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

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A B S T R A C T
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/m², 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. Microarc oxidation (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.

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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-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...
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 oxidation (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/cm³ were purchased from Shenzhen Esun Industrial Co., Ltd., China. The viscosity average molecular weight (Mn) 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 4.7 vol%. The composite specimens were fabricated by the lamina stacking method. The middle plane of the stack along the height direction was 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.

2.2.1. Materials preparation

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 KH₂PO₄ in 1000 mL distilled water) and stock solution B (1.1876 g Na₂HPO₄ in 1000 mL distilled water) at a volume ratio of 18.2:1. 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. Before the immersion solution was changed, the pH value was measured. The viscosity average molecular weight (Mn) of the PLA during immersion was calculated by the Mark-Houwink-Sakurada formula [39] based on the intrinsic viscosity at 25 °C monitored by an Ubbelohde viscometer. The initial mass (m₀) of the sample with dimensions of 25 mm × 12 mm × 2 mm for the mass loss test was recorded and the final mass (mₐ) 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:

\[ \omega = \frac{(m₀ - mₐ)mₐ}{100\%} \]  

2.2.2. 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 K₃Fe(CN)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/dm². Afterwards, the wires were removed and washed with deionized water.

2.2.3. In vitro degradation tests

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\[ \omega = \frac{(m₀ - mₐ)mₐ}{100\%} \]  

2.2.5. Determination of mechanical properties

Before the mechanical tests of the composites, the tensile properties of the initial MAW/PLA composites with length of 120 mm × 12 mm × 2 mm, were determined by the tensile testing machine, as shown in Fig. 2. The mechanical tests were performed on the 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 Sorensen’s phosphate-buffered solution (SPB) 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 (Sₜ) of the samples in the wire direction was measured. The bending strength (S₅) of the samples was measured by the three-point bending method according to the ASTM D790-2010 for a span of 32 mm. The shear strength (S₅) 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. [43]. The plate sample was fixed and sheared successively 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.
3. Results

3.1. Mechanical properties

$M_v$ of the PLA in the fabricated composites and pure PLA samples can be controlled to be between 50,000 and 55,000 g/mol. This enables more direct investigation of the MAW effects on the mechanical strength of the composites, as shown in Table 3. The increase in the tensile strength ($S_t$) is proportional to the MAW content and a high strength of nearly 110 MPa is achieved at 40 vol%. The load-displacement curves of the composites under tension are shown in Fig. 3. The load increases linearly at first, exhibits an abrupt drop, and then declines gradually. The sharp drop may be due to breakage of PLA because it is the same as the bearing load of the PLA matrix in the composite when failure occurs. The ratio of the bearing load of each component in the composite to the maximum load of the composite ($\sigma_{\text{Load}}$) at this time can be calculated. $\sigma_{\text{Load}}$ of the PLA matrix in the composite ($\sigma_{\text{Load-PLA}}$) is calculated by dividing the reduced value by the maximum load value of the composite and $\sigma_{\text{Load}}$ of the MAWs in the composite ($\sigma_{\text{Load-Mg}}$) can be obtained. At 5 vol%, $\sigma_{\text{Load-Mg}}$ is 43.7%, indicating that the MAWs constitute the main underpinning body. When the MAW content goes up to 10 vol%, $\sigma_{\text{Load-Mg}}$ increases significantly to 70.5%. If the MAW content is increased from 20 to 40 vol%, $\sigma_{\text{Load-Mg}}$

<table>
<thead>
<tr>
<th></th>
<th>Poisson ratio</th>
<th>Density (g/cm$^3$)</th>
<th>Elastic modulus (GPa)</th>
<th>Yield strength (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Tensile strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAW ($\phi$ 0.3 mm)</td>
<td>0.35</td>
<td>1.8</td>
<td>45</td>
<td>270</td>
<td>270</td>
<td>316</td>
</tr>
<tr>
<td>PLA</td>
<td>0.36</td>
<td>1.24</td>
<td>4.0</td>
<td>–</td>
<td>–</td>
<td>46</td>
</tr>
</tbody>
</table>
increases slightly from 83.1% to 84.0%. The final gradual decline in the curve may stem from gradual fracture and evulsion of the MAWs due to poor interface bonding between the MAWs and PLA.

