Preparation and characterization of bio-composite PEEK/nHA

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Abstract. PEEK/nHA composite material, with excellent mechanical property as polyetheretherketone (PEEK) and biological activity as hydroxyapatite (HA), has attracted wide attention of medical experts and materials science experts. The addition of hydroxyapatite was the decisive factor for biological activity in PEEK/nHA composite. In this paper, acicular nanohydroxyapatite was prepared by chemical precipitation method with Ca(NO₃)₂, (NH₄)₂HPO₄ as raw material; PEEK/nHA composite was prepared by solution blending and vacuum sintering method. The composite was characterized with FT-IR, XRD, DSC, TG and mechanical property test. Results showed that the composite has good thermal stability and compressive property when the mass ratio of PEEK to nHA is 10:3; and high nHA content can improve the biological activity of the composite, which can meet the basic requirements for bone tissue engineering scaffold.

1. Introduction

Polyetheretherketone (PEEK) is a kind of semi-crystalline thermoplastic material with high performance which has not only good processing performance and excellent high temperature resistance, but also many other excellent performance such as good abrasion performance [1-2], chemical resistance, fire resistance, hydrolysis resistance, radiation resistance [3]. For its biocompatibility and characteristics similar to human bone strength and modulus, artificial bone made of PEEK has not only advantages as light-weight, non-toxic, corrosion resistance and so on, but also can be integrated with organism. So using PEEK to fabricate human skeleton instead of metal is one of the most important applications in medical field [3-6]. But the lack of biological activity in PEEK limits its use. Hydroxyapatite (HA), a kind of bioactive material with excellent biological compatibility, which can form strong bond with bone tissue and has osteoconductivity and osteoinductivity, is widely used in clinic [7-8]. But pure HA with low bending strength and large brittleness can’t meet the requirements for clinical applications [9]. To overcome these shortcomings, HA and PEEK were compounded, which can not only increase the toughness of composite, but also endow the composite with biological activity, while increase the rigidity of PEEK. Thus a composite can not only play a supporting role but also has certain biological function in vivo was obtained.

Traditional PEEK/nHA composites were prepared by in-situ polymerization and melt-blending mostly. For the different shapes of human bones and complex surfaces composing the bones, the
precise tailor can’t be achieved according to traditional processing method. Therefore, in this paper, nanohydroxyapatite with biological activity was prepared, and then the nanohydroxyapatite slurry was blended with PEEK. The composite powder was put into mold for extrusion forming after drying. The formed solid was sintered in a Muffle furnace. After all that, composites PEEK/nHA with good dispersion and thermal stability were prepared.

2. Experiment

2.1. Reagents
Calcium nitrate, purity quotient≥99%, Tianjin Fuchen Chemical Reagents Factory; ammonium phosphate, purity quotient=98%, J&K Scientific (Beijing); anhydrous methanol, analytical reagent, Beijing Chemical Works; ammonium hydroxide, analytical reagent, Beijing Chemical Works; PEEK, made by our own; acetone, analytical reagent, Beijing Chemical Works; ethanol, analytical reagent, Beijing Chemical Works.

2.2. Preparation of PEEK/nHA Composite

2.2.1. Preparation of nano HA. 0.6mol/L calcium nitrate aqueous solution and 0.36mol/L ammonium phosphate aqueous solution were prepared. 50mL calcium nitrate aqueous solution and 50mL ammonium phosphate aqueous solution were respectively added into different constant pressure funnels. Flask with three necks was put in thermostatic waterbath at a certain temperature. Calcium nitrate aqueous solution and ammonium phosphate aqueous solution were dropped slowly into the flask with three necks at the same speed while stirring. In the process of reaction, add ammonium hydroxide to maintain the pH value of the reaction system at about 11, and continue to react for 6 hours after two kinds of solution finished dropping. Keep the system static for 24 hours at room temperature. Wash it with de-ionized water repeatedly until the liquid poured out is neutral. White powder of nanohydroxyapatite was obtained after vacuum filtration and drying.

2.2.2. Preparation of PEEK/nHA. 4 conical flasks (250mL) with PEEK powder and HA in certain quality as 4 group tests, appropriate amount of ethanol as dispersant, magnetic stir at room temperature for 4 hours hermetically, and homogeneous dispersion liquid was obtained. Then vacuum filter it and dry the solid, PEEK/nHA composite powder with mass ratios of PEEK to nHA as 10:1, 10:2, 10:3 and 10:4 in the 4 groups respectively were prepared. Then the 4 groups of PEEK/nHA composite powder were milled and pressed into blocks in mold to form certain shapes. Finally, the blocks were put in vacuum annealing furnace for vacuum sintering with a sintering temperature at 350℃. In addition, a group of pure PEEK was prepared and sintered in the above manner as contrast.

