Fabrication of corrosion-resistant chitosan–gelatin–bioactive glass-ZnO/CeO₂ hybrid coating on magnesium ZK60 alloy by AC-EPD

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ABSTRACT
A hybrid coating was fabricated on ZK60 magnesium (Mg) alloy using alternating current electrophoretic deposition (AC-EPD). The hybrid coating comprised chitosan, gelatin (Type-B), bioactive glasses (BG(a,b)) and nanoparticles of ZnO/CeO₂. Fourier-transform infrared (FTIR) spectra confirmed the presence of the above-mentioned materials on coated samples. Scanning electron microscopy (SEM) images showed that coating morphology was homogeneous and covered the maximum surface area. Potentiodynamic polarization measurements (PDP) of coated samples were investigated in Ringer’s solution at 25°C. PDP results showed that lowest corrosion current density values of 1.39 and 1.84 μA cm⁻² were observed for suspensions CS₀.₈–G₀.₈–BG(b)₁.₀–ZnO₀.₆ and CS₀.₈–G₀.₈–G(a)₁–CeO₂(₂₀.₆), respectively. SEM analysis and PDP results confirmed that best AC-EPD parameters for ZK60 are (Voltage = 35 V, Frequency = 300 Hz, DC off-set = 2 V, Time = 480 s, Distance = 10 mm). DC off-set with the same direction to high amplitude peak was a promising addition in AC-EPD parameters.

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Highlights
- Fabrication of corrosion-resistant hybrid coatings on ZK60 by AC-EPD
- All suspensions significantly decrease the corrosion process of ZK60
- ZnO with CS–G–BG(b) showed best ZK60 corrosion protection among all
- Suitable suspension, correct AC-EPD parameters lead to promising anti-corrosion coating

1. Introduction
Natural or synthetic biomaterials are used for different biomedical applications. Metallic biomaterials, due to their load-bearing mechanisms, are good candidates for orthopaedic implants. Nickel, titanium alloys and stainless steel are used for long-term implant applications. Magnesium (Mg) alloys are used as short-term implant materials due to their low corrosion rate [1–3]. Magnesium alloys are bio-absorbable implant materials due to their limited corrosion rate and reduce the risk of second surgery to remove the implants. In bone mineralization magnesium plays an important role; its density and mechanical properties (density: 1.8–2.0 g cm⁻³; E-modulus: 7–30 GPa; ultimate bearing strength: 164–600 MPa) are very nearer to human bones [4]. Magnesium alloy ZK60 with elemental composition: wt.% (Mg-94, Zn-4.8–6.2, Zr ≥ 0.45) is also a good
choice for bio-implant material due to its density and E-modulus values (1.83 g cm$^{-3}$, 44.8 GPa) [5–7]. Here, the E-modulus value is very important; it helps to decrease the stress shielding which is often not observed in other metallic implants.

In physiological pH magnesium implants degrade randomly due to corrosion process [8]. Fast corrosion reduces the mechanical properties and causes premature fracture and healing complications [9]. To overcome such type of complications, alloy manufacturing and surface modification by biocompatible materials [10,11] are very helpful. Alloy manufacturing is a primary tool for corrosion prevention and composition can be adjusted by suitable concentration of other elements such as aluminium, calcium, silicon, zinc, zirconium and rare earth metals (Ce, Nd, Sm, Gd, Dy, Y) [12]. Nowadays, researchers are emphasizing on surface modification to control the corrosion process through electrochemical treatment (anodic oxidation), alkali heat treatment, conversion coating, microarc oxidation, spurtting-spinning coating and electrophoretic deposition (AC-EPD) [13–17]. Electrophoretic deposition is most promising among these techniques because it is simple and cost effective and is also applicable to implants with different shapes [18]. Through the AC-EPD process, more adhesive microstructural layers can be possible with no side reactions. Alcoholic media, as electrolyte for electrophoretic deposition, is helpful to reduce the electrolysis of water and increases the range of voltage for investigation. Moreover, the deposition of microstructural layers by the AC-EPD can be possible at room temperature without the production of toxic by-products. The AC-EPD has great potential for future nanocomposite coatings of biomedical devices, electronics, energy storage and harvesting devices, sensors and other surface modification applications. There are different parameters, such as voltage, frequency, wave function, distance, time and concentration of electrolyte, playing a decisive role to finalize a bubble-free homogeneous AC-EPD coating. A constant moderately applied voltage with high frequency is promising for uniform deposition as compared to high voltage and low frequency. Different wave functions are important for the kinetic movement of charge particles, which enhance the synergistic effect of deposition. Concentration of electrolyte and distance between the electrodes and duration of deposition process are linearly effective for mass density transfer for deposition during the initial time [19–22].

