process with only one time constant (Fig. 4b) [24]. The circuit depicted in Fig. 4c was used to fit the impedance curves. In this circuit, $R_p$ represents the solution resistance, $C_s$ is the coating capacitance, $C_{dl}$ is the double layer capacitance and $R_{ct}$ is the charge transfer resistance which is attributed to the electrochemical corrosion rate. The equivalent circuit in Model A is employed to characterise the uncoated sample while, Model B could describe the coated samples. Clearly, the incorporation of a Si coating increased the charge transfer resistance ($R_{ct}$) of the PCL

### Table 2

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Corrosion potential, $E_{corr}$ (mV vs. SCE)</th>
<th>Current density, $i_{corr}$ ($\mu\text{A/cm}^2$)</th>
<th>Cathodic slope, $j_{c,n}$ (mV/decade) vs. SCE</th>
<th>Anodic slope, $j_{a,n}$ (mV/decade) vs. SCE</th>
<th>Polariation resistance, $R_p$ (k$\Omega$ cm$^2$)</th>
<th>Corrosion rate, $P_i$ (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg–Ca–Bi alloy</td>
<td>$-1502.4$</td>
<td>$389.7$</td>
<td>$62.1$</td>
<td>$53.1$</td>
<td>$0.32$</td>
<td>$8.90$</td>
</tr>
<tr>
<td>PCL coated</td>
<td>$-1501.2$</td>
<td>$32.7$</td>
<td>$87.9$</td>
<td>$162.4$</td>
<td>$7.58$</td>
<td>$0.74$</td>
</tr>
<tr>
<td>Si/PCL coated</td>
<td>$-1352.8$</td>
<td>$0.43$</td>
<td>$95.8$</td>
<td>$185.7$</td>
<td>$639.01$</td>
<td>$0.009$</td>
</tr>
</tbody>
</table>
coated sample (2265.12 kΩ cm²), indicating reduced coating porosity and improved barrier performance for corrosion protection of the substrate. However, the diameter of the semicircle in the Nyquist plots decreased to 5.21 kΩ cm² after Si coating, indicating degradation of the coating. This can be attributed to the ionic transport in the coating including for example chloride ion penetration through pinholes [25]. However, the lowest charge transfer resistance is observed for the uncoated sample (2.11 kΩ cm²). The rate of the electrochemical processes

Fig. 5. Scanning electron micrographs of (a) uncoated Mg–1.2Ca–2Bi, (b) Si-coated and (c) Si/PCL-coated Mg–1.2Ca–2Bi after immersion into Kokubo for 240 h. EDS analysis of (d) Point A, (e) Point B, and (f) Point C.

Fig. 6. Scanning electron micrographs of (a) Si-coated, (b) Si/PCL-coated after immersion in Kokubo for 720 h, and corresponding EDS analysis of (c) Si-coated and (d) Si/PCL-coated Mg–1.2Ca–2Bi.
at the substrate/electrolyte interface is controlled by the charge-transfer resistance which is the key factor in determining the corrosion resistance [25,26]. This suggests that the dual-layered coating can significantly impede the charge-transfer process at the substrate-electrolyte interface.

The surface morphologies of the uncoated, single-layer, and dual-layer-coated samples were examined following immersion in SBF for 240 h (Fig. 5). The uncoated alloy exhibited extensive surface cracking that was accompanied by pitting corrosion (Fig. 5a). Mg and O, and trace amounts of C were present on the uncoated alloy. Thus, the corrosion products were mainly composed of magnesium hydroxide Mg(OH)₂, indicated by the O:Mg molar ratio of ~2:1 (Fig. 5d). The Si-coated alloy exhibited a less uniform film with more pits, allowing the solution to make contact with the substrate and accelerating the corrosion reaction (Fig. 5b). The EDS analysis of the precipitate morphology indicates the presence of Mg, Si, Ca, P, O, and C elements with Ca/P atomic ratio of ~1.23 that implies the formation of calcium phosphate (Fig. 5e). Cracks are clearly observed in the structure of dual layer coating that would enhance corrosion of the substrate (Fig. 5c). The EDS analysis of dual layer coating revealed the presence of Mg, Ca, O, and C (Fig. 5f).

Elemental maps of the surface of the Si-coated and Si/PCL-coated Mg–1.2Ca–2Bi were collected following 30 days of immersion (Fig. 6). The Si-coated alloy exhibited large, deep, elliptically-shaped corrosion pits (Fig. 6a). Mg and O were the main constituents of the corrosion products on the sample surface (Fig. 6c). The existence of Mg on the sample surface implies that the corrosion medium easily in-}

![Image](115x615 to 471x741)

**Fig. 7.** (a) Change in pH value and (b) hydrogen evolution measurements of uncoated Mg–1.2Ca–2Bi, Si coated and Si/PCL coated Mg–1.2Ca–2Bi in Kokubo solution.

