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In vitro corrosion and antibacterial performance of polysiloxane and poly(acrylic acid)/gentamicin sulfate composite coatings on AZ31 alloy

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ABSTRACT

An investigation on the corrosion resistance and antibacterial properties of polyelectrolytes and polysiloxane coatings on magnesium alloy with gentamicin was made. The microstructure and composition of the multilayer coatings were characterized by using Fourier transform infrared spectroscopy, X-ray diffractometer and scanning electron microscopy. The analysis of electrochemical measurement in HBSS suggested that the composite coatings improved the corrosion resistance of AZ31 alloy. Finally, the result of plate-counting method demonstrates the effective antibacterial properties of the functionalized substrates. Thus, it can be concluded that the multilayer-treatment reported here is a versatile approach to develop antibacterial and anticorrosion coatings on magnesium implants.

1. Introduction

Nowadays, stainless steels, titanium and titanium alloys are the most extensively used artificial implant materials in orthopedic fields [1–3]. Compared with these permanent metallic materials, biodegradable magnesium (Mg) alloys show several advantages, such as low density, high specific strength and avoiding second surgery for implant removal [4,5]. However, the poor corrosion resistance limits the applications of Mg alloys [6]. Thus, numerous investigations on improving the corrosion resistance of Mg alloys have been carried out. The strategies include elemental alloying, post treatment and surface modification [7–10].

On the other hand, the antibacterial properties are also necessary for Mg implant when exposed to the living tissue [11]. The formation of bacterial biofilm at the implant/tissue interface may lead to persistent infections around implants [12]. Thus, several methods have been investigated to fabricate a new class of coating to suppress the bacterial growth [13,14]. An effective way to reduce the implant-associated infections would be the local delivery of antibiotics [15,16]. Gentamicin is a simple water soluble aminoglycoside that kills bacterial cells by inhibiting their protein synthesis; it has been used in the treatment of severe infections caused by both Gram-positive and, especially, Gram-negative bacteria [17–19].

Layer-by-layer (LbL) assembly opens new opportunities for fabricating multilayer thin films with controlled architecture and composition. A general LbL deposition is achieved using oppositely charged materials (polymers, proteins, nanoparticles, etc.) that deposit via electrostatic interactions [20]. Many kinds of building blocks can be fabricated into multilayer films in a designed way, thus the obtained multilayer nanonetwork could exhibit tunable corrosion protection and antibacterial properties because of the nature and versatility of the polyelectrolyte complex [21–23].

For corrosion protection purposes, polysiloxane-based hybrid materials are of particular interest due to their dense structure of siloxane cross-linking by a condensation process [24,25]. And these materials have a history of medical uses in many aspect [26]. Depending on the type of silanes used as monomer, some functional groups of the polysiloxane side chains can react with polymer films to form chemical covalent or ionic bonds, promoting e.g. paint adhesion, high oxidative stability and excellent thermal stability [27]. The protective characteristics of polysiloxane films have been reported in various studies [28–30]. On the other hand, polysiloxane matrices were also considered as promising materials for the development of functionalized bioactive hybrids. Chisholm's work [31] shows that polysiloxane could be used to construct surface coatings containing pendant levofloxacin to combat

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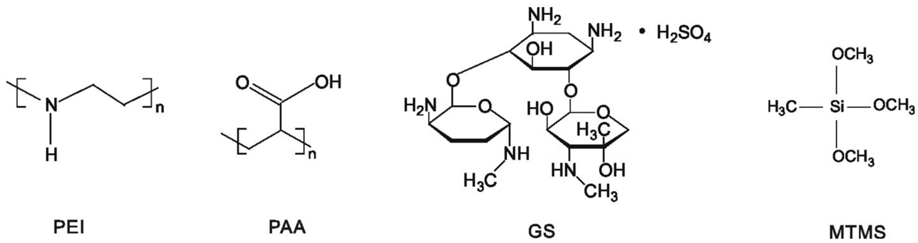

Fig. 1. Chemical structures of PEI, PAA, GS and MTMS.

implanted device related infection; The work of Vallet-regi [32] shows that the polysiloxane hybrid materials are a promising alternative in bone tissue regeneration because of their tailored in vitro bioactivity and degradability; and some bioactive materials containing polysiloxanes have been developed for bone tissue regeneration [33,34].

In this study, getamicin, poly(acrylic acid) and polysiloxane were successfully introduced on Mg alloy surfaces to improve their antibacterial activity and corrosion resistance using a LbL method and polymerization process. The blending of siloxane modifier with LbL systems has, to the knowledge of the authors, never been reported before. And the getamicin and poly(acrylic acid) used here have been proved no apparent cytotoxicity in P.T. Hammond's work [35].The physicochemical properties of the composite films were characterized using different analytical techniques. The corrosion performance and antibacterial properties of the resultant substrates were investigated using electrochemical techniques and plate-counting method.