The bending strength ($S_b$) of the composites increases to about 190 MPa at 40 vol% and it is about twice that of pure PLA. The load-deflection curves of the composites under bending loads are presented in Fig. 4. The load increases linearly initially and then decreases gradually at 0 and 5 vol% but stepwise at 10 and 20 vol%.

This decrease may be related to breakage of the PLA on the bottom surface of the composite as shown in the upper right picture in Fig. 4. The later stepwise decrease may be associated with gradual rupturing of the MAWs along the bending direction of the composite. Fig. 5(a) and (b) depict the bending fracture morphology of the 20 vol% composite. Fig. 5(a) shows decreased wire diameter at the fracture section, suggesting that the wires undergo plastic deformation during the bending tests.

The impact strength ($S_i$) of the composites increases significantly from 18 kJ/m² for 5 vol% to 150 kJ/m² for 40 vol%. The value of the 40 vol% composite is approximately 29 times larger than that of pure PLA, indicating that the composite has good rigidity and ductility. Fig. 5(e) and (f) show the shear fracture morphology of the 20 vol% composite. The MAWs have an oval shape and there are many disordered cracks in the matrix.

### 3.2. Theoretical mechanical strength assessed by FEM

In spite of the aforementioned encouraging results, the properties, especially $S_t$ and $S_b$, are not ideal due to the poor interface between the MAWs and PLA and so the force cannot be efficiently transferred from the matrix to the reinforcements [30,31]. Hence, it

<table>
<thead>
<tr>
<th>Mean volume fraction of MAWs (vol%)</th>
<th>$S_t$ (MPa) Mean</th>
<th>SD</th>
<th>FEM Mean</th>
<th>SD</th>
<th>$S_b$ (MPa) Mean</th>
<th>SD</th>
<th>$S_i$ (kJ/m²) Mean</th>
<th>SD</th>
<th>$S_s$ (MPa) Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PLA</td>
<td>46 (±5.66)</td>
<td>47</td>
<td>88 (±0.95)</td>
<td>5</td>
<td>19 (±4.24)</td>
<td>18</td>
<td>45 (±0.74)</td>
<td></td>
<td>56 (±0.13)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>50 (±2.05)</td>
<td>57</td>
<td>99 (±2.16)</td>
<td>27</td>
<td>26 (±10.19)</td>
<td>63</td>
<td>73 (±0.91)</td>
<td></td>
<td>63 (±1.55)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>65 (±0.06)</td>
<td>68</td>
<td>119 (±7.54)</td>
<td>90</td>
<td>26 (±26.94)</td>
<td>73</td>
<td>73 (±0.91)</td>
<td></td>
<td>73 (±0.91)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>80 (±3.54)</td>
<td>91</td>
<td>136 (±0.41)</td>
<td>150</td>
<td>40 (±40.38)</td>
<td>67</td>
<td>67 (±0.70)</td>
<td></td>
<td>67 (±0.70)</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>108 (±3.73)</td>
<td>136</td>
<td>190 (±0.38)</td>
<td>150</td>
<td>40 (±40.38)</td>
<td>67</td>
<td>67 (±0.70)</td>
<td></td>
<td>67 (±0.70)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3

Mechanical properties of MAWs/PLA composites.
is essential to conduct a theoretical evaluation of the mechanical strength in order to improve the interface. The theoretical $S_t$ of the composites derived by FEM is shown in Table 3. At a content below 10 vol%, the FEM results are almost in line with experimental data. However, there is a marked increase at 40 vol% reaching 136 MPa that is 0.26 times larger than that of the experimental value, suggesting the possibility to further improve $S_t$.

$S_t$ is an important index for bone fixation devices. However, the present composites are anisotropic and the bending strength is related to various factors such as the volume fraction and distribution of the MAWs as well as distance between the MAWs and neutral plane of the composite samples $(h_i)$. The different distributions along the cross section (involving different $h_i$, MAW-containing lamina number, and MAW number per lamina) of the MAWs in the 40 vol% composite are shown in Fig. 6. A large value of 300 MPa can theoretically be attained at 40 vol% and it is much larger than the experimental value, indicating that the mechanical properties can be further improved by modifying the internal structure. Moreover, the theoretical properties can be tailored since $S_t$ varies between 200 MPa and 300 MPa.

