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A study on nano-composite of hydroxyapatite and polyamide

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A new kind of nano-composite of nano-hydroxyapatite (n-HA) and polyamide$_{8063}$ (PA) was prepared directly using nano-hydroxyapatite slurry and co-solution method under normal atmospheric pressure. The results show that the n-HA content in the composite can reach 65 wt%, similar to the apatite content in natural bone. Interface chemical bonding forms between n-HA and polyamide, the n-HA keeps the original morphological structure with a crystal size of 10–30 nm in diameter by 50–90 nm in length with an aspect ratio of 2.5, and distributes uniformly in the composite. The synthetic nano-composite could be one of the best bioactive materials for load-bearing bone repair or substitution. © *2003 Kluwer Academic Publishers*

1. Introduction

Being the main inorganic constitution of hard tissues, hydroxyapatite (HA) has been attractive in hard tissue repair. Fundamental studies and clinical applications have demonstrated that HA biomaterials are biocompatible and osteoconductive [1, 2]. However, due to the brittleness of HA ceramic, it has been restricted in non load-bearing sites for bone repair or substitute [3, 4]. In order to enhance its toughness, study on HA and polymer composite is highlighted, such as HA reinforced polyethylene, polylactide and polyactive®, etc. The combination of (HA) bioactivity and (polymer) toughness may result in a new load-bearing bioactive material with good mechanical properties [5–7].

It is known that the higher the HA content in the polymer, the better the composite bioactivity. However, the increase of HA content in the polymer is affected by the particle size and the interface between HA and polymer which may also cause the change of mechanical strength of the composite [5, 8, 9]. It has been also speculated that the smaller of the HA particles, the higher of the HA content in the composite, and the better the homogeneity of the composite. In an effort to introduce strong interfacial bonding between the two phases, nano-grade hydroxyapatite (n-HA) crystals and polar polymer that may form chemical bonding with n-HA should be selected to make nano-composite.

Hydrothermally synthesized nano-grade apatite crystals have a similar size, composition and crystal structure to bone apatite, and probably have better osteoconductivity and bioactivity [10, 11]. Therefore, n-HA crystals should be used to make n-HA/polymer composite. However, when the n-HA slurry is dried in air, it will clog due to its high surface activity into micrometer-sized HA particles that are difficult to make a nano-composite with good homogeneity and high HA content. In this study, n-HA slurry and polar polymer polyamide$_{8063}$® (PA) with high toughness and good mechanical properties are selected to prepare nano-composite by co-solution method.

2. Materials and methods

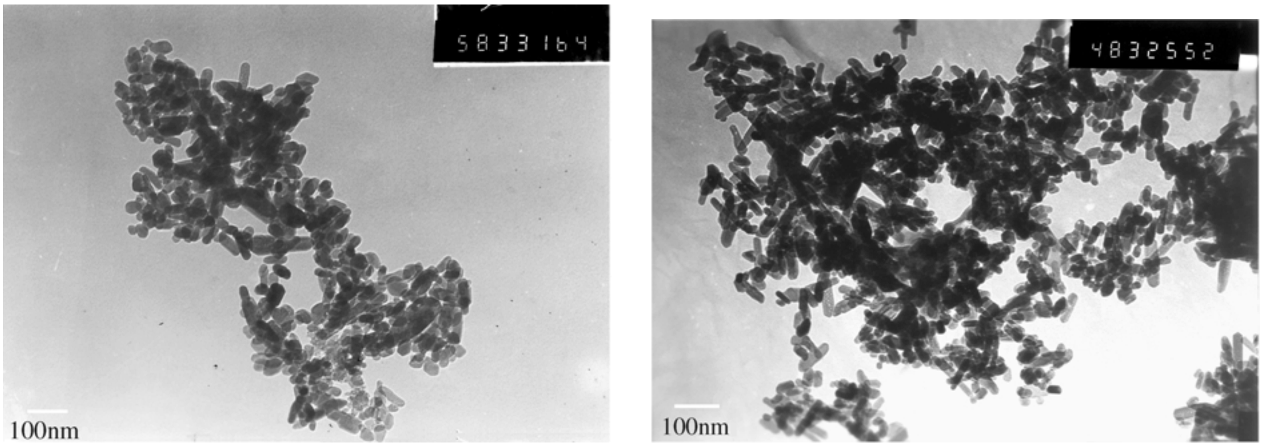
HA precipitation was prepared by the following reaction:

