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Self-reinforced biodegradable Mg-2Zn alloy wires/polylactic acid composite for orthopedic implants

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ABSTRACT

Biodegradable composite rods with polylactic acid as matrix and Mg-2Zn wires as the reinforcement body were prepared by hot press and hot drawn method in this article. The main purpose is to improve the mechanical properties based on the strengthen and toughness effect of the directionally distributed Mg-2Zn wires in PLA matrix and the improved interfacial bonding strength by MAO treated Mg-2Zn wires as well as the self-reinforcement effect of PLA after hot drawn process. The effect of hot drawn on the orientation, crystallinity and melting temperature changes of PLA were investigated by XRD and DSC method. The relationship between the bending strength and the volume content of Mg-2Zn wires in the composite rods as well as the influence of hot drawn on the mechanical properties were compared and analyzed theoretically. The regularly arrangement of PLA chains after hot drawn is benefit to increase the crystallinity, the elastic modulus as well as the mechanical strength in essence. Theoretical calculation results could provide a reference value and guide us to adjust the Mg-2Zn wires content and prepare the composite rods according to the actual application requirements.

1. Introduction

The biodegradable orthopedic implants with clinical permission mainly focus on polylactic acid (PLA), polyglycolic acid (PLGA) [1] as well as PLA/phosphate composites [2–4]. However, their mechanical properties could not satisfy the actual requirements. Although PLA is biodegradable and biocompatibility, the obvious weakness are their low strength and long-term acidic micro-environment with low pH value around the implant in the fracture zone, which is susceptible to induce second bone-fracture and local inflammation with serious effect on the bioactivity of osteoblast [5,6]. Moreover, the low degradation rate mismatching the new bone tissue formation rate during healing process even makes it need more than three years to completely disappear due to its hydrophobic property.

The application potential of biodegradable magnesium alloy as the orthopedic implants have attracted large numbers of peers' attention and exploration all over the world [7–9]. Biodegradable magnesium alloy possesses many advantages such as suitable elastic modulus (about 41–45 GPa) and moderate density (1.74–2.0 g/cm^3) compared to human natural bone [10], high tensile strength (200–400 MPa) and stiffness could satisfy the mechanical strength requirement used for load bearing applications, as well as excellent biocompatibility as one of the necessary elements in human body [11–13]. Zheng et al. deeply investigated the new bone formation mechanism promoted by magnesium alloys based on fibrocartilaginous enthesis regeneration in the anterior cruciate ligament reconstruction rabbit model [14] and local neuronal production of CGRP to improve bone-fracture healing in rats [15]. However, low corrosion resistance made its mechanical strength loss fast and hydrogen gas aggregation around the implant is susceptible to induce the gap formation between the implant and bone tissues, both of them limit the actual application [16].

We proposed an innovative approach to prepare biodegradable composite rods for orthopedic implant with idea performances combing the advantages of polylactic acid and magnesium alloy. The mechanical property of composite is related to the matrix, strengthen part and the interface bonding effect. The property of matrix is of great importance to the whole mechanical property considering the low modulus and anti-deforming ability to the load. The method to improve the mechanical property of the composite including increasing the molecular weight or adopting self-reinforcing method to improve the orientation and crystallinity of it, as well as improving the interface bonding effect. However, it is difficult and not economical to simply increase the

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molecular weight of PLA. Self-reinforcing technology is a good choice. In order to improve the mechanical strength of PLA or its related composites, commonly used self-reinforcing methods including fibrillated method [17,18], solid state extrusion [19,20], die-drawing technique [21–23] and hydrostatic extrusion [24]. Therefore, how to realize the self-reinforcing effect as to the composite is a question worth investigating.

In this article, the mechanical properties of composite rods have been apparently improved by the strengthen and toughness effect of directionally distributed Mg-2Zn wires in the PLA matrix, the improved interfacial bonding strength after MAO treated Mg-2Zn wires as well as the self-reinforcement effect of PLA after hot drawn process [25–27]. The mechanical performances of Mg-2Zn wires/PLA composite rods could be controlled by adjusting the content of Mg-2Zn wires to satisfy the actual application requirements.

2. Materials and methods

2.1. Materials

Mg-2Zn (98 wt% Mg and 2 wt% Zn) wires with a diameter of 0.3 mm, tensile strength up to 250 MPa and breaking elongation above 10% were prepared in our laboratory by melting, hot extrusion, cold-drawn and heat treatment. The number average molecular weight (M_n) of NatureWorks PLA (Grade 3251D) was 7.8×10^4. Dichloromethane and chromatographically pure tetrahydrofuran (THF) were purchased from chemical reagent co., LTD.