FEM is performed to investigate the bending behavior of the composites by changing the volume fraction and diameter of the MAWs (assuming no change in the tensile properties of the MAWs with diameters between 0.3 mm and 0.5 mm). Fig. 7 shows that 200 MPa which is sufficient for load-bearing bone fixation applications can be achieved from the 20 vol% composite. In order to study the influence of various parameters, the equivalent section method (ESM) commonly used to calculate $S_t$ of reinforced concrete in computational mechanics is adopted [43]. Compared to reinforced concrete, these composites share some similarities such as the brittle matrix, high strength, and directional reinforcement, whereas the main difference is that the MAWs here and steel bars in concrete exhibit plastic deformation and elastic deformation,

Fig. 4. Load-deflection curves of the composites with different MAW contents under bending load.

Fig. 5. Fracture morphology of the composites with 20 vol% MAWs: (a) Bending fracture (low magnification); (b) Bending fracture (high magnification); (c) Impact fracture (low magnification); (d) Impact fracture (high magnification); (e) Shear fracture (low magnification); (f) Shear fracture (high magnification).
respectively, when the matrix fractures. If deformation of MAWs can be treated as an elastic behavior, $S_{b}$ of the composites can be determined by ESM and in this case, the effective elastic modulus is adopted.

The PLA on the bottom surface of the composite only experiences tensile stress during bending followed by early-stage fracture. The stress on the bottom surface ($s$) during failure is about the same as that of pure PLA. As the MAWs in the composite are symmetrically arranged about the neutral plane, $S_{b}$ of the composites can be calculated as follows:

$$s = \frac{M \cdot y}{I_z} = \frac{S_{b-PLA}}{C_0}; \quad (2)$$

$$I_z = IM_g + IPLA = bh^3/12 + \sum_i (n - 1) \pi r_i^2 h_i^2; \quad (3)$$

$$M = FL/4; \quad (4)$$

$$S_{b} = 3FL/2bh^2 = 12S_{b-PLA}I_z/bh^2. \quad (5)$$

where $M$ is the bending moment (N·mm), $y$ is the distance between the bottom surface and neutral plane (mm), $I_z$ is the equivalent inertia moment of the composite (mm$^4$), $S_{b-PLA}$ is the bending strength of pure PLA (MPa), $h_{MG}$ is the inertia moment of the MAWs (mm$^4$), $I_{PLA}$ is the inertia moment of the PLA (mm$^4$), $b$ is the width of the specimen (mm), $h$ is the thickness of the specimen (mm), $n$ is the ratio of the effective elastic modulus of the MAW to the elastic modulus of the PLA matrix, $r_i$ is the radius of MAW (mm), $h_i$ is the distance between MAW and neutral plane (mm), $F$ is the bending load (N), $L$ is the support span (mm). The ESM calculation process is illustrated in Fig. 8. The first step is to obtain $S_{b}$ of the predetermined composites by FEM, followed by derivation of the corresponding $I_z$ and $n$. Thereafter, $n$ is manipulated by a least-square method to obtain a value of 6.667, suggesting that the effective elastic modulus of the MAW is 26.67 GPa. $S_{b}$ is recalculated using $n = 6.667$ and the results are shown in Fig. 7. The ESM results are in general agreement with those by FEM thus validating that the proposed model is feasible and reliable.

### 3.3. Interface improvement by MAO

The importance of interface improvement is apparent according to the experimental and FEM results. In this respect, MAO can produce a rough and porous surface on the MAWs to improve the bonding between the MAWs and PLA in the composites. The surface morphology of the MAWs before and after MAO are depicted in Fig. 2. A rough and porous surface can be observed from the MAWs after MAO and the tensile strength of the MAWs decreases to about 310 MPa. The load-displacement curves of the composites reinforced with the MAO MAWs (composites-MAO) under tension and pictures of the broken specimens are shown in Fig. 9(a). Compared to the composites reinforced with the untreated MAWs, no obvious evulsion can be observed when failure occurs, indicating improved interfacial bonding between the matrix and reinforcements.

$S_{t}$ and $S_{b}$ of the MAO composites are shown in Fig. 9(b). At 20 vol% $S_{t}$ is nearly 100 MPa that is 14% larger than that of the composite without undergoing MAO. However, $S_{t}$ of the MAO composites is a little larger than that provided by FEM. This may be attributed to the larger contact regions and special interfacial micro-anchoring action between the PLA and MAWs. This phenomenon provides clues about the benefits of using MAO to strengthen the interface. Since the samples are prepared under the same conditions, the change in $S_{t}$ reflects the effects of MAO on the mechanical properties of the samples. Obviously, $S_{b}$ of the MAO composites is larger than that without undergoing MAO. $S_{b}$ of the 20 vol% MAO composite is about 150 MPa which is 11% larger than that without MAO.