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

In an autoclave, the HA precipitation in a solid-solution ratio of 1 wt% was treated hydrothermally at 140°C under 0.3 MPa for 2–4 h [11]. After treatment, the HA precipitation became n-HA crystals in a slurry state. n-HA slurry and DMAC(N, N-dimethyl acetamide) were put into a three-neck flask, when the mixture was stirred, the temperature was gradually increased to 100–120°C. After the water was completely removed, the n-HA/ DMAC slurry was obtained.

Composites were prepared by the co-solution method that is mixing n-HA/DMAC slurry with PA (18 kDa, purchased from Du Pont Company, USA) DMAC solution. When the mixture was stirred, the temperature was gradually increased to 130–160°C for 4 h, then cooled down to room temperature. After fully washed by hot deionized water and ethanol, the products were dried at 110°C for 48 h. Composites with different n-HA content were prepared with a similar method.

The composites were characterized by infrared spectroscopy (IR), X-ray photoelectronic spectroscopy



(a) (b)

Figure 1 TEM photographs of n-HA crystals and n-HA/polyamide composite n-HA crystals: (a) nano-composite and (b) Bar: 100 nm.

(XPS), transmission electron microscopy (TEM) and X-ray diffraction (XRD). IR spectra were scanned by a Nicolet 170SX FI-IR spectrometer. XPS were carried out with XSAM 800 Instrument. TEM was taken by JEM-100CX and XRD were scanned through Philips XRD analyzer. n-HA content in the composite was tested by Burning Test at 800°C under air (O_2) atmosphere.

3. Results

3.1. Burning test analysis

Table I is the n-HA content in the composite tested by burning at 800°C under air (O_2) atmosphere. The data show that the n-HA content in different the parts of same the sample is almost the same. This indicates that the composites prepared by the co-solution method have a good homogeneity and an expected n-HA content n-HA content in the composite can reach 65 wt% through this method.

3.2. TEM analysis

Fig. 1 is the TEM pictures of n-HA crystals (a) and n-HA/polyamide composite (b). It can be seen that the hydrothermally synthesized n-HA crystals have a crystal size of 10–30 nm in diameter by 50–90 nm in length with an aspect ratio of ~2.5, and a similar diameter and length can also be seen in the composite. This indicates that the n-HA crystals are still nano-grade and scatter homogeneously in the composite.

3.3. XRD analysis

Fig. 2 shows the XRD results of the n-HA (a), polyamide (b), and n-HA/polyamide composite (c). The polyamide$_{8063}$ is an amorphous polymer without crystalline peak as shown in (b). Comparison of XRD curve of n-HA (a) with that of the composite (c), it can be seen that the patterns of starting n-HA are very similar to that of the composite. the peaks position of the starting n-HA does not change in the composite. This means the n-HA still keeps its original crystal structure in the composite.

TABLE I n-HA content in the composites

Sample	1	2	3	4
n-HA (wt%)	45.07	51.55	38.78	64.15
	45.05	52.05	38.48	64.05
	45.05	51.74	38.88	64.56
Average (wt%)	45.06	51.78	38.71	64.25