The compressive strength of the uncoated, Si-coated and Si/PCL-coated alloy before and after immersion in Kokubo solution for 10 days was measured (Fig. 9). As expected, the Si and Si/PCL coatings did not affect the bulk compressive properties of the alloy. The compressive strengths of Si/PCL-coated and Si-coated alloy decreased from 263 MPa prior to immersion to 258 and 201 MPa, respectively, following 10 days of immersion in the SBF. Therefore, the compressive strength of the Si/PCL coated samples is 0.16 ml/cm². This indicated that the uncoated Mg–Ca–Bi and Si had undergone severe corrosion in the SBF. However, Si/PCL films could effectively inhibit the degradation of uncoated sample. In addition, it can be observed that the degradation rate amplified after 120 h for the dual-layered Si/PCL coated sample, respectively. This indicates that dual-layered coating remarkably suppressed the hydrogen evolution (0.16 ml/cm²) over the long immersion period, considerably lower compared to all the other samples.

The XRD pattern of uncoated, Si underlayer and PCL overlayer in SBF for 10 days are shown in Fig. 8. The XRD pattern confirmed the presence of Mg(OH)₂ (PDF No. 44-1482) [28] as the main corrosion product of the uncoated and, clearly, no common types of calcium phosphate was observed in this diffraction pattern. Strong peaks of Mg(OH)₂ were also observed, indicating severe corrosion attack that occurred due to the fact that the uncoated sample directly exposed to SBF solution [29–31]. However, the corrosion products of single layer Si and dual-layer Si/PCL coated include hydroxyapatite (HA) and Mg(OH)₂. Low intensity of Mg(OH)₂ in single layer and dual-layer coated samples were observed, confirming the existence of a thick PCL coating on an intermediate Si coating.

### 3.3. Mechanical properties as a function of corrosion protection

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![X-ray diffraction patterns attained from the corrosion products of uncoated Mg–1.2Ca–2Bi alloy. Si coated and Si/PCL coated specimen after full immersion exposure to SBF solution for 240 h duration.](303x85 to 551x253)

**Fig. 8.** X-ray diffraction patterns attained from the corrosion products of uncoated Mg–1.2Ca–2Bi alloy. Si coated and Si/PCL coated specimen after full immersion exposure to SBF solution for 240 h duration.
the specimens was comparable to that of human cortical bone (100–230 MPa) [14]. In contrast, the compressive strength of the uncoated alloy decreased to 178 MPa following 10 days of immersion in the SBF. The presence of extensive corrosion pitting is likely to be the cause of the decrease in mechanical properties. Interestingly, the results here indicate that the PCL coating is able to delay the loss of the mechanical properties of the substrate. The strength of the bond between substrate and Si coating was ~6.8 MPa. The higher strength of Si is due to the formation of thin films which were produced by physical deposition method. As a result of the poor bonding strength between polymer and silicon further corrosive medium infiltrate to the substrate and subsequently degrading of the coating [32,33]. In view of this, Degner et al. showed [23] that although PCL coating has low bonding strength to the magnesium substrate, it can effectively protect of the substrate if the polymer film thickness is sufficient.

4. Conclusions

This study investigated the effectiveness of synthesising dual layer Si/PCL coatings on Mg–1.2Ca–2Bi via a combination of PVD and dip-coating methods. The microstructure of the PCL layer consisted of pore networks, while the Si underlayer provided the Mg–1.2Ca–2Bi substrate with a denser barrier to SBF. A greater retention of the mechanical properties of Mg–1.2Ca–2Bi following exposure to SBF is also provided by using a hybrid Si/PCL coating (σ咳嗽 = 258.2 MPa) when compared to that of the Si coating (σ咳嗽 = 201.3 MPa) or uncoated alloy (σ咳嗽 = 178.1 MPa). The Si coating exhibited significantly higher coating-substrate bond strength when compared to the adherence of the PCL layer to the Si bond coat. The immersion and hydrogen evolution results demonstrate that a hybrid Si/PCL coating provides improved resistance to degradation of Mg–1.2Ca–2Bi when compared to the uncoated Mg alloy substrate or a Si-coating.

Acknowledgments

The authors would like to acknowledge the Universiti Teknologi Malaysia (UTM) and Nippon Sheet Glass Foundation for providing research facilities and financial support under Grant No. R.J.130000.7324.4B136.

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