



Fabrication of polylactic acid/hydroxyapatite/graphene oxide composite and their thermal stability, hydrophobic and mechanical properties

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ABSTRACT

A series of polylactic acid/hydroxyapatite/graphene oxide composite (PLA/HA/GO) were fabricated via solution blending and casting method using *N,N*-dimethyl-formamide (DMF) and CH_2Cl_2 as mutual solvents. The physicochemical properties of the resulting composites were characterized by means of FT-IR, SEM, TEM, Raman spectra, XRD and N_2 -physisorption. Particularly, the thermal stabilities, hydrophobic and mechanical properties of PLA/HA/GO composites were systematically investigated. The influences of GO content on thermal stabilities, hydrophobic and mechanical properties of the composites were also evaluated. The results showed that the addition of GO and HA not only improved the thermal stability of PLA, but also improved the hydrophobic property of PLA-based composites. By compared with the PLA/HA/GO composite, the tensile strength of pristine PLA is slight high. The tensile strength and hardness of PLA/HA/GO composites increased with the increase of GO content. The obtained PLA/HA/GO composite may be a promising material for load-bearing orthopedic implants.

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1. Introduction

It is well known that biodegradable polymer materials such as poly (glycolic acid) (PGA), poly (ethylene glycol) (PEG), poly (lactic acid) (PLA) and poly (ϵ -caprolactone) (PCL) [1,2], etc. can be decomposed by microorganisms without the negative environmental impact, and have brought wide applications in biomedical area due to their relatively good properties such as biodegradability, environmental friendliness and acceptable physical mechanical performance. Among the above polymer materials, poly lactic acid (PLA), one of the synthetic aliphatic polyester polymers prepared from renewable resources, is one of the most common biodegradable polymer materials. Recently, owing to its excellent biodegradability, biocompatibility, bioresorbability and ductility, PLA has received much attention in the food and medical area, such as widely used in anti-microbial, bone fixation, surgical suture, meniscus repair, and drug delivery [1,3–6], etc. Also, the advantage of PLA is that the mechanical property and degradation rate of PLA can be adjusted and controlled via adjusting the molecular weight

and choosing different forms of polymeric and molding methods to satisfy its requirement in clinic.

Hydrolysis is one of the main characteristics of PLA which affects not only the biodegradation but also the mechanical property. According to the structure of PLA and degradation mechanism, PLA in the presence of water undergoes chemical hydrolysis which results in the reduction of polymer molecular weight and the release of lactic acid [7]. During its hydrolysis process, due to the sensitivity between ester bond in the chain segments of PLA and water, the carboxyl end groups produced during this process promote the auto catalytic hydrolysis of the ester bond [8]. Meanwhile, oligomer produced during the degradation process can further promote the degradation of PLA, and the inner acidic substances will accelerate continuously the degradation rate of PLA. In conclusion, the hydrolysis of PLA is dependent of various factors, such as chemical structure, morphology, hydrolysis conditions [9]. Therefore, a tremendous amount of works have been done to study the improvement of the physical properties of PLA such as polymer blending, copolymerization, plasticization and reinforced composites. Of which, fabrication of PLA-based composite with nanoparticles is the most effective and promising method to expand the applications of PLA. In recent years, a lot of nanoparticles, such as nano-silica, titanium dioxide, silver nanoparticles, nano calcium carbonate, hydroxyapatite, nano crystalline cellulose,

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layered silicate, carbon nanotubes, montmorillonite, nano carbon fiber and graphene nanosheet, have been introduced in PLA-based composite [10–17].

Some literatures have reported that the crystallization rate, mechanical properties and thermal stability of PLA nanocomposites could be enhanced apparently by multi-walled carbon nanotubes [18–20]. Compared to carbon nanotubes, graphene oxide (GO) is cheap, and can be obtained in large quantities by chemical oxidation of graphite and can be functionalized in various ways to enhance its interaction with other molecules displaying higher Young's modulus, flexibility and hardness [21]. GO, a single layer composed of sp^2 -hybridized carbon atoms mixed with more polar patches of sp^3 -hybridized carbon atoms closely packed into a two-dimensional structure [22], is a fantastic member with extraordinary mechanical properties, bioactivity and biocompatibility. On the other hand, GO holds some oxygen functional groups such as epoxy, hydroxyl and carboxylic groups between the lamellas, which can be easily exfoliated and functionalized to form homogeneous suspensions in both water and organic solvents. As a consequence, it is considered as a promising candidate to take over carbon nanotubes as reinforcing nanofiller in fabrication of multifunctional polymer nanocomposites.

Hydroxyapatite (HA) which is a type of biological ceramic materials possesses good osteoconductivity, osteoinductivity, biodegradability and biocompatibility. Based on these characteristics, it can promote the growth of bone and adhesion of tissue owing that Ca^{2+} of HA can react with a carboxy-containing amino acid, protein, organic acid and so on, so that HA can be widely used to repair and replace the skeletal and dental tissue [23]. Moreover, it can also be the scaffold materials of tissue engineering because of its high mechanical strength [24]. However, due to the poor mechanical properties of the HA, especially low toughness and high elastic modulus which restricted its application to the human body [25]. To improve its practicability, many efforts have been carried out by researchers for modification of HA-based composites [26,27].