Natural polymers, such as chitosan and gelatin, are good candidates for the fabrication and matrix preparation of biomaterials, due to their biocompatibility and biodegradability. There single use in biomedical applications is often not fulfilling the desired requirements, such as corrosion rate, bioactivity and mechanical properties. To fulfill these requirements several types of bioactive inorganic materials are used with biopolymers, such as micro- or nanoparticles of biocompatible metal oxides [23–28]. In well-known bioactive inorganic materials, bioactive glasses (BG) are promising metal oxides; they can be used as inorganic fillers in different biopolymer blends and composites. Bioactive glass not only increased the mechanical properties of the composite but also enhanced the bone repairing and tissue regeneration around the implant sites [29]. These types of biopolymer/BG composites show excellent mechanical and osteoconductive properties [30]. It is also observed that corrosion-resistant property of synthetic polymer coatings is enhanced by the addition of zinc oxide (ZnO) and ceria (CeO$_2$) nanoparticles [31,32]. During the degradation process, nanoparticles of CeO$_2$ stabilize the corrosion products so that the corrosion process is inhibited locally [32]. Furthermore, these types of nanoparticles in coating materials are also important for antibacterial activities, bone mineralization, radical scavenging activities and self-healing processes [33–36]. Suspension composition, AC-EPD parameters and the type of substrate play an important role to improve corrosion-resistant coating. The current work reports corrosion-resistant biocompatible coatings (CS–G–BG–ZnO/CeO$_2$) on ZK60 through modified AC-EPD parameters. We believe that such type of surface modification of ZK60 for improved corrosion resistance has not yet been reported, as obvious from the previous literature.

2. Materials and methods

2.1. Materials

A disc-type magnesium alloy ZK60 with composition (wt%): (Mg-94.05, Zn-5.5, Zr-0.45) was used with surface area (2 cm$^2$) for coating process. As coating materials, chitosan (degree of deacetylation 75–85%, Sigma-Aldrich) and gelatin (Type-B, from bovine skin, Sigma-Aldrich) biopolymers with bioactive glasses BG (a,b) powders with the same composition, (SiO$_2$-53, CaO-20, Na$_2$O-23, P$_2$O$_5$-4), but preparation method was different: (a) milled at 1500°C, (b) calcinated at 600°C [37] and nanoparticles of ZnO and CeO$_2$ with particle size (\(<100\) nm) (Sigma-Aldrich) are used.

2.2. Suspension preparation

Biopolymer–BG composite suspensions were prepared for all experiments. In ultrapure water (Milli-Q, Merck Millipore) and acetic acid solution (99–100%, Chem-Lab), chitosan and gelatin were dissolved separately. Then these solutions were mixed and a required amount of absolute ethanol (99–100%) was added to avoid the bubble formation of hydrogen gas during the electrolysis of water [34]. After that, powder of BG was dissolved in the above suspension and again
Table 1. Composition of suspensions used for ZK60 coatings through the AC-EPD.

| Suspensions | Chitosan (g L⁻¹) | Gelatin (gL⁻¹) | BG a (gL⁻¹) | BG b (gL⁻¹) | ZnO (gL⁻¹) | CeO₂ (gL⁻¹) |
|-------------|-----------------|---------------|------------|------------|-----------|----------|
| 1           | 0.8             | 0.8           | –          | 1          | –         | –        |
| 2           | 0.8             | 0.8           | –          | 1          | 0.6       | –        |
| 3           | 0.8             | 0.8           | 1          | –          | –         | 0.6      |

stirred for 30 min to make the suspension more homogeneous. For nanoparticle-modified coatings, biopolymer–BG suspensions were further utilized and calculated quantity of nanoparticles (ZnO/CeO₂) was added and again stirred for 30 min. The pH of all the suspensions was maintained at 5.5, to make the net positively charged suspension for cathodic deposition [38]. The summary of the best finalized suspensions based on AC-EPD coatings results is present in Table 1.

