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Effect of n-HA with different surface-modified on the properties of n-HA/PLGA composite

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ABSTRACT

Three different surface modification methods for nano-hydroxyapatite (n-HA) of stearic acid, grafted with L-lactide, combining stearic acid and surface-grafting L-lactic were adopted, respectively. The surface modification reaction and the effect of different methods were evaluated by Fourier transformation infrared (FTIR), X-ray photoelectron spectra (XPS), thermal gravimetric analysis (TGA), transmission electron microscopy (TEM). The results showed that n-HA surfaces were all successful modified, and the modification method of combining stearic acid and surface-grafting L-lactic had the greatest grafting amount and the best dispersion among the three modification methods. Then, the n-HA with three different surface modification and unmodified n-HA were introduced into PLGA, respectively, and a serials of n-HA/PLGA composites with 3% n-HA amount in weight were prepared by solution mixing, and the properties of n-HA/PLGA composites were also investigated by electromechanical universal tester and scanning electron microscope(SEM), comparing with PLGA. The results showed that the n-HA/PLGA composite with the n-HA surface modified by combining stearic acid and surface-grafting L-lactic had the highest bending strength and the best dispersion and interfacial adhesion among the three different modification methods, suggesting the surface modification of combining stearic acid and surface-grafting L-lactic was the most ideal method in this study, which has a great deal of enhancement of bending strength than PLGA, and it would be potential to be used in the field of bone fracture internal fixation in future.

1. Introduction

It is a common in clinic to the bone fracture caused by many reasons such as trauma, disease and aging. For a long time, the metallic materials are the traditional fracture internal fixation for their high mechanical strength [1]. However, previous studies have shown that metallic materials did not provide the optimum therapy for internal fixation due to their inherent shortcomings, such as stress shielding resulted from the dismatch of mechanics strength between the metallic materials and the bone, and local tissue inflammation resulted from the release of metallic ion, which may cause the spontaneity secondary bone fracture to occur during the latter healing of bone fracture. Moreover, due to its non-biodegradability in the human body, a second operation would be needed to take out the metal bolt, which would be a very pain and financial losses for patients. Therefore, more and more researches have been focused on developing a kind of biodegradability materials in the human body for fracture internal fixation, and they are likely to replace metal implants in the near future, due to their advantages over metal materials, such as no stress-shielding effect, no metallic corrosion, and no need for removal after surgery [2–4].

Aliphatic polyesters, such as poly(lactic acid)(PLA), poly(glycolic acid) (PGA) and their copolymers (PLGA), are biodegradable and essentially non-toxic one of the main polymer groups, such as bone screws, bone plates and pins made of PLA or PDLLA have been widely used in bone fracture fixation [5–7]. However, PLLA and PDLLA have still their weaknesses, for example, for PLLA, it would take 5 years or so to be completely degraded due to its crystallinity, which would bring inflammatory reaction in body [8], although it has high mechanical strength. For PDLLA, its mechanical properties are too low to be sufficient for more demanding load application due to its non-crystallinity, although it can be completely degraded in one or two years [9].

Poly-lactic-co-glycolic acid (PLGA), a copolymer composed of LA and GA, has attracted increasing attention due to its controllable degradation rate by altering the ratio of LA to GA, and its mechanical properties are not lower than PLLA [10,11]. Moreover,

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PLGA was approved by U.S. Food and Drug Administration (FDA) for clinical research, and so far it has been one of the most commonly used in biomedical fields such as bone screws, due to the combination of its bioabsorbabtily, biodegradable, biocompatible and mechanical properties [12]. However, for PLGA, there are still some critical subjects to be solved so as to be used as bone screws in body, for example, much acidic degradation products, and the poor cell attachment ability and bioactivity due to its hydrophobic properties [13,14]. To overcome these inherent disadvantages, the prevalent method is to introduce the inorganic fillers into PLGA to fabricate filler/polymer composites, such as hydroxyapatite, β-tricalcium phosphate, bioglass, titanium dioxide, and so on [15–18]. Among the inorganic filler/PLGA composites, nano-hydroxyapatite (n-HA) is a major inorganic component of natural bone, so it was thought to have good bioactivity and osteoconductivity properties due to their chemical and structural similarity to the mineral phase of native bone. Moreover, n-HA is a weak alkali inorganic filler, which can buffer acidic in body[19–21]. Therefore, to improve the shortcomings of PLGA, the n-HA/PLGA composite have been extensively investigated, which are expected to reinforce mechanical properties, improve cell adhesion and endow it with bioactivity as well as adjust the degradation rate by inducing n-HA nanoparticles [22–24].