To the best of our knowledge, most of the previous efforts aimed at the preparation and application of PLA/GO, PLA/HA or HA/GO composites but there are few publications involving fabrication of PLA/HA/GO nanocomposites because it is difficult for HA and GO to disperse in PLA matrix. Therefore, it would be significant to prepare PLA/HA/GO nanocomposites and investigate its fundamental performance to provide a good foundation. For this purpose, in the present work, a series of polylactic acid/hydroxyapatite/graphene oxide composites (PLA/HA/GO) with different GO contents were fabricated *via* solution blending and casting method. First of all, graphene oxide/hydroxyapatite nanocomposite was prepared by a wet-chemical precipitation method. During this process, cetyltrimethyl ammonium bromide (CTAB) was adopted to modify the surface of GO to expand the layer spacing of GO, which is beneficial to the following graft of hydroxyapatite on GO nanosheets. Then, PLA was successfully buried in the porous of inorganic particles and firmly adsorbed on the surface of GO and HA *via* ultrasonication and magnetic stirring to obtain the PLA/HA/GO composites. The effects of different contents of GO on the morphology, crystallinity, thermal stability, hydrophobic property and mechanical property of the PLA/HA/GO composites were investigated.

2. Experimental

2.1. Materials

Particle size of natural flake graphite (G) about $44\ \mu\text{m}$ was purchased from Qingdao Zhongtian Co. Ltd.; cetyltrimethyl ammonium bromide (CTAB), HCl ($1\ \text{mol L}^{-1}$), H_2SO_4 (98%),

KMnO_4 , NaNO_3 , H_2O_2 (30%), calcium nitrat ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$), $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25%), *N,N*-dimethyl-formamide (DMF), dichloromethane (CH_2Cl_2) (AR, Sinopharm Chemical Reagent Co., Ltd.) and poly L-lactic acid (PLLA), $M_w = 155,000\ \text{g/mol}$ (Shanghai Dibai Chemical Technology Co., Ltd.). Simulated Body Fluid (SBF): NaCl, NaHCO_3 , Na_2SO_4 , $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, KCl, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 , HCl ($0.1\ \text{mol/L}$) and tris (hydroxymethyl) aminomethane: $(\text{HOCH}_2)_3\text{CNH}_2$ (AR, Sinopharm Chemical Reagent Co. Ltd.).

2.2. Preparation of graphite oxide

Graphite oxide was prepared by a modified Hummers' method from natural flake graphite in our previous report [28]. In brief, 98% H_2SO_4 (115 ml) was added into the graphite (2.5 g) in an ice bath, and then KMnO_4 (15 g) and NaNO_3 (2.5 g) were slowly added with stirring. The mixture was warmed to $35\ ^\circ\text{C}$ and continuously stirred for another 30 min. After that, 125 ml deionized water was slowly added into the above mixture, the reaction was heated to $95\ ^\circ\text{C}$ and kept at the temperature for 30 min with stirring. Further, 800 ml deionized water was added and then 15 ml H_2O_2 (30%) and 1 ml HCl ($1\ \text{mol L}^{-1}$) were added to reduce the excess KMnO_4 . The resulting sample was washed with deionized water and centrifuged at 3000 rpm for 10 min, and then the precipitate was fully dried in an oven at $60\ ^\circ\text{C}$ for overnight, designated as graphite oxide (GtO).

2.3. Synthesis of hydroxyapatite/graphene oxide (HA/GO) composites

The quantitative graphite oxide was dispersed into deionized water *via* ultrasonication in a bath sonicator for 1 h to obtain a uniform and stable yellow–brown suspension, indicating the exfoliation of graphite oxide powder into flake of graphene oxide (GO) in aqueous solvents. Then, the bath temperature was heated to $70\ ^\circ\text{C}$, a given amount of CTAB ($0.1\ \text{mol L}^{-1}$, CTAB/GO = 50 mmol/g) was added into the GO suspension under magnetic stirring and kept at the temperature for 12 h with stirring and aged for 1 day. After centrifugation, the obtained precipitate was dispersed into 100 mL of distilled water *via* ultrasonication for 2 h to obtain a suspension. Ammonia was added in order to keep the reaction pH between 10 and 11. The synthesis of the HA/GO composites was carried out by a wet-chemical precipitation method. The details as follows: diammonium hydrogen phosphate ($0.3\ \text{mol L}^{-1}$) and calcium nitrate ($0.5\ \text{mol L}^{-1}$) were separately dissolved into distilled water and ethyl alcohol according to the molar ratio of Ca/P is 1.67. Then, the prepared $\text{Ca}(\text{NO}_3)_2$ solution was added into the GO suspension in a water bath at $45\ ^\circ\text{C}$, and the suspension was constantly stirred for 2 h. Subsequently, the prepared $(\text{NH}_4)_2\text{HPO}_4$ solution was added drop by drop into the mixture at the velocity of 1 mL/min with a continuous vigorous stirring and the pH value of the mixed solution was kept at 10 *via* addition of ammonia. The mixed solution was stirred for 8 h and aged at $45\ ^\circ\text{C}$ for 2 day. The desired precipitate was filtered and washed with deionized water several times to remove the residual NH_4^+ and NO_3^- until the pH of solution is neutral. The product was washed with CH_2Cl_2 for 3 times to remove the residual water and dried at $80\ ^\circ\text{C}$ for overnight under vacuum, denoted as HA/GO.

2.4. Preparation of poly (lactic acid)/hydroxyapatite/graphene oxide) PLA/HA/GO composites

PLA/HA/GO nanocomposite films were prepared *via* solution blending and casting using CH_2Cl_2 as a mutual solvent. The amounts of PLA, HA, GO and CTAB are listed in Table 1. Briefly, the above HA/GO composite was dispersed into DMF and CH_2Cl_2 ($V_{\text{DMF}}: V_{\text{CH}_2\text{Cl}_2} = 2:3$) using ultrasonication for 90 min below $5\ ^\circ\text{C}$ to obtain

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