2.3. Coating preparation

Through AC-EPD parameters different coatings were prepared. A disc of Mg-alloy ZK60 was clipped as the cathode in a cylindrical EPD cell (Ø = 16.2 mm) with stainless-steel as the anode having an inter-electrode distance of 10 mm. Under voltage-controlled conditions all AC-EPD coatings were done at room temperature. An asymmetric triangular wave function having asymmetry of 3 was used as AC signal. A superimposed DC off-set was also applied with high amplitude AC signal in the same direction to the high amplitude peak significantly participated in the parameters and effectively produced a crack-free coating.

Finalized AC-EPD parameters were set as asymmetric triangular wave function (Figure 1(b)) with inter-electrode distance 10 mm; peak-to-peak voltage 35 V, Frequency 300 Hz, deposition time 8 min, and DC off-set (+2 V) the same direction to the high amplitude peak are depicted in Table 2.

3. Results and discussion

3.1. Optimization of AC-EPD parameters

Through AC-EPD parameters different compositions of suspensions were investigated for ZK60 coatings and among them three suspensions were finalized based on bubble-free coatings (Table 1). These suspensions were finalized through modified AC-EPD cell (Figure 1(a)) in 80% ultrapure Milli-Q water (MQ, Merck Millipore), absolute ethanol (99–100% purity, Fisher Chemical) and acetic acid solution (99–100% p. CHEM-LAB, NV) with volume ratio 80:19:1. The pH of every suspension was maintained at 5.5 prior to further experimentation.

In all AC-EPD coatings, ZK60 substrate was connected as cathode to reduce the risk of oxidation during electrochemical reactions. Finally, AC-EPD coatings showed that a superimposed DC off-set (2 V cm⁻¹) in the same direction to the high amplitude peak significantly participated in the parameters and effectively produced a crack-free coating.

Table 2. Finalized AC-EPD optimal parameters for composite coatings on ZK60.

| Peak-to-peak voltage (V cm⁻¹) | DC off-set (V cm⁻¹) | Frequency (Hz) | Duration (min) |
|-------------------------------|--------------------|---------------|---------------|
| 35.00                        | 2.00               | 300           | 8             |
nanoparticles of ZnO in the coating layer enhanced the overall coating morphology with smooth surface coverage (Figure 2(b)). Furthermore, Figure 2(b) shows that, on the top of the biopolymer layer, a mixture of ZnO and BG b is present. The SEM image of coated ZK60 with suspension 3 showed that BG a and CeO$_2$ nanoparticles mixture was also distributed across the coated layer (Figure 2(c)) also having no cracks and pits. The SEM analysis showed that overall BGs and nanoparticles of ZnO/CeO$_2$ in all coatings were equally distributed on the coating layer and more dominantly observed in the case suspension 2. In all coated samples, the maximum surface area of ZK60 is covered by hybrid coatings and EDX graphs also confirmed the presence of coated layer elements, Figure 2 (a’–c’).
FT-IR spectra (Figure 3) of coated samples of ZK60 showed that a combination of four peaks was observed from 1664 to 1507 cm\(^{-1}\). Peaks at 1559, 1507, 1457 cm\(^{-1}\) correspond to amides (1–3) of gelatin and one at 1664 cm\(^{-1}\) associated with imine (–N\(=\)CH–) bond due to self-crosslinking of chitosan during the AC-EPD. The last peak of self-crosslinking of chitosan can be produced by the amine (–NH\(_2\)) and carbonyl (–C\(=\)O) group present in the chitosan chain by the dehydration during the AC-EPD process [39]. Crosslinking of a polymer like chitosan can help to improve the attachment of coated layer with the substrate [40].

Corrosion process can be controlled by thick, compact and crack-free coatings [35]. The coated surface with suspension 2 was further subjected to check the coating thickness by the SEM-based surface profilometry test which is equal to 19.5 μm (Figure 4).
3.3. Corrosion investigations

Generally, the homogeneity and coating thickness of a developed coating layer described its corrosion inhibition efficiency. Corrosion protection efficiency of coated ZK60 samples was evaluated by potentiodynamic polarization curves through Tafel extrapolation.