3.4. IR analysis

Fig. 3 is the IR spectra of n-HA (a), polyamide (b) and n-HA/polyamide (PA) composite (c). The peaks of 2858 cm^{-1} and 2930 cm^{-1} represents the $-CH_2-$ group in PA, but it moves to the 2859 cm^{-1} and 2932 cm^{-1}in the composite; the stretch vibration peaks of N—H and —C=O in PA are at 1544 cm^{-1} and 1640 cm^{-1} [12], but shift to 1545 cm $^{-1}$ and 1641 cm^{-1} in composite separately. In addition, the peaks of 1636 cm^{-1}, 1266 cm^{-1}, 1368 cm^{-1}, 472 cm^{-1} in n-HA move to 1641 cm^{-1}, 1269 cm^{-1}, 1372 cm^{-1} and 474 cm^{-1} in the composite respectively. The peaks at 3571 cm^{-1} and 633 cm^{-1}

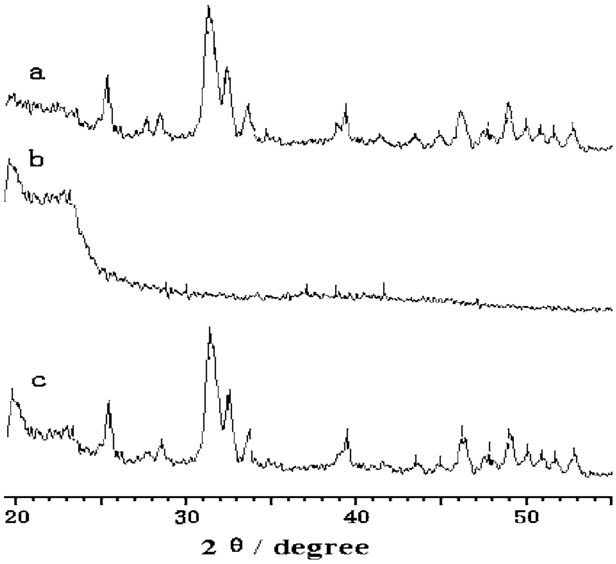


Figure 2 XRD patterns of n-HA, polyamide and the n-HA/polyamide composite. n-HA (a), polymaide (b), and nano-composite (c).

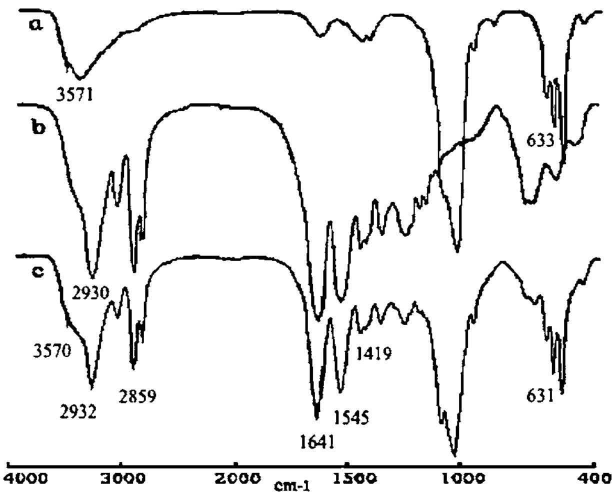


Figure 3 The IR spectra of n-HA (a), polyamide (b), and n-HA/polyamide composite (c).

are from the —OH group in n-HA, but it appears at 3570 cm^{-1} and 631 cm^{-1} in the composite. Comparison of IR spectrum of original n-HA with that of the composite, it can be seen that the two peaks have a slight displacement and become weak in the composite. In addition, there appears a new peak at 1419 cm^{-1}in the composite, comparing with the spectra of n-HA and polyamide, the new peak should belong to the —COO$^-$ stretch vibration.