2.2. Methods

2.2.1. Preparation method

Mg-2Zn wires were firstly treated by microarc oxidation (MAO) method in the alkaline electrolyte solution containing Na_2SiO_3 of 13 g/L, Na_3PO_4 of 5 g/L, and NaOH of 2.5 g/L. The current density value was set at 4.0 A. Working mode adopted the direct current mode and the frequency was 500 Hz. The operation could stop while the working voltage increased up to 280 V. The treated wires were rinsed with deionized water for several times and then dry in air. During the composite rod fabricating process, Mg-2Zn wires were firstly wound directionally around an aluminum plate and covered with PLA/dichloride solution (0.125 g/mL). They were dried at room temperature for 48 h. Then the PLA lamina containing magnesium alloy wires and blank PLA lamina were stacked according to the pre-calculated content (initial wires volume content was 5 vol%, 10 vol%, 15 vol% and 20 vol %, respectively). Mg-2Zn wires/PLA composite rods with the sizes of 6 mm in diameter and 120 mm in length were fabricated by hot press (HP) method in a certain mold at 165 °C for 20 min. After cooling down to 80 °C, the samples were taken out for characterization or further hot drawn (HD). The samples were sequentially drawn through molds of different sizes at 165 °C for 2 min of each pass to keep the diameter at 5 mm, 4 mm and 3.2 mm, respectively. Preparation method and pictures of real samples were illustrated in Figs. 1 and 2.

2.2.2. Determination of mechanical properties

The mechanical properties of the composite rods including bending strength, tensile strength and shear strength were measured by CMT4503 electronic universal testing machine at room temperature with the crosshead speed of 2, 5 and 2 mm/min respectively until the experimental specimen failed. The diameters of test were 60 mm in length for specimen and 32 mm in span according to ASTMD790-10 for bending strength. The load-displacement curves were recorded simultaneously and the strength values were the averages of three measurements.

2.2.3. Microstructure characterization

The surface and cross-section morphologies were studied by Sirion200 Field Emission Scanning Electron Microscope (SEM). The element composition in micro-area was determined by energy dispersive spectroscopy (GENESIS 60S EDS), at an accelerating voltage of 20 kV. The crystal condition of PLA molecular chains during the hot drawn process were investigated by X-ray diffraction (XRD, Bruker, D8-discover, Cu Kβ radiation) with the voltage of 40 KV and the current of 30 mA. The intensity was collected in the range of 10–90° at a glancing angle of 0.02°and the scanning speed was 0.15 s/step. Differential scanning calorimeter (DSC 8000) gives the information about the thermal behaviors of microstructure including the crystallinity and melting temperature of the composite rods at HP and HD state. The test was carried out at a heating rate of 10 °C/min under constant flow of N_2 (10 mL/min).

2.2.4. Statistical analysis

Data from mechanical properties of the composite rods were expressed as mean ± standard deviation (SD), and *t*-test was performed to assess statistical significance. Statistical analysis was performed with SPSS 17.0 software (Chicago, IL, USA). $P < 0.05$ was considered significant.

3. Results

3.1. Microstructure changes of PLA chains

Pure PLA cannot be hot drawn through the molds using the method in this article because of the inherent property above soften temperature. On the contrary, the composite could easily pass through molds due to performance of Mg-2Zn wires in which may drive the movement of PLA molecular chains along the drawn direction (Fig. 2). The peaks appeared at $2\theta = 16.63°$ and 19.00° represent the characteristic peaks along (200)/(110) and (203) in the αcrystal of PLA according to the XRD results (Fig. 3). The initial intensity ratio of the above two characteristic peaks ($I_{(200)/(110)}$: $I_{(203)}$) was 3.04 for the hot pressed composite rods with 5 vol% initial wires content (HP-5 vol%), and then dramatically improved to 14.71 after hot drawn three passes (Table 1). As to the hot pressed composite rods with 10 vol% initial wires content (HP-10 vol%), the value of ($I_{(200)/(110)}$: $I_{(203)}$) was 7.12, maybe due to the increased amount of Mg-2Zn wires induced the orientation of PLA chains. While it increased from 2.91 for the HD-10 vol%-one pass to 4.02 for the HD-10 vol%-three passes sample. All of these proved that the orientation preferred in (200)/(110) [28–30]. Essentially, the intensity of (200)/(110) plane was higher than other planes because two PLA chains pass through the plane of (200)/(110) but only one at the most in other planes in the α-type PLA crystal cell structure (Fig. 4). Additionally, it will promote the orientation arrangement of PLA chains along the direction of out force during the hot drawn process, which is parallel to C axis from the lamellae structure. The regularly arrangement of PLA chains is benefit to increase the crystallinity from 9.51% for HP-5 vol% to 46.00% for HD-5 vol%-three passes specimen and it increased from 13.30% for HP-10 vol% to 86.00% for HD-10 vol%-three passes specimen (Fig. 5 and Table 1). Simultaneously, the density in crystal region is larger than that of amorphous region.

3.2. Revolution of the crystallinity, melting temperature of PLA

During the cooling down process after HP, the interface stress produced from the shrinkage of PLA matrix and the thermal expansion coefficient differences between wires and PLA matrix. The interface stress promoted the nucleation, crystal growth and the trans-crystal layers formation around the wires. The thickness of the trans-crystal layer is related to the cooling rate and the normal spherical produced in the PLA matrix is far away from the wires [32]. The wires played an important role in inducing crystallization from 5% of pure PLA rod to 9.51% and 13.30% of HP-5 vol% and HP-10 vol%. In addition, the crystallinity gradually increased for the composite rods after HD one,