2. Material and methods

2.1. Materials and chemicals

The as-extruded AZ31 alloy used has nominal chemical composition (wt.%): Al 2.5–3.0, Zn 0.7–1.3, Mn > 0.20 and balanced Mg. Poly(acrylic acid) (PAA, MW = 800–1000), poly(ethyleneimine) (PEI, MW = 600) and methyltrimethoxysilane (MTMS) were purchased from Qingdao Jingke Chemical Reagent Co., Ltd. Gentamicin sulfate (GS, MW = 575.67) was purchased from Chengdu Aike Chemical Technology Co., Ltd. Fig. 1 shows the chemical structures of PEI, PAA, GS and MTMS used in this work. All chemicals were of analytical grade and distilled water was used throughout to prepare the solutions and wash the samples.

2.2. Preparation of composite coatings

The AZ31 alloy (20 mm × 20 mm × 3 mm) used as substrates were ground with SiC papers up to 1500 grit, washed with ethanol to remove excess impurities and dried in air. Prior to the assembly, the substrates were treated in 1 M NaOH solution for 30 min at room temperature and then rinsed in distilled water and dried by warm air. The hydroxide layer on AZ31 surface was expected to promote surface condensation of PEI.

LbL coatings were created via a dip-coating method. The substrates were first immersed into PEI solution (5 g/L) for 30 min to obtain a precursor layer with stable positive charges. For the $(PAA/GS)_{20}$ multilayer film, the PEI-primed substrates were alternately dipped in PAA (pH = 7.0) and GS solutions at 1 g/L for 5 min. After each deposition step, the substrates were thoroughly rinsed with distilled water and dried with air. The deposition of each bilayer containing oppositely charged polymers, positive GS and negative PAA, was repeated until the desired $(PAA/GS)_{20}$/Mg samples were obtained.

After that, a mixture of MTMS, ethanol and water (3:10:20, v/v/v) was aged 20 min at 40 °C in the water bath. The $(PAA/GS)_{20}$/Mg samples were immersed in the mixture for another 2 h and rinsed by ethanol. After the thermal treatment at 120 °C for 2 h, the PMTMS/$(PAA/GS)_{20}$ multilayer film was constructed.

2.3. Surface characterization

The surface and cross-section morphologies of the samples were observed by means of scanning electron microscopy (SEM, Nova NanoSem 450, USA) equipped with energy-dispersive X-ray spectroscopy (EDX). The phase composition of the samples were analyzed by means of X-ray diffractometer (XRD, Model D/max 2500PC Rigaku, Japan), with a Cu target at a scanning rate of 8°/min. The diffraction patterns were

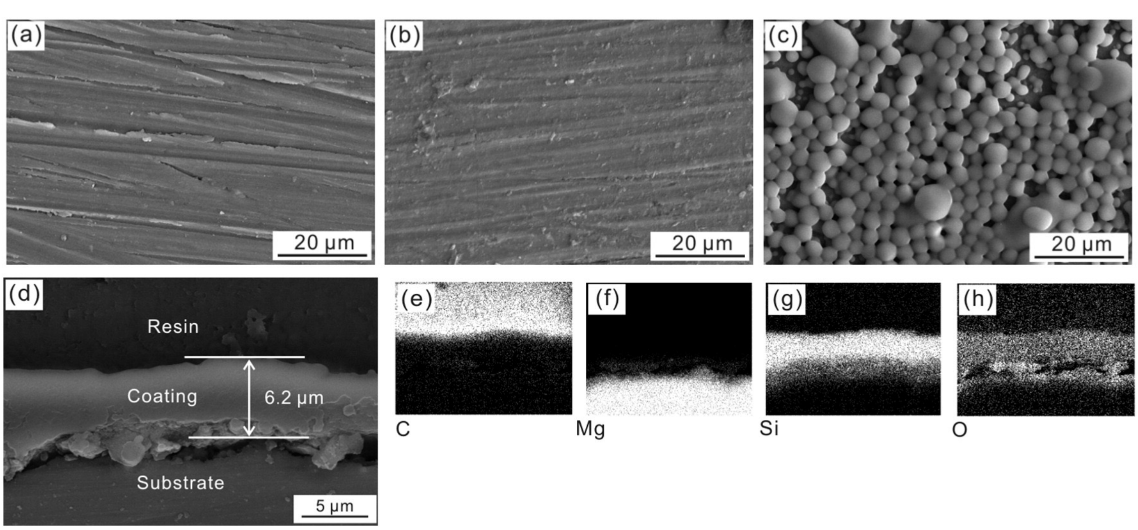

Fig. 2. SEM images of (a) AZ31 alloy, (b) $(PAA/GS)_{20}$/Mg and (c) PMTMS/$(PAA/GS)_{20}$/Mg, (d) cross-sectional SEM image and (e–h) element mapping of PMTMS/$(PAA/GS)_{20}$/Mg.