### 3.4. Degradation characteristics

Although degradation of PLA is relatively complex, the main changes are reduction in the molecular weight initially as well as
loss of mechanical strength and subsequently real mass [9,44]. There are many factors that influence the degradation rate of PLA. High crystallinity, low stress, and orientation may suppress the degradation rate [45,46], while high temperature [41] and acidity [11] tend to increase the degradation rate. To investigate the effects of the molecular weight and crystallinity of the PLA, immersion for 21 days (3 weeks) at 50 °C for accelerated degradation and 56 days (8 weeks) at 37 °C for normal degradation is performed. The MAW reinforcements in the immersed specimens undergo MAO to improve the interface and prevent the MAWs from rapid corrosion. The degradation behavior is examined as a function of MAW content (0–20 vol%) in relation to $\omega$, $M_v$, $S_b$, and the results are summarized as follows.

The percentage mass loss ($\omega$) during accelerated and normal degradation is shown in Fig. 10(a). Both $\omega$ values exhibit a slight increase proportional to the MAW content. As there is hardly any mass loss from pure PLA, this slight increase may be related to degradation of the MAO MAWs. However, the largest $\omega$ is no more than 1% indicating a fairly low degradation rate of MAWs during immersion and suggesting long-term reinforcing action of MAWs and good strength retention ability of the composites.

The change in $M_v$ of the pure PLA and the PLA in the 20 vol% MAWs/PLA composite versus immersion temperature is shown in Fig. 10(b). $M_v$ decreases significantly with immersion time and a larger decrease rate is observed at a higher temperature. Obviously, $M_v$ of the PLA in the composite shows a similar trend as pure PLA in the early stage. A smaller decrease rate after 7 days at 50 °C or 14 days at 37 °C indicates a different degradation behavior. After immersion for 21 days at 50 °C, the $M_v$ values of pure PLA and PLA in the composite are 25% and 45% of the initial values, respectively. The values are 49% and 66% after 56 days at 37 °C, indicating relatively larger $M_v$ retention at 37 °C. Moreover, during the immersion period, the pH of the solution is measured. The average pH of the solution immersed with pure PLA varies in the range between 7.32 and 7.39 during the immersion period, whereas that immersed with the composite (20 vol%) changes from 7.38 to 7.60. These variations are within the controlled pH range of the solution (7.4 ± 0.2), indicating that little degradation products are released from both samples into the solutions during immersion.

The change in $S_b$ of the composite versus immersion time is shown in Fig. 11(a) and (b). $S_b$ of pure PLA at 37 °C and 50 °C decreases with a similar concave shape, whereas $S_b$ of the 20 vol% composite shows a convex decrease. At 37 °C, $S_b$ of pure PLA and the composites decreases gradually versus immersion time. After 56 days, the $S_b$ values of pure PLA and 20 vol% composite are 56 MPa and 110 MPa, respectively, which are 64% and 74% of the initial values, indicating good strength retention ability. This ability is further verified by the integrity of the MAWs. There are MAO coating fragments and no visible corrosion pits on the wire surface after immersion. At 50 °C, a faster decrease in $S_b$ is observed. After 21 days, the $S_b$ values of pure PLA and the 20 vol% composite are 10 MPa and 96 MPa, respectively, which are 11% and 65% of the initial values. The higher level of strength retention may be
attributed to the MAWs which retain the integrated and continuously reinforced PLA during immersion. $S_b$ of the composites after 14 days at 50 °C is the same as that of the composites after 56 days at 37 °C and hence, $S_b$ of the composite after immersion for 2 weeks at 50 °C reflects that of the corresponding composite after 2 months at 37 °C.

4. Discussion

4.1. Strengthening and toughening of the composites

High-strength biodegradable PLA-based composites have been investigated. The materials can be classified as self-reinforcing, particle-reinforcing, and fiber-reinforcing and the materials described here are considered fiber-reinforcing. The MAW reinforcements have large diameters and deliver better failure strain than conventional fibers. For instance, the tensile strain of the MAWs is 0.16 that is 14 and 15 times larger than that of pure PLA and carbon fibers, respectively [47]. The toughened 40 vol% composite has a remarkable impact strength of 150 kJ/m$^2$ which is nearly 5 times larger than that of PLA incorporated with the same amount of carbon fibers [47], although carbon fibers have larger tensile strength and elastic modulus. The value of 150 kJ/m$^2$ is sufficient to satisfy the impact-resistant requirements of human bones enabling effective protection against external impact.

