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Biodegradable poly-lactic acid based-composite reinforced unidirectionally with high-strength magnesium alloy wires

X. Li [a, b], C.L. Chu [a, b, *], L. Liu [a, b], X.K. Liu [a, b], J. Bai [a, b, *], C. Guo [a, b], F. Xue [a, b], P.H. Lin [a, b], Paul K. Chu [c]

[a] *School of Materials Science and Engineering, Southeast University, Nanjing 211189, China*
[b] *Key Laboratory for Advanced Metallic Materials, Southeast University, Nanjing 211189, China*
[c] *Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China*

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ABSTRACT

Biodegradable poly-lactic acid (PLA) – based composites reinforced unidirectionally with high-strength magnesium alloy wires (MAWs) are fabricated by a heat-compressing process and the mechanical properties and degradation behavior are studied experimentally and theoretically. The composites possess improved strengthening and toughening properties. The bending strength and impact strength of the composites with 40 vol% MAWs are 190 MPa and 150 kJ/m^2, respectively, although PLA has a low viscosity and an average molecular weight of 60,000 g/mol. The mechanical properties of the composites can be further improved by internal structure modification and interface strengthening and a numerical model incorporating the equivalent section method (ESM) is proposed for the bending strength. Micro arc oxidization (MAO) of the MAWs is an effective interfacial strengthening method. The composites exhibit high strength retention during degradation and the PLA in the composite shows a smaller degradation rate than pure PLA. The novel biodegradable composites have large potential in bone fracture fixation under load-bearing conditions.

1. Introduction

Orthopedic implants play important roles in restoring the normal activity and improving the quality of life of millions of people. Orthopedic implants are commonly categorized as reconstructive or fracture management ones. One desirable characteristic is the ability to degrade spontaneously in the physiological environment to avoid a second operation for removal and reduce the risk of local inflammation which may appear after long-term implantation of non-biodegradable implants [1–3]. Poly-lactic acid (PLA), one of the naturally degradable materials having excellent biological properties and versatility, is used in commercial applications [4–7]. However, the mechanical properties of pure PLA cannot meet the stringent requirements of weight-bearing bone fracture fixation devices. One reinforcing technique is to orient the chains of PLA [8–10]. For instance, Weiler et al. [8] used a solid-state extrusion technique to prepare PLA rods and the bending strength and modulus of the rods were 200 MPa and 9 GPa, respectively, compared to 140 MPa and 5 GPa, respectively, for rods prepared by conventional injection molding. Another effective approach is to incorporate filler materials such as bioactive glass, bioceramics, and fibers into PLA. Shikinami et al. [11] reported a PLA-based composite composed of high molecular weight poly-L-lactic acid (PLLA) as the matrix and 40 wt% hydroxyapatite (HA) as the reinforcement. This composite prepared by a forging technique had an initial bending strength of 270 MPa and it remained over 200 MPa for up to 24 weeks after soaking in a phosphate-buffered saline (PBS) at 37 °C. Addition of HA fillers can suppress heterogeneous degradation which has been reported to be related to the acidic degradation products from PLA resulting in a local low pH environment and probable bone resorption [12,13]. Besides HA, many other filler materials such as calcium carbonate [14], chitosan [15], titania nanoparticle [16], bioglass [17], and magnesium alloy fibers [18] have been investigated to overcome the low pH problem and among them, magnesium-based fillers which are themselves biodegradable have attracted much interest.

Magnesium is an essential element and plays an important role in human metabolism by participating in protein synthesis and

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* Corresponding authors. School of Materials Science and Engineering, Southeast University, Nanjing 211189, China. Tel./fax: +86 25 52090689.
E-mail addresses: clchu@seu.edu.cn (C.L. Chu), baijing@seu.edu.cn (J. Bai).