3.5. XPS analysis

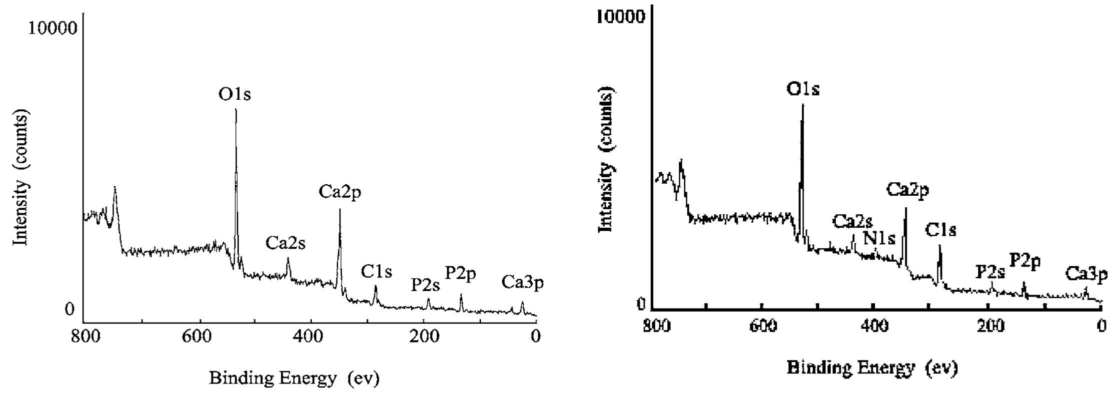
Fig. 4 is the XPS curve of n-HA (a) and the n-HA/polyamide composite (b). The binding energy of calcium atom (Ca), phosphor atom (P), oxygen atom (O) has some difference between original n-HA (O: 531.5, Ca: 351.8 and 347.3, P: 134.5 ev) and in the composite (O: 531.6, Ca: 351.9 and 348.4, P: 135.5 ev) [13]. The binding energy of O in the composite is higher than that of n-HA (a) by 0.1 ev, Ca by 0.1 ev and 1.1 ev, and P by 1 ev respectively. Comparison of the binding energy of Ca, O and P in n-HA with that in the composite shows that the binding energy of Ca, O and P increases in the composite, this means that there are some interface interaction or bonding present between the n-HA and polyamide.

4. Discussion

To achieve the desired bioactivity, it is necessary to improve the n-HA content in the composite; the n-HA can provide bioactivity with living tissue, such as can form strong bone-bonding with natural bone. Clearly, the smaller the HA particles and the higher the HA content is in the polymer, the better the composite bioactivity [8, 13]. Conventional melting method by mechanically mixing HA powders with polymer to prepare HA/polymer composite is difficult to ensure high HA content in the composite with good homogeneity and mechanical strength [13]. Therefore, undried n-HA slurry was directly utilized to prepare n-HA/Polyamide composite in solution under normal atmospheric pressure in this experiment. The result reveals that inorganic/polymer composite prepared by using co-solution method is more helpful than mechanically mixing with clogged powders under high temperature and high pressure. The burning test indicates that the n-HA content in different parts of the same sample is almost the same, this means that the prepared composites with a high n-HA up to 65% have a good homogeneity. TEM and XRD analysis indicates that n-HA keeps its original morphological structure and uniformly distributes in the polyamide matrix, this is similar to the natural bone in which n-HA uniformly distributes in the collagens [14]. Therefore, directly using n-HA slurry in solution is an effective method to prepare a homogeneous nano-composite with high HA content.

In making n-HA/polymer composite, the interface between the inorganic mineral and organic polymer should be first optimized in order to create a proper bonding between the two phases. The Polyamide$_{8063}$ (PA) is a polymer with high polarity because of some polar groups in its molecular chain. The polar polymer has relatively high affinity to polar fillers (n-HA), and can form chemical bonding with n-HA inorganic polar fillers, therefore PA was chosen as the polymer matrix to prepare nano-composite in this experiment.

IR results show that some peaks in the composite have slight displacement comparing with those peaks in n-HA and polyamide; the peaks at 3570 cm^{-1} and 631 cm^{-1} of the —OH group become weak in the composite; and a new peak at 1419 cm^{-1} which belongs to the carboxyl (COO$^-$) stretch vibration appears in the composite. This may be caused by the formation of



(a)

(b)

Figure 4 XPS curve of n-HA (a) and n-HA/polyamide composite (b).

some interface interaction or bonding between the –OH in the HA and the amide (—CONH—) in the polyamide, therefore the vibration of —OH was hampered, and there is also some attraction between calcium ions (Ca^{2+}) in n-HA and $—COO^-$ group in composite. From above fact, it may be deduced that interface bonding between composite and n-HA have been formed.