Even though the molecular weight of PLA is only about 60,000 g/mol that is smaller than those of other materials (Table 4), $S_b$ of 190 MPa which is sufficiently large in practice arises from the strengthening effects of MAWs as their tensile strength is as large as 316 MPa. The low molecular weight leads to large degradation rate which bodes well for temporary bone fixation.

One strengthening approach is internal structure modification. $S_b$ of the composites can go up to 300 MPa in the 40 vol% composites by adjusting the internal MAW distribution. It is a convenient way to obtain composites with variable strength to cater to different applications and would be difficult to achieve using a single type of materials. The numerical model on $S_b$ proposed here enables quick evaluation of the materials. Different biomedical devices have special requirements such as geometry, size, and mechanical properties and this model can be used to assess the mechanical properties to validate and expedite the design.

Another approach to strengthen the composite is interface strengthening. Poor interfacial bonding between the PLA and MAWs compromises the mechanical integrity. Conventional interface strengthening methods utilize covalent bonding between the modified region and substrate, for example, by applying a compatible layer to the interface or incorporating the appropriate functional groups to create strong adhesion between the substrate and layer [46]. In this work, MAO is employed to prepare a rough and porous coating on the MAWs to anchor the PLA while ingredients in the PLA solution penetrate the pores, as shown in the upper right of Fig. 9(b). The micro-anchoring provides strong physical bonding to strengthen the interface, transfer the loading from the matrix to reinforcements, strengthen the MAWs, and ultimately enhance mechanical properties of the composites.

High-strength PLA-based composites are commonly produced by self-reinforcing at a low temperature, as shown in Table 4, but our composites are prepared at a relatively high temperature. The self-reinforcing process can alter the chain orientation to improve the mechanical properties of the PLA. Although the degradation rate increases slightly by increasing the molecular weight or changing the orientation, the materials can satisfy the requirements of long-term weight-bearing bone fixation.

Table 4

<table>
<thead>
<tr>
<th>Shape</th>
<th>Initial Mw (1000 g/mol)</th>
<th>$S_b$ (MPa)</th>
<th>$S_t$ (MPa)</th>
<th>$S_f$ (kJ/m$^2$)</th>
<th>Fabricating process</th>
<th>Fabricating temperature (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA/HA-30 wt%</td>
<td>Rod</td>
<td>400</td>
<td>121</td>
<td>299</td>
<td>166</td>
<td>Forging</td>
<td>103</td>
</tr>
<tr>
<td>PDLA</td>
<td>Rod</td>
<td>280</td>
<td>–</td>
<td>180</td>
<td>–</td>
<td>Solid-state extrusion</td>
<td>120</td>
</tr>
<tr>
<td>SR-PILLA</td>
<td>Pin</td>
<td>660</td>
<td>–</td>
<td>280</td>
<td>–</td>
<td>Die-drawing</td>
<td>–</td>
</tr>
<tr>
<td>PLA</td>
<td>Rod</td>
<td>220</td>
<td>–</td>
<td>240</td>
<td>–</td>
<td>Die-drawing</td>
<td>100</td>
</tr>
<tr>
<td>PLLA</td>
<td>Rod</td>
<td>133</td>
<td>69.8</td>
<td>–</td>
<td>–</td>
<td>Mold-compressing</td>
<td>200</td>
</tr>
<tr>
<td>SR-PLLA</td>
<td>Rod</td>
<td>260</td>
<td>–</td>
<td>271</td>
<td>–</td>
<td>Mold-compressing</td>
<td>162–174</td>
</tr>
<tr>
<td>PLA/unidirectional carbon fibers-40 vol%</td>
<td>Plate</td>
<td>100</td>
<td>220</td>
<td>–</td>
<td>–</td>
<td>Mold-compressing</td>
<td>110</td>
</tr>
<tr>
<td>PLA/unidirectional MAWs-40 vol%</td>
<td>Plate</td>
<td>60</td>
<td>108 (–136°)</td>
<td>190 (–300°)</td>
<td>150</td>
<td>Mold-compressing</td>
<td>Present</td>
</tr>
</tbody>
</table>