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activating some enzymes [19]. The biocompatibility of magnesium and its alloys has been investigated and verified [20–23]. In addition, the fracture toughness of magnesium is greater than that of most bioceramics and its mechanical strength is better than that of biopolymers. The elastic modulus and density are also close to those of natural cortical bones. These advantages suggest potential use of Mg and Mg alloys in biodegradable applications [24–27] as well as reinforcement for ceramic [28] and polymeric [18] implants. Currently, the major drawback of magnesium and its alloys is the low corrosion resistance and production of hydrogen in the corrosion process [29–31]. Much effort has been made to overcome the hurdles by for example, alloying [32–34] and surface treatment such as deposition of protective coatings [35–38]. Alkaline degradation of magnesium by adjusting the local pH of the immersion medium has been reported [18] and this may provide a new way to solve the low pH problem associated with long-term degradation of PLA.

In this work, low-molecular-weight PLA-based biocomposites are reinforced unidirectionally with high-strength Mg alloy wires (MAWs) and studied experimentally and theoretically by the finite element method (FEM). Micro arc oxidization (MAO) is conducted on the MAW reinforcements to strengthen the composites. Accelerated and regular degradation tests are performed to assess the degradation behavior with the objective of developing novel biodegradable composites for load-bearing applications.

2. Materials and methods

2.1. Materials

MAWs composed of AZ31 (96% Mg, 3% Al and 1% Zn by weight) with a diameter of 0.3 mm were fabricated by continuous smelting, casting, hot extrusion, wet drawing, and annealing. PLA particles with a density of 1.24 g/cm^3 were purchased from Shenzhen Esun Industrial Co., Ltd., China. The viscosity average molecular weight ($\overline{M}v$) of PLA was calculated to be 60,000 g/mol using the Mark-Houwink-Sakurada formula [39] according to the intrinsic viscosity at 25 °C using an Ubbelohde viscometer. The crystallinity and glass transition temperature of the PLA were 38% and 64 °C based on differential scanning calorimetry (DSC) [11].

2.2. Methods

2.2.1. Materials preparation

The MAW contents in the composites were predetermined to be 5, 10, 20, and 40 vol% (mean volume fraction). The dimensions of the samples were 120 mm × 12 mm × 2 mm (length × width × height) and the approximate amounts of MAWs were 16, 34, 68, and 136 to obtain mean volume fractions of 5, 10, 20, and 40 vol%, respectively. The true volume fraction of the MAWs was calculated by dividing the real volume of the MAWs by the volume of the specimen and the results are shown in Table 1. For a mean volume fraction of 5 vol%, the true volume fraction was 4.7 vol%. The composite specimens were fabricated by the lamina stacking method. The dimensions of the lamina were 120 mm × 12 mm × 0.4 mm. Two kinds of laminas including MAW-containing laminas and pure-PLA laminas were utilized to ensure the total thickness of the laminas to be about 2 mm. The amount of the MAW-containing laminas in the different composites and corresponding quantity of MAW per lamina are shown in Table 1. The MAWs in each lamina were uniformly distributed and the MAW-containing laminas were symmetrically distributed about the middle plane of the stack along the height direction.

Preparation of the composite is schematically illustrated in Fig. 1. The PLA particles were dissolved in chloroform. The MAWs were directionally arranged and PLA/chloroform solution was poured to overlay the directional MAWs, followed by evaporating in air for 12 h to form the thin pre-impregnating composite laminas. The pure-PLA laminas were fabricated by the same process. Afterwards, the laminas were stacked in a mold cavity. The stack was heated and compressed for 15 min at 5 MPa and 190 °C. Finally, the stack was cooled naturally to room temperature along with the mold in an oven at 5 MPa. After demolding, the plate specimens with the predetermined dimensions of 120 mm × 12 mm × 2 mm were produced and pure PLA specimens were prepared by the same process as controls. The dissolving process was to further determine the surface morphologies of MAWs in the composite after immersion tests. The composites reinforced with the micro-arc oxidized (MAO) MAWs were fabricated by the same procedures.

Table 1
Characteristics of MAWs/PLA composites.

Mean volume fraction (%)	True volume fraction (%)	MAW-containing lamina numbers	MAW numbers per lamina
Pure-PLA	–	–	–
5	4.7	2	8
10	10	2	17
20	20	4	17
40	40	4	34

2.2.2. Finite element method (FEM)

The theoretical strength of the composite, including the tensile and bending strength, was calculated by the finite element method (FEM) using Ansys software with the implicit solver. The beam element and solid element were, respectively, assigned to MAWs and PLA. The elastic model of PLA and elasto-plastic model of Mg alloy wires were applied. The interfaces between the MAWs and PLA during simulation were theoretically treated implying complete bonding.

