



# Effect of n-HA content on the isothermal crystallization, morphology and mechanical property of n-HA/PLGA composites

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## ABSTRACT

A series of g-n-HA/PLGA composites with surface-modified g-n-HA of 1%, 3%, 6%, 10% and 15% in weight were prepared by solution mixing. The isothermal crystallization, morphology and mechanical property of g-n-HA/PLGA composites were investigated by differential scanning calorimeter (DSC), scanning electron microscope (SEM) and electromechanical universal tester. The results showed that Avrami equation was suitable for describing the isothermal crystallization process in this system, and the crystallization rate of g-n-HA/PLGA composites containing more than 3 wt% g-n-HA was basically accord with the relational expression of  $T_{110\text{°C}} > T_{105\text{°C}} > T_{115\text{°C}} > T_{120\text{°C}}$ . Moreover, at the same  $T_c$ , crystallization rate was greatly enhanced with the increasing of g-n-HA acting as nucleate. However, the addition of higher content of g-n-HA would cause more agglomeration in PLGA matrix, so that the mechanical properties of g-n-HA/PLGA composites would gradually decrease. In conclusion, the addition of higher content of g-n-HA was favorable to promote the crystallization better in g-n-HA/PLGA composites, but it could also cause more agglomeration in PLGA matrix, result in worse mechanical properties, and the addition content of 3 wt% g-n-HA to PLGA matrix was an appropriate proportion, which had the highest bending strength among these g-n-HA/PLGA composites, and it might be potential to be used in biomedical fields in future.

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## 1. Introduction

Poly-lactic-co-glycolic acid (PLGA), a copolymer composed of polylactic acid (PLA) and polyglycolic acid (PGA), is one of well-known materials among synthetic biodegradable polymers, and so far it has been extensively used in biomedical fields due to its good biocompatibility and biodegradability [1–4]. However, there are still some inherent disadvantages to be improved, such as relatively insufficiency mechanical properties, poor bioactivity and much acidic degradation products [5,6]. Therefore, more and more researchers are focusing on the preparation of inorganic–organic hybrids composite based on PLGA, for example, calcium phosphate/PLGA polymer composites [7,8]. Among the calcium phosphate inorganic materials, nano-hydroxyapatite (n-HA), the most similar material to the mineral component of bones, has been widely applied in bone regeneration surgery owing to its good bioactivity and osteoconductivity. However, it has also been limited to low-load applications because of its intrinsic brittleness in itself [9–11]. To achieve an ideal biomaterials with good mechanical properties and biodegradability as well as bioactivity,

aimed to be applied in the field of bone, it is a hotspot of research to introduce n-HA into PLGA. Accordingly, the n-HA/PLGA composite have usually been investigated [12–15].

In our recent study, we reported on three different surface modification methods of n-HA and the g-n-HA/PLGA composites [16], and we concluded that the surface modification of combining stearic acid and surface-grafting L-lactic was an ideal method, which could obtain g-n-HA/PLGA composite with high bending strength. However, the addition content of g-n-HA is still an important factor to improve the mechanical properties of g-n-HA/PLGA composite, which may induce some subtle variation associated with crystallization behavior and microstructure [17], so as to change the mechanical properties of g-n-HA/PLGA composites. Moreover, up to now, there is no report on the effect of n-HA content on the isothermal crystallization, morphology and mechanical property of n-HA/PLGA composites with n-HA modified by this new surface modification method.

Based on this, in the present work, the influence of different contents addition of g-n-HA on properties of g-n-HA/PLGA composites containing 1%, 3%, 6%, 10% and 15% g-n-HA in weight were studied, including isothermal crystallization behavior, the dispersion of g-n-HA nanoparticle in PLGA matrix and the mechanical properties of g-n-HA/PLGA composites with different contents of g-n-HA. The main purpose of the study is to understand

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the relation between the content of g-n-HA and the isothermal crystallization behavior, microstructure as well as mechanical properties, so as to select an ideal g-n-HA/PLGA composite with an appropriate proportion of g-n-HA in g-n-HA/PLGA composite, which has the high mechanical strength, and it would be more widely used in the biomedical fields in future.

## 2. Experimental

### 2.1. Materials

PLGA was prepared in our laboratory, whose copolymer composition (LA:GA) is 95:05 (mol:mol),  $M_w = 3.6 \times 10^5 - 3.9 \times 10^5$ , determined by intrinsic viscosity method. g-n-HA was also prepared in our laboratory, and the average size of nanoparticle was about 100–120 nm in length and 20–40 nm in width. Other agents were all of analytical grade.

### 2.2. Preparation of g-n-HA/PLGA composites

The nanocomposites of g-n-HA/PLGA containing 1%, 3%, 6%, 10% and 15% g-n-HA in weight were prepared by solution mixing method. First, the neat PLGA was completely dissolved in dichloromethane with an initial concentration of polymer solution was 2% (w/v). Then, pre-calculated g-n-HA, dispersed highly in absolute ethanol and dichloromethane, were slowly added in above polymer solution with the help of magnetic stirring and ultrasonic treatment for more than 4 h, and g-n-HA were uniformly suspended in the PLGA solution. Finally, the mixture were precipitated with an excess of absolute ethanol, washed, and dried in a vacuum oven at 40 °C for 48 h, and the g-n-HA/PLGA containing 1%, 3%, 6%, 10% and 15% g-n-HA were labeled as g-n-HA/PLGA-1%, g-n-HA/PLGA-3%, g-n-HA/PLGA-6%, g-n-HA/PLGA-10% and g-n-HA/PLGA-15%, respectively.