* No mention.
* In theory.
4.2. Analysis of the degradation behavior and biocompatibility

The ideal temporary bone fixation device should have high strength retention during healing and undergo fast degradation after healing. Therefore, it is imperative to fathom the degradation behavior. The main degradation mechanism of PLA is hydrolysis [7,11,51] which involves hydrolytic cleavage of the ester linkage to form acidic carboxyl end groups and oligomers. The soluble degradation products close to the surface escape readily but those in the bulk cannot diffuse out of the PLA, resulting in high internal acidity and reduced pH. Moreover, the acid products catalyze the ester hydrolysis reaction [11]. The PLA in the composites described here have a different degradation behavior for its higher mass loss rate and slower molecular weight decrease than pure PLA. According to the MAO coating fragments on the surface of MAWs after immersion for 56 days at 37 °C and visual integrity of MAW substrate after 21 days at 50 °C, the degradation process is shown in Fig. 12. Initially, water molecules penetrate the PLA to trigger hydrolytic degradation of the ester linkage and form acidic carboxyl end groups [11]. As time elapses, the water molecules diffuse through the PLA into the MAO coating causing degradation of the MAO coating. The initial MAO coating is a basic oxide. Cracks emerge locally and propagate resulting in eventual disintegration which deteriorates the bonding between the MAO coating and MAW substrate. During degradation of the MAO coating, some soluble ions such as OH\(^{-}\) and Mg\(^{2+}\) are released and diffuse to the SPB resulting in the obvious mass loss from the composites compared to pure PLA.

The slower degradation rate of the PLA in the composite mitigates the pH decrease. It has been reported that the delayed adverse biological response such as bone resorption arises from pH reduction [52,53]. Many types of filler materials such as ceramics and bioglass have been proposed to overcome the hurdle. Henna et al. [14] reported that PLA-based composite filled with a bioactive glass led to a more constant pH in the buffer solution and slower decreasing rate of the viscosity average molecular weight than pure PLA in vitro. Agrawal and Athanasiou [54] studied the in vitro degradation of PLA-PGA composites incorporated with calcium carbonate, sodium bicarbonate, and calcium hydroxyapatite and showed that the three ingredients altered the rate of pH decrease in the vicinity of the PLA-PGA implants. Our composites exhibit effective long-term stability due to degradation of the MAO coating or MAWs. Hydroxide ions (OH\(^{-}\)) released during degradation diffuse into the PLA to counteract the acidic hydrogen ions released from the acidic carboxyl end groups. This neutralization maintains a steady pH to mitigate degradation of the PLA matrix and enhance the strength retention ability of the composites.

The biocompatibility of PLA and magnesium has been studied. Although the toxicity rendered by aluminum in Mg alloys is controversial, Mg–Al alloys are generally considered biocompatible based on in vitro and in vivo experiments [21,55,56]. Degradable porous scaffolds made of the magnesium alloy AZ91D were implanted into the distal femur condyle of rabbits [57] and no significant harm or inflammation was observed. Osteolysis around the implants in rabbits was observed [55] and Xue et al. [58] investigated the in vivo biocompatibility of AZ31 and AZ91D alloys at different places of the mouse. Histological results obtained from the liver, heart, kidney, skin, and lung of the mouse after two months suggested that the Mg–Al–Zn alloys had good biocompatibility. Furthermore, the dispersive MAWs prevent a large amount of hydrogen release which would otherwise occur on bulk magnesium alloys. Consequently, the risk of tissue reaction caused by needle-shape fibers or fragments is reduced substantially reduced.

5. Conclusion

Biodegradable PLA-based composites reinforced with high-strength magnesium alloy wires are produced for load-bearing bone fixation applications. The materials have excellent strength, toughness, and impact strength due to the unidirectional reinforcing effects rendered by the MAWs. Analysis by FEM indicates that the strength of the composite can be further improved. A numerical model about the bending strength is formulated and predicts that the bending strength can be larger than 300 MPa for 40 vol% MAWs, although the PLA has a low viscosity average molecular weight of 60,000 g/mol. Micro arc oxidation conducted on the MAWs improves the interfacial bonding between the MAWs and PLA and consequently, the tensile strength and bending strength of the composites are enhanced. The materials have high strength retention ability according to the accelerated and normal degradation tests and moreover, the degradation rate of PLA decreases after incorporation of the MAO treated MAWs. The reinforced composites are promising biodegradable materials in load-bearing applications.

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References


