Materials Science and Engineering C 70 (2017) 141–147

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Mechanical and degradation properties of biodegradable Mg strengthened poly-lactic acid composite through plastic injection molding

Muhammad Shoaib Butt [a,b], Jing Bai [a,b,*], Xiaofeng Wan [c], Chenglin Chu [a,b], Feng Xue [a,b], Hongyan Ding [d], Guanghong Zhou [d]

[a] School of Materials Science and Engineering, Southeast University, Jiangning, Nanjing, 211189, Jiangsu, China
[b] Jiangsu Key Laboratory for Advanced Metallic Materials, Jiangning, Nanjing 211189, Jiangsu, China
[c] School of Mechanical Engineering, Nantong University, Nantong 226019, Jiangsu, China
[d] Jiangsu Provincial Key Laboratory for Interventional Medical Devices, Huaiyin Institute of Technology, Huaian 223003, Jiangsu

ARTICLE INFO

Article history:
Received 10 May 2016
Received in revised form 15 July 2016
Accepted 20 August 2016
Available online 25 August 2016

Keywords:
Poly-lactic-acid
Magnesium alloy
Degradation
Coating
Composite rod
Plastic injection molding

ABSTRACT

Full biodegradable magnesium alloy (AZ31) strengthened poly-lactic acid (PLA) composite rods for potential application for bone fracture fixation were prepared by plastic injection process in this work. Their surface/interfacial morphologies, mechanical properties and vitro degradation were studied. In comparison with untreated Mg rod, porous MgO ceramic coating on Mg surface formed by Anodizing (AO) and micro-arc-oxidation (MAO)treatment can significantly improve the interfacial binding between outer PLA cladding and inner Mg rod due to the micro-anchoring action, leading to better mechanical properties and degradation performance of the composite rods.With prolonging immersion time in simulated body fluid (SBF) solution until 8 weeks, the MgO porous coating were corroded gradually, along with the disappearance of original pores and the formation of a relatively smooth surface. This resulted in a rapidly reduction in mechanical properties for corresponding composite rods owing to the weakening of interfacial binding capacity. The present results indicated that this new PLA-clad Mg composite rods show good potential biomedical applications for implants and instruments of orthopedic inner fixation.

1. Introduction

Recently, full-biodegradable materials, as medical implants into human body, have been studied widely due to their advantages in eliminating the adverse effects of removing implants by second surgery or permanent remaining of implants in body. The most common biodegradable polymers in medical applications are the poly(α-hydroxyacid)s, including polyglycolic acid (PGA),polylactic acid (PLA), and polydioxanone (PDS). Poly-lactic acid offers unique features of biodegradability, biocompatibility, thermoplastic and process ability that present potential applications as medical industry. Unfortunately, the mechanical properties of most investigated PLA were poor, and they could not effectively meet the requirements of human bones, limiting its use in certain applications. Many reinforced materials such as calcium carbonate, chitosan, titanium nanoparticle, bioglass, and magnesium alloy [1–5] have been investigated to overcome these problems.

Among them magnesium based reinforced are more attracted because of low density, high specific strength and good biocompatibility. They are mostly studied in the development of cardiovascular stents, bone fixation materials and porous scaffolds for bone repair. However, the application of Mg alloys in clinical practice is seriously challenged by their fast corrosion rates and insufficient mechanical properties, especially when exposed to aggressive environments such as those including chloride [Cl^-] ions. In addition, strong affinity of localized corrosion makes the corrosion of magnesium alloy frequently inhomogeneous. Similarly, the large corrosion rate during the initial implantation stage lead to high level of pH value surrounding the human tissues and rapid decline of their mechanical strength, both of which are undesired for the healing of the implanted area [6].

The corrosion resistance and degradation rate of magnesium alloys can be controlled by surface modification [7]. A variety of surface modification techniques have been proposed, e.g. electro-chemical deposition [8], conversion coatings [9] laser surface alloying [10], alkaline treatment [11], micro-arc oxidation [12], anodizing [13] and sol gel coating [14]. Among them anodizing (AO) and micro-arc-oxidation (MAO) is convenient and cost saving. Shi et al. [15] reported rough and anisotropic distribution of micrometer pores in their anodized

* Corresponding author at: School of Material Science and Engineering, Southeast University, Jiangning, Nanjing 211189, Jiangsu, China.
E-mail address: baijing@seu.edu.cn (J. Bai).

