Processing properties of nano apatite-polyamide biocomposites

W. JIE, L. YUBAO*, H. YI
Research Center for Nano-Biomaterials, Analytical & Testing Center, Sichuan University, Chengdu 610064, People's Republic China
E-mail: nic7504@scu.edu.cn, nic7505@263.net

Hydroxyapatite (HA) ceramics are attractive in hard tissue repairing because of its excellent biocompatibility and osteoconductivity. However, due to the brittleness and fatigue failure when impanted in vivo, HA ceramics have been restricted to be used in non load-bearing sites for bone repairing [1, 2]. In order to enhance the toughness of HA bioceramics, studies on HA and polymer composite are highlighted. Up to date, various composites have been explored as bone substitute materials, including HA reinforced polyethylene, polylactide, collagen and polyactive$^{®}$, etc [3–5].

It is clear that the higher the HA content in the polymer, the better the bioactivity of the composite. To achieve the desired bioactivity, it is necessary to increase HA content in composite. However, at present, most HA/polymer composites are prepared by direct mixing HA powder and polymer resin, which are difficult to fabricate composite with high HA content [6]. It is known that the smaller the HA particles are, the higher the HA content could be in the polymer [7]. Therefore, nano-hydroxyapatite (n-HA) crystals should be selected to fabricate high bioactive composites. However, due to its high surface activity, when n-HA slurry is dried in air, it will clog into micrometer-sized HA particles. Try to solve this problem, n-HA slurry (not dried HA powders) is used directly to prepare HA/polymer composite in this study.

To ensure good mechanical properties, the interface between the HA and polymer in n-HA/polymer composite should be first optimized to create proper chemical bondings between the two phases. n-HA is a polar inorganic material, which has relatively high affinity to polar organic polymer and may form chemical bondings with polar polymer (e.g. polyamide) [8].Therefore, n-HA slurry and polar polymer polyamide66 (PA66) with high toughness and polar groups in its molecular chains are used to prepare biocomposite by co-solution method in this study.

HA precipitation was prepared by the following reaction:

$$\begin{aligned}&10\mathrm{Ca(NO_3)_2} + 6\mathrm{(NH_4)_2HPO_4}\\&+8\mathrm{NH_4OH} \rightarrow \mathrm{Ca_{10}(PO_4)_6(OH)_2}\\&\qquad +20\mathrm{NH_4NO_3} + 6\mathrm{H_2O}\end{aligned}$$

The calcium nitrate, ammonium dibasic phosphate and DMAC are from Chengdu Chemical Agent Co. Ltd, China, AR grade. In an autoclave, HA precipitation in a solid-solution ratio of 1wt% is treated hydrothermally at 140°C under 0.3 MPa for 2 hr. After treatment, HA precipitates into n-HA crystals in a slurry state [9]. n-HA slurry and DMAC(N, N-dimethyl acetamide) are then mixed in a three-neck flask. When the mixture is stirred, the temperature is gradually increased to 100–120°C. After the water is completely evaporated, n-HA/DMAC slurry is obtained. Composites is prepared by co-solution method by mixing n-HA/DMAC slurry with PA66 (18kDa, purchased from Du Pont Company, USA) DMAC solution. When the mixture is stirred, the temperature is gradually increased to 130–150°C for 4 hr, then the mixture is cooled down to room temperature. After fully washed by hot deionized water and ethanol, final products are dried at 80°C for 48 hr. Composites with different n-HA content are prepared with the similar method. n-HA/PA66 composite samples are fabricated with an injection moulding machine. The injection temperature ranged from 260 to 290°C under15 MPa pressure.

The composites are analyzed with Fourier Transform Infrared absorption spectra (FT-IR, Nicolet 170SX), Differential Scanning Calorimetry (DSC,SEIKO EXSTAR6000), X-ray Photoelectronic Spectroscopy (XPS, XSAM 800), Transmission Electron Microscopy (TEM, JEM-100CX) and X-ray Diffraction (XRD, Philips XRD analyzer). The mechanical properties of the composite are measured by Universal Material

TABLE I n-HA content in composite and mechanical properties of dense composite sample (mean ± SD)

Sample	n-HA content (%)	Tensile strength (MPa)	Bending strength (MPa)	Compressive Strength (MPa)	Elastic modulus (GPa)
1	32.51	65 ± 5	72 ± 5.0	90 ± 4	3.1 ± 0.2
2	40.26	70 ± 2	81 ± 2.3	97 ± 2	3.8 ± 0.3
3	51.48	73 ± 1	88 ± 3.6	101 ± 1	4.7 ± 0.5
4	64.35	77 ± 2	94 ± 5.2	106 ± 3	5.5 ± 0.3

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*Author to whom all correspondence should be addressed.