2.2.3. Micro arc oxidation

The MAWs were gently washed with acetone, distilled water, and ethanol and ultrasonically cleaned three times. The wires were suspended in an aqueous electrolyte composed of sodium silicate (15 g/L), sodium phosphate (5 g/L), sodium hydroxide (2 g/L), and K_2ZrF_6 (3 g/L) and subsequently processed in the WHD-30 type MAO equipment [40] for 3.5 min. The constant current mode was used and the forward and negative current was 6 A/dm^2. Afterwards, the wires were removed and washed with deionized water.

2.2.4. In vitro degradation tests

The MAWs in the specimens for the *in vitro* degradation tests were pretreated using MAO. The individual samples were placed in 50 mL screw-top plastic bottles and fully immersed in the Sorensen's phosphate-buffered solution (SPB). The SPB was prepared by mixing stock solution A (9.078 g KH_2PO_4 in 1000 mL distilled water) and stock solution B (11.876 g Na_2HPO_4 in 1000 mL distilled water) at a volume ratio of 18.2–81.8. The bottles were kept at a constant temperature of 37 °C for normal degradation or 50 °C in accelerated degradation [41]. The ratio of the solution in milliliters to the mass of the specimen in grams was greater than 30:1. The immersion durations for normal degradation were 7, 14, 28, and 56 days, whereas those for accelerated degradation were 1, 7, 14, and 21 days. The solution was changed every 1 day to keep the pH value at 7.4 ± 0.2. Before the immersion solution was changed, the pH was measured.

The viscosity average molecular weight ($\overline{M}v$) of the PLA during immersion was calculated by the Mark-Houwink-Sakurada formula [39] based on the intrinsic viscosity at 25 °C monitored by the Ubbelohde viscometer. The initial mass (m_0) of the sample with dimensions of 25 mm × 12 mm × 2 mm for the mass loss test was recorded and the final mass (m_t) of the sample after immersion was obtained after drying for 48 h in an oven at 37 °C. The overall percentage mass change (ω) was calculated by the following equation:

$$\omega = ((m_0 - m_t)/m_0) \times 100\%. \quad (1)$$

2.2.5. Determination of mechanical properties

Before the mechanical tests of the composites, the tensile properties of the initial MAWs with a length of 120 mm and PLA with dimensions of 120 mm × 12 mm × 2 mm fabricated by the same fabrication process were determined. The typical tensile curve of MAWs is depicted on the left of Fig. 2. The MAWs show approximately bilinear-plastic deformation under tension and the mechanical properties of the MAWs and PLA for Finite Element Method (FEM) analysis are listed in Table 2.

The fabricated specimens were cut into dimensions of 60 mm × 12 mm × 2 mm, 60 mm × 12 mm × 2 mm, and 30 mm × 12 mm × 2 mm for the bending, impact, and shear tests, respectively conducted on the CMT4503 electronic universal testing machine at room temperature. In order to produce similar wet testing conditions for the immersed specimens according to the literature [9,42], the as-prepared composites were immersed in the SPB solution for 1 h before their mechanical properties were determined. The crosshead speed was, respectively, 5, 2, and 5 mm/min and the Charpy impact test was performed on the unnotched samples using the ZBC impact testing machine, as shown in Fig. 2. The tensile strength (S_t) of the samples in the wire direction was measured. The bending strength (S_b) of the samples was measured by the three-point bending method according to the standard ASTMD790-2010 for a span of 32 mm. The shear strength (S_s) of the composites subjected to transversal shear loading was measured by the dual shear test. The shear test was similar to that used by Weir et al. [41]. The plate sample was fixed and sheared simultaneously on both ends of the crosshead under constant speed control. All the mechanical strength values were the averages of three measurements.

2.2.6. Microstructural characterization

Small pieces of the wires were mounted on stubs using adhesive tapes. The stubs and composites were sputter-deposited with a thin gold layer in an argon atmosphere. The wire and fracture morphology was examined on a Philips XL30 FEG scanning electron microscope (SEM) at an accelerating voltage of 20–25 kV.