XPS analysis shows that binding energy of Ca, O and P in the composite increases compared with that of n-HA. This means that there would be some interaction or chemical bonding forming between n-HA and polyamide. This may be caused by the affinity between Ca^{2+}, —OH, PO_4^{3-} in n-HA and $—COO^-$, —CONH— in the polyamide. From this result and that of IR spectra, it can be concluded that some chemical bonding is present between n-HA and polyamide. As a filler, synthesized n-HA can only be used to reinforce a polymer without enough bioactivity when its content in the composite is lower than 10 wt%. However, when the n-HA content in a composite is higher than 40 wt%, the composite can be used as a bioactive medical material.

It is well known that bone at structural level is a composite of n-HA crystals reinforced collagen [10] the n-HA used in this experiment is a hydrothermally synthesized, nano-grade HA crystal, similar to bone apatite in morphology, composition, crystal structure and crystallinity [11]. Polyamide has good compatibility with the human body, it is an excellent medical polymer and usually used as biomedical materials,for instance, the surgical sutures, and PA also has some similarity to collagen in structure, such as containing —CONH—, COO^- groups, etc. [12–14] in this study, n-HA and polyamide were used to prepare a bone-like composite, it seems that the more similar the composition between biomaterial and bone, the better the bio-performance of the material in osseous environment. therefore, the synthetic n-HA/polyamide composite may have better biological properties and be superior to other conventional HA biomaterials.

5. Conclusion

Direct use of n-HA slurry and polyamide solution by the co-solution method to prepare nano-composite is a very useful way to make bioactive composite with high HA content, good homogeneity and chemical interface bonding. When compared to natural bone, the synthetic nano-composite can be said to be a bone-like biomaterial, the n-HA provides the bioactivity for the composite, forming bone-bonding with natural bone and the polymer is responsible for mechanical strength and toughness. Therefore, the synthetic nano-composite may be one of the best bioactive materials for load-bearing bone repair or substitute.

Acknowledgments

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References

1. C. J. DAMIEN and J. R. PARSONS, *J. App. Biomter.* **2** (1991) 187.
2. G. DACULSI and N. PASSUTI, *Bioceramics* **2** (1989) 3.
3. M. JARCHO, *Clin Orthop* (1981) 185.
4. H. OONISHI, S. KUSHITANI, H. IWAKI, K. SAKA, ONOH, A. TAMURA, T. SUGIHARA, L. L. HRNCH, J. WILSON and E. TSUJI, *Bioceramics* **8** (1995) 137.
5. W. BONFEILD, *Biomater. Biomech.* (1983) 421.
6. G. K. ANTONIS, *Biomaterials* **15** (1994) 55.
7. LIU QING, *ibid.* **19** (1998) 1067.
8. LI YUBAO, YAN YONGGANG and FENG JIANGQING, “The Fourth Asian Symposium on Biomedical Materials” (Singapore, 1999) p. 89.
9. M. WANG, *Biomaterials* **19** (1998) 2357.
10. LI YUBA and K. DE GROOT, *J. Mater. Sci. Mater. Med.* **5** (1994) 326.
11. WANG XUEJIANG, LI YUBAO and WEI JIE, *Biomaterials* **23** (2002) 4787.
12. LI YUBA, J. DE WIJN, C. P. A. JKLEIIN, S. V. MEER and K. DE GROOT, *J. Mater. Sci. Mater. Med.* **5** (1994) 252.
13. WANG JIANGXIN, LI YUBAO and FENG JIANQIN, *High Technology Lett.* **5** (1999) 103.
14. WEI JIE, LI YUBAO and YAN YONGGANG, *High Technol. Lett.* **4** (2001) 8.

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