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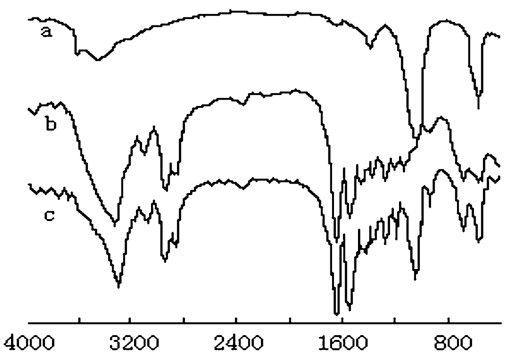

Figure 1 IR spectra of (a) n-HA, (b) PA66 and (c) n-HA/PA66 composite.

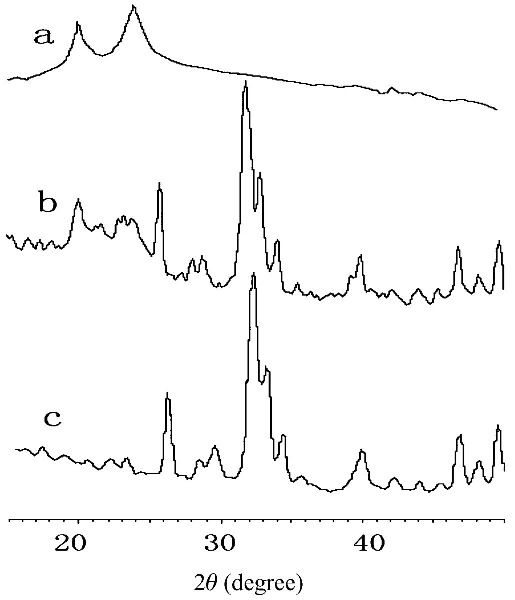

Figure 2 XRD spectra of (a) PA66, (b) n-HA/PA66 composite and (c)n-HA.

Test machine with a average value of 4 specimens. n-HA content in the composite is tested by burning the composite at 800°C in air with a average value of 3 specimens (n-HAwt%= burned product/composite × 100%).

Table I is the n-HA content in the composite tested by burning the composite at 800°C in air. Data shows that the n-HA content in different parts of the same sample is very similar. This indicates that the composite has good homogeneity and expected n-HA content (up to 65wt%) in the composite can be obtained by co-solution method used in this experiment.

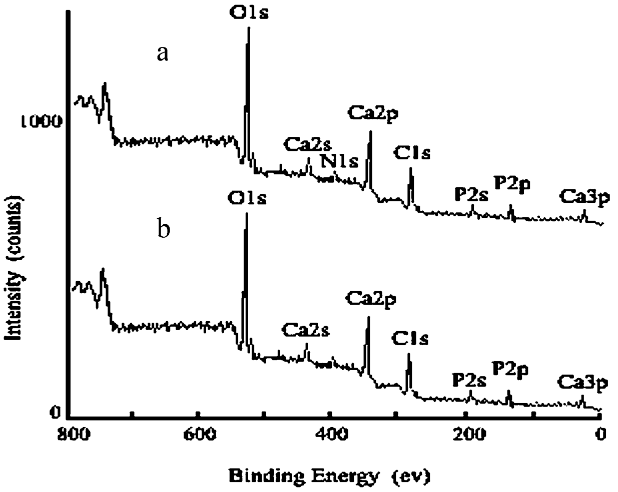

Figure 4 XPS spectra of (a) n-HA/PA66 composite and (b) n-HA.