### 2.3. Characterization of g-n-HA/PLGA composites

The isothermal crystallization behavior of the pure PLGA and g-n-HA/PLGA composites with g-n-HA of 1%, 3%, 6%, 10% and 15% were measured with a differential scanning calorimetric (DSC) analyzer (Q20, TA Instruments-Waters, USA) under nitrogen atmosphere, and the gas feed rate was 20 ml/min. About 4–10 mg of each sample was used. The samples were heated from

room temperature to 190 °C with a rapidly heating rate of 200 °C/min and kept at this temperature for 5 min to eliminate previous thermal history, then cooled to predetermined crystallization temperature ( $T_c$ ) (105, 110, 115, 120 °C) at cooling rate of 200 °C/min, and maintained at  $T_c$  till the time necessary for complete crystallization of the polymer matrix. The heat enthalpy of crystallization ( $\Delta H_c$ ) evolved during the isothermal crystallization was recorded as a function of time ( $t$ ) at different  $T_c$ .

The dispersion of the n-HA nanoparticles in the PLGA matrix was investigated by SEM (KYKY-2800 KYKY, China). Fracture surface of g-n-HA/PLGA composites were used for the observation at an acceleration voltage of 20 kV, after been uniformly sputtered with a gold layer.

The bending strength of pure PLGA and g-n-HA/PLGA composites with g-n-HA of 1%, 3%, 6%, 10% and 15% were measured by an electromechanical universal testing machine (CMT6000, Sans, China). The three-point bending strength of rectangular bars of 4 mm × 6 mm × 60 mm were measured at a crosshead speed of 20 mm/min at 19 °C and a relative humidity of 60%, which is in accordance with GB/T6569-1986. Five parallel samples of each specimen were tested and the mean values were given.

## 3. Results and discussion

### 3.1. Isothermal crystallization analysis

The isothermal crystallization heat flow curves of pure PLGA and g-n-HA/PLGA composites were obtained at different crystallization temperature, shown in Fig. 1. It is seen that the crystallization exothermic peak location were shifted to right and became wider and wider, as the increase of the crystallization temperature, and it was basically in accord with the relational expression of  $T_{105^\circ\text{C}} > T_{110^\circ\text{C}} > T_{115^\circ\text{C}} > T_{120^\circ\text{C}}$ , which indicates the crystallization rate slowed with increasing crystallization temperature. The possible reason was that the higher temperature is disadvantage to crystallization, which is caused from the abrupt movement of molecular chain, as to the unstable of crystal nucleus formed, and the molecular chain was fixed, and the more time was needed to finish the total crystallization process and crystallization peak became flatter [18]. In addition, comparing the crystallization exothermic peak location and shape of g-n-HA/PLGA composites containing different contents of g-n-HA, it can be found that crystallization exothermic peak location were shifted to left and

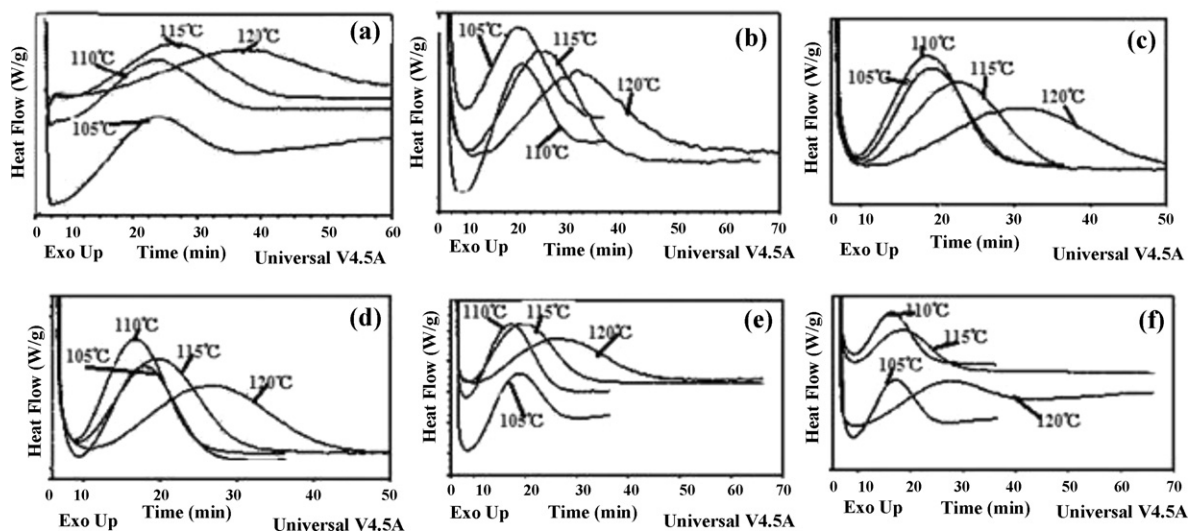


Fig. 1. Isothermal crystallization DSC curves of PLGA and g-n-HA/PLGA composites. (a) PLGA, (b) g-n-HA/PLGA-1%, (c) g-n-HA/PLGA-3%, (d) g-n-HA/PLGA-6%, (e) g-n-HA/PLGA-10%, and (f) g-n-HA/PLGA-15%.

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