http://dx.doi.org/10.1016/j.msec.2016.08.051
0928-4931/

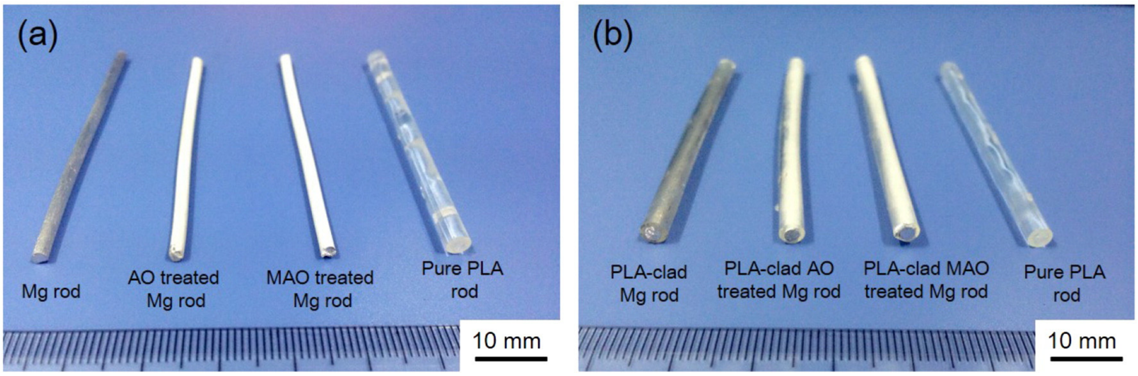

Fig. 1. Photographs of prepared samples: (a) Mg rod, AO and MAO treated Mg rods, and pure PLA rod. (b) PLA-clad Mg rod, PLA-clad AO and PLA-clad MAO treated Mg rods, and pure PLA rod.

coatings. Likewise, many researchers have examined that the pore characteristics of anodic film are the basic concern in perfect evaluation of its corrosion performance [16–17].Most notably the MAO ceramic coatings have characteristics to improve the wear resistance, corrosion resistance and high interfacial bond strength with the substrates [18].

In this paper, matrix material, polylactic acid (PLA) is reinforced with different Mg rods including untreated, AO and MAO surface treated, to prepare the composites rods. These composite rods were fabricated by plastic injection molding (PIM) process which offers an interesting manufacturing route for multi-functional components in a few processing steps. It can offer: savings in cost and weight, consolidation of part, better dimensional stability, high component integration, and faster assembly as a result of there being fewer parts. The surface and interface microstructures of these experimental composite rods during degradation period were characterized, and their mechanical and degradation properties were also evaluated.

2. Materials and methods

2.1. Coating preparation

The AZ31 (96%Mg, 3%Al and 1%Zn all in wt.%) magnesium alloy rod with diameter of 2.44 mm, height 60mmwere first prepared by smelting, casting, hot extrusion, wet drawing and annealing. The AO treatments were performed at a constant current density of 3 A/cm^{2}in an electrolyte containing 20 g/L NaOH, 24 g/L Na_2SiO_3,16 g/L $Na_2B_4O_7$ and 4.8 g/L $C_6H_8O_7.H_2O$.The Mg rod was used as the working electrode and stainless steel as the counter electrode. Afterwards, the Mg rod were detached and washed with deionized water. The MAO treatments were performed at constant current density 3 A/cm^{2}the magnesium alloy acting as the anode and stainless steel sink as the cathode. The samples were detained and suspended in the electrolyte during MAO at temperature of 20–40 °C. After MAO for a predetermined duration, the specimen was removed and washed with deionized water. The macroscopic photos of original Mg rod and surface treated Mg rods by AO and MAO processes are shown in Fig. 1(a).

2.1.1. Plastic injection molding

The Mg rods with and without surface coating were used to fabricate PLA-clad Mg composite rods by PIM process. The PLA particles (Shenzhen Esun Industrial Co., Ltd., China) with a density of 1.24 g/cm^3 and a viscosity average molecular weight of 60,000 g/mol were first introduced into hopper. Barrel made of steel cylinder to withstand the pressure and temperature involved in melting the PLA particles. After PLA particles were completely melted at the set temperature, the entire screw moves forward and push the molten PLA into the mold where Mg rod was located in the middle of the lower die in advance. The PIM parameters are given in Table.1.The macroscopic photos of three kinds of composite rods are shown in Fig.1(b).The PIM parameters are given in Table.1.The macroscopic photos of three kinds of composite rods are shown in Fig. 1(b).

A simple schematic showing the preparation process of the present composite rod by PIM is illustrated in Fig. 2 with the diameter of the present Mg and composite rod. Pure PLA specimens, as shown in Fig. 1(a) and (b), were also prepared under the same conditions and parameters in Table 1 as controls.

2.2. Microstructures characterization

The surface/interface morphology and thickness of the experimental rods were examined by FEI SIRION field-emission scanning electron microscope (SEM). The elemental composition of the coatings was determined by energy-dispersive X-ray spectroscopy (EDS) equipped on SEM. The X-ray diffractometer (XRD) was used to determine the phase structures of the coatings using the following conditions: Cu Kα radiation, wavelength of 0.15418 nm, acceleration voltage of 40 kV, and current of 30 m/A, and scanning step of 0.02 (C°)/step and scanning speed of 2 s/step. The measured angle error was less than ±0.01.

2.3. Determination of mechanical properties

The mechanical properties of composite rods were determined through tensile tests using CMT4503 universal testing machine.The tensile tests were carried out at a rate of 1 mm/min until the experimental sample failed.

2.4. Immersion tests

In immersion tests for both coated and uncoated samples were placed in the polyethylene bottle with 15 ml of SBF and place in the thermostat oscillation slot at a temperature of (37.5 ± 0.5)°C. The SBF was replenished once a day. The evolved hydrogen volumes were

Table 1
Plastic Injection parameters to fabricate PLA-clad Mg composite rods.

Injection speed	Temperature	Back pressure	Back pressure time	Cooling time	Cylinder temperature
20 mm/s	185 °C	750 bar	3 s	10s	200–195–190–185–35 °C