The IR spectrum of the n-HA is shown in Fig. 1a. It is observed that the peaks at 566 cm^{-1}, 1034 cm^{-1} and 1095 cm^{-1} belonging to PO_4^{3-} of pure n-HA, move to 568 cm^{-1}, 1037 cm^{-1} and 1092 cm^{-1} in n-HA in the composite [10]. Bands around 2924 cm^{-1} and 2851 cm^{-1} represent carbon hydrogen ($-CH_2-$) vibration of PA, the two peaks move to 2931 cm^{-1}and 2858 cm^{-1} in composite as shown in Fig. 1c. The band around 1544 cm^{-1} representing the stretching vibrations of carbon-nitrogen (C—N) and hydrogen-nitrogen (H—N) of PA in Fig. 1b moves to 1537 cm^{-1} in composite. These results indicate that some molecular interactions may be presented between the n-HA and PA66 in the composite.

The absorption peaks at 3571 cm^{-1} and 632 cm^{-1}, representing bending vibration of hydroxyl ($-OH^-$) of n-HA, obviously decrease in composite as shown in Fig. 1c. The —NH— characteristic adsorption peak of PA at 3300 cm^{-1} shifts to 3313 cm^{-1}, the —C =O vibration peak at 1640 cm^{-1} displaces to 1636 cm^{-1} in the composite. These results mean that hydrogen bonding may be formed between the $-OH^-$ group of n-HA and —C=O and/or —NH— groups of PA66. A new peak for $-COO^-$ stretching vibration appears at 1417 cm^{-1} in the composite, which may result in the bonding of $-COO^-$ group of PA66 with the calcium ion in n-HA. Therefore, it could be deduced that n-HA may be linked

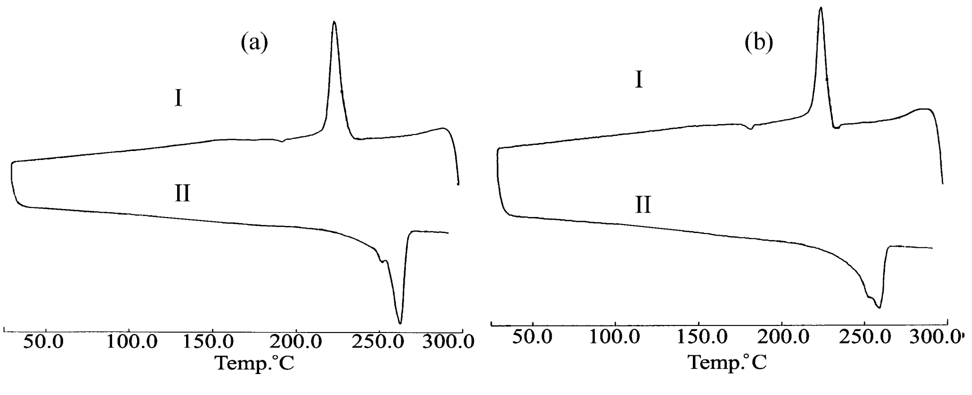

Figure 3 DSC curves of (a) PA66 and (b) n-HA/PA66 composite (I) cooling; (II) melting.

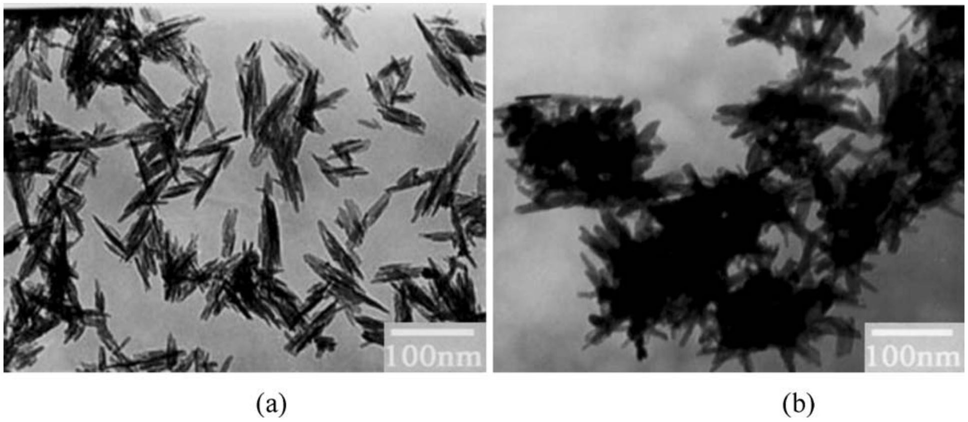

Figure 5 TEM micrographs of (a) n-HA crystals and (b) n-HA/PA66 composite.

to PA66 by hydrogen bonding and by the formation of carboxyl-calcium-carboxyl linkage as following:

$$\mathrm{PA{-}COO^{-}[Ca^{2+}(n\text{ - }HA)]^{-}OOC\text{ - }PA}$$

These linkages have strong effects on interface behavior and mechanical properties of the composite.