The potentiodynamic polarization curves presented a positive shift towards less negative value in corrosion potential ($E_{corr}$) and indicated that all suspensions covered the maximum area of coated ZK60 (Figure 5). The corrosion results, derived directly from polarization curves through Tafel region extrapolation in Ringer’s solution of bare and coated samples, are presented in Table 3. Normally, cathodic polarization curve corresponded to the hydrogen evolution reaction during water reduction and anodic polarization curve, due to the formation of Mg$^{2+}$ ions during the dissolution of Mg in corrosive media [38]. Corrosion results confirmed that hybrid coating created a barrier between the bare substrate and corrosive media and significantly increased corrosion potential ($E_{corr}$) and decreased corrosion current density ($i_{corr}$) values.

Furthermore, the value of anodic Tafel slopes ($\beta_a$) of bare ZK60 (378.9 mV dec$^{-1}$) decreases with all suspensions (1–3) from 168.3 to 123.4 mV dec$^{-1}$. This indicates that maximum surface area of bare ZK60 will be covered by coating and the oxidation process will be further inhibited. Corrosion results also confirmed that corrosion process was inhibited more significantly with suspension 2 ($i_{corr} = 1.39 \mu A cm^{-2}$) than suspension 3 ($i_{corr} = 1.84 \mu A cm^{-2}$). The corrosion results with suspension 2 could be described based on amine group (–NH$_2$) present in polymers (chitosan and gelatin) and small size of BG b with a combination of ZnO also help to make a hybrid positive charge composite coating for cathodic deposition. In the polymer chain NH$_2$ group supports to neutralize the pH during corrosion process like conversion of NH$_2$ to NH$_3^+$ in acidic media and NH$_3^+$ to NH$_2$ in basic media which is further helpful to heal/repair of corroded sites through passivation and enhances the mobility of polymeric chains [41]. It is also reported that ZnO-modified coatings contributed effectively to control the electrolyte diffusion, enhanced the antibacterial properties and inhibited the corrosion process [35].

The SEM images of bare and coated samples of ZK60 after 10 min immersion in Ringer’s solution are presented in Figure 6. ZK60 surface indicated that it is oxidized in Ringer’s solution and produced more Mg(OH)$_2$ (EDX graph Figure 6). The coated surface with suspension 1 is very less affected by Ringer’s solution and small crystals of NaCl are deposited on the coated surface (Figure 6(a)). Figure 6(b) indicates that there is no prominent difference on the surface of coated ZK60 with suspension 2, after contacting with Ringer’s solution, which confirmed compact, homogeneous and less affected coating in the presence of ZnO and BG b particles. The similar behaviour of SEM image in Ringer’s solution was observed in suspension 3 (Figure 6(c)), with nanoparticles of CeO$_2$. But the corrosion results showed that this suspension inhibited the corrosion process lesser than suspension 2. Finally, EDX point analysis graphs confirmed the presence of corrosion products (Mg(OH)$_2$, NaCl) and coated elements on the coated surface after corrosion test, as shown in Figure 6 (a’–c’).

Overall, results showed that the biopolymer (chitosan, gelatin) composite coatings are feasible by AC-EPD and created a metal–ligand interaction to protect the substrate from further degradation. In AC-EPD parameters DC signal with asymmetric triangular wave function also helps for protective coating. Finally, ZnO nanoparticle-modified biopolymer/BG coating showed...
a potent corrosion protection capability as compared to CeO₂. Furthermore, there is a need to investigate such type of coating for cytocompatibility and osseointegration properties.

4. Conclusions

The surface morphology of all coated samples has indicated that the first layer is formed by polymers and the second layer by bioactive glass-ZnO/CeO₂. The best-optimized AC-EPD parameters for coating of ZK60 are (Voltage = 35 V, Freq. = 300 Hz, DC off-set = 2 V, t = 8 min. Distance = 10 mm). All suspensions showed promising corrosion resistance towards ZK60 with low $i_{\text{corr}}$ values. Among all, suspension CS₀.₈–G₀.₈–BG(b)₁–ZnO₀.₆ (2) gives excellent corrosion resistance with lowest $i_{\text{corr}}$ of 1.39 $\mu$A cm⁻². Overall, for corrosion protection of ZK60, ZnO nanoparticles are more useful than CeO₂. These types of hybrid coatings are beneficial for corrosion protection and also biocompatible for implant devices.

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