However, there are two most problematic issues in manufacturing n-HA/PLGA composite, the one is the agglomeration of the HA nanoparticles in the PLGA matrix, and another is a weak adhesion between the hydrophilic n-HA and hydrophobic polymer, which will result in early failure at the interface and thus deteriorate the mechanical properties and limit its load-bearing applications. To solve these problems, it is necessary to hunt for an appropriate modification method for n-HA to improve the dispersion and the compatibility between the filler and the polymer, and it has been becoming the key of research work. Accordingly, many methods have already been applied [25–30], including a diverse class of coupling agents, zirconyl salt, poly acids, dodecyl alcohol, polyethylene glycol and isocyanate, and so on. However, among these techniques, the modification effects were all not very ideal, and there is few literature to report on the enhancement of bending strength. However, bending strength of materials is a very important factor in selecting internal fixation materials in clinic.

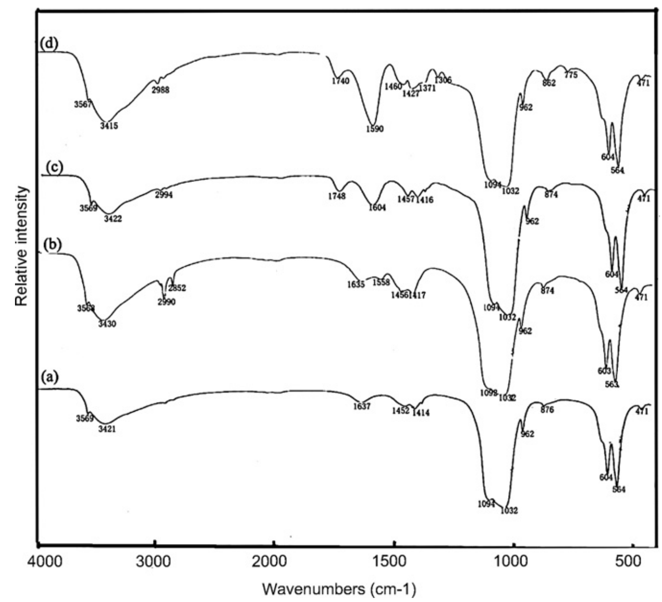

Fig. 1. IR spectra of (a) unmodified n-HA, (b) n-HA modified with stearic acid, (c) n-HA grafted with L-lactide, (d)n-HA modified by combining stearic acid and grafted L-lactide.

Based on this, in the present work, three different surface modification methods for n-HA of stearic acid, grafted with L-lactide, combining stearic acid with surface-grafting L-lactic were adopted, respectively. The surface modification reaction and the effect of different methods were evaluated by Fourier transformation infrared (FTIR), X-ray photoelectron spectra (XPS), thermal gravimetric analysis (TGA), X-ray diffraction pattern (XRD), transmission electron microscopy (TEM). Then, a serials of n-HA/PLGA composites with 3% n-HA in weight were prepared by solution mixing, and the properties of n-HA/PLGA composites were also investigated by

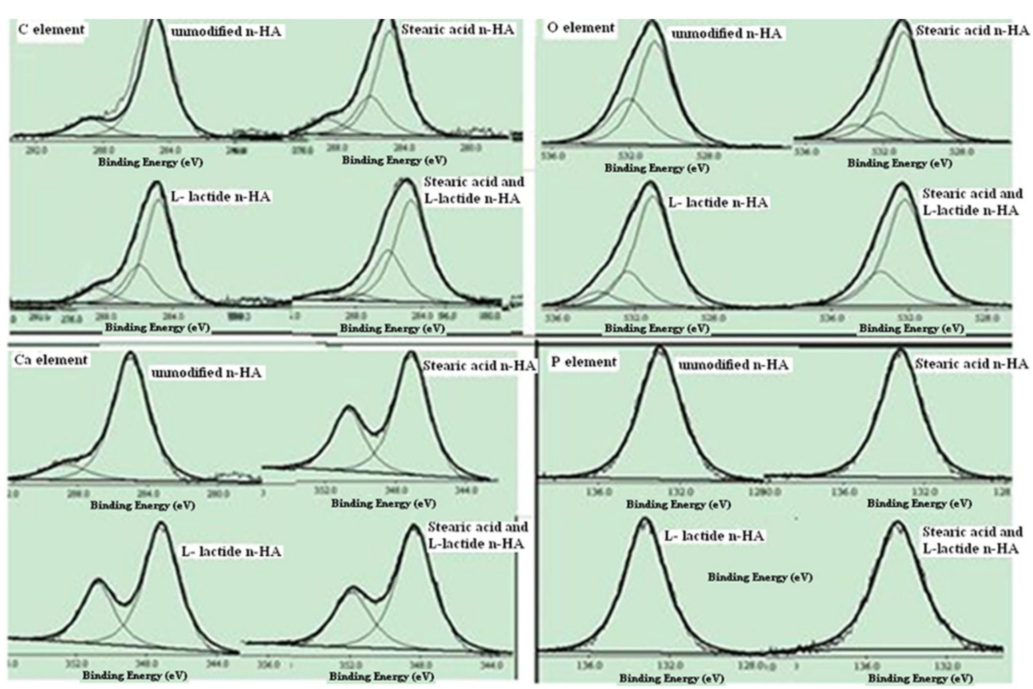

Fig. 2. C O, Ca and P elements fitting spectrum of XPS of n-HA and n-HA modified by different methods.