Fig. 2 shows the relevant XRD patterns, in which 2a is PA66, 2b is n-HA/PA66 composite and 2c is n-HA. The PA66 in Fig. 2a and 2b have two characteristic peaks at $2\theta = 20^\circ$ and 24° [11]. The crystalline peaks of n-HA at $2\theta = 25.9^\circ, 32^\circ, 33^\circ, 34^\circ, 35.5^\circ$ and 40° are shown in Figure 2b and 2c, exhibiting a HA structure. From the XRD patterns, it can be calculated by Scherrer equation that the mean size of n-HA crystals and n-HA crystals in composite is about 45nm. Fig. 3 is the DSC curves of PA66 and n-HA composite, the result shows that the crystallinity of pure PA66 and PA66 in the composite is 35% and 24% respectively. When pure PA66 and PA66 in the composite are compared, the crystallinity of PA66 decreased in the composite, which indicates that the crystal structure of PA66 changes after forming composite with n-HA. Because the hydrogen bonds in PA66 contribute to its crystallinity, the appeared interfacial chemical bondings between the n-HA and PA66 in the composite may result in the decrease of the number of hydrogen bonds of PA66, and thus the crystallinity of PA66 decreases.

Fig. 4 is the XPS curve of n-HA/PA66 composite and n-HA. The binding energy of calcium atom (Ca), phosphorous atom (P) and oxygen atom (O) has some difference between n-HA (O: 531.2, Ca: 351.5 and 347.5, P: 134.5ev) and the composite (O: 531.6, Ca: 351.8 and 348.2, P: 135.4ev). The binding energy of O in the composite is higher than that of n-HA by 0.4ev, Ca by 0.3ev and 0.7ev, and P by 0.9ev respectively. The increase of the binding energy of Ca, O and P in the composite indicates that chemical bonds are present between the n-HA and PA66. Combining the IR,XRD,DSC and XPS analysis results, it can be concluded that strong molecular interactions and chemical bondings are presented between the n-HA and PA66 interface in the composite.

The TEM photographs of (a) n-HA crystals and (b) n-HA/PA66 composite are shown in Fig. 5. The size of the needle-like n-HA crystals and n-HA crystals in the composite is approximately $\Phi 5$–10 nm × 70–90 nm, and the n-HA crystals are uniformly distributed in PA66 matrix and combined closely with the PA66.

Chemical bonding and strong molecular interaction between n-HA and PA66 obviously ensure good mechanical properties of the composite. The mechanical properties of the composite samples are shown in Table 1. The bending strength, tensile strength and compressive strength of the composite with 64.35wt% n-HA content are 94MPa, 77MPa and 106MPa, respectively, which is close to the natural bone (80–100 MPa, 60–120 MPa, 50–140 MPa separately [12]). The elastic modulus of the composite prepared in this study is 5.5Gpa (similar to that of natural bone: $3 \sim 25$ GPa). However, the elastic modulus of bioceramics and medical metals is much higher ($70 \sim 300$ GPa), which usually causes stress stimulating or stress shielding effect and finally result in bone resorption and loosening of implants in clinics [13]. Therefore, the composite prepared in this study can match well mechanically to that of human bone.

In a summary, the novel biocomposite of n-HA and PA66 prepared by co-solution method has good homogeneity, high n-HA content, and excellent mechanical properties, which are close to the natural bone. Strong molecular interactions and chemical bondings are presented between the n-HA and PA66 interface in the composite. The n-HA/PA66 composite can be used in load-bearing sites as bone substitute.

Acknowledgments

The financial support from the Ministry of Science and Technology of China and the Ministry of Education of China are gratefully acknowledged.

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Received 17 November 2003
and accepted 20 July 2004