2.3. Performance and Characterization
Nicolet-380 Fourier transform infrared spectrometer (FT-IR) from Thermo Electron Corporation was used to determine the molecular structure of nanohydroxyapatite and its composite; D8 KP2025-0NS 16-1-Z X-ray diffractometer from Bruker AXS Diffraktometer were used to determine the crystalline structure (scanning range as 10-60°, scanning speed as 4 deg/min); TGA/DSC1/SF/1100 thermogravimetric analyzer from METTLER TOLEDO Instrument Co., Ltd. was used to determine the thermal stability (heat from room temperature to 800℃ at a rate of 10℃/min); differential scanning calorimeter DSC131 from SETARAM Instrumentation was used to determine the melting point and crystallization temperature (nitrogen flow rate at 50mL/min, keep in 35℃ for 35s, then heat up to 400℃ at a rate of 10℃/min and keep for 20s, then cool down to 30℃ at rate of 10℃/min); microcomputer control electronic universal testing machine RG-300 from Shenzhen Reger Instrument Co., Ltd. was used to determine the mechanical property (according to GB/1041-2008 standard, test temperature at 23℃, humidity as 20%, at a test speed as 1mm/min).
3. Results and Discussion

3.1. Tests and characterization of nHA

3.1.1. Characterization of nHA. Figure 1 is the IR spectrum of HA sample we prepared. In the figure, the absorption peak at 3434.40 cm\(^{-1}\) is corresponding to the contracting vibration peak of O-H in H\(_2\)O; the absorption peaks at 962.20 cm\(^{-1}\) and 1032.20 cm\(^{-1}\) are corresponding to the key band of PO\(_4^3^-\); the absorption peak at 873.07 cm\(^{-1}\) is corresponding to the key band of PO\(_4^2^-\); the absorption peaks at 563.30 cm\(^{-1}\) and 602.83 cm\(^{-1}\) belong to the bending vibration absorption peak of PO\(_4^3^-\). From the analysis above, it is confirmed that the prepared sample do be hydroxyapatite.

In figure 2, HA-40, HA-60, HA-70 are the XRD diffraction patterns of nanohydroxyapatite obtained in 40\(^\circ\)C, 60\(^\circ\)C and 70\(^\circ\)C respectively. The sharp peaks at 25.8\(^\circ\), 31.5\(^\circ\), 32.8\(^\circ\), 34.1\(^\circ\), 39.5\(^\circ\), 46.6\(^\circ\), 49.3\(^\circ\) as 2\(\theta\) are the characteristic diffraction peaks of HA. As seen in table 1, the grain size of HA gradually increased with the increase of reaction temperature.

![Figure 1. IR spectrum of nHA.](image1)

![Figure 2. XRD diffraction of HA.](image2)

| Table 1. Grain size of HA (2\(\theta\)=31.5\(^\circ\)). |
|-----------------------------------------------|
| Sample | Grain size (nm) |
|--------|----------------|
| HA-40  | 10.6           |
| HA-60  | 15.9           |
| HA-70  | 21.6           |

3.1.2. SEM. As seen in figure 3, the nanohydroxyapatite we prepared is acicular crystal, and its acicular section diameter is less than 100nm, which can be proved that the sample we prepared is nanohydroxyapatite.
3.2. Tests and characterization of PEEK/nHA composite

3.2.1. Characterization of PEEK/nHA. Figure 4 is the IR spectrum of PEEK/nHA. In it, the stretching vibration peak for C=O is at 1649.80 cm⁻¹; the aromatic ring framework vibration peak is at 1597.62 cm⁻¹ and 1490.41 cm⁻¹; asymmetric stretching vibration peak for R-O-R is at 1222.91 cm⁻¹; symmetric stretching vibration peak for R-CO-R is at 927.07 cm⁻¹; bending vibration absorption peaks for C-H out of the benzene ring plane is at 836.92 cm⁻¹ and 767.34 cm⁻¹, respectively, at 836.92 cm⁻¹ is the characteristic peak of aromatic ring para-position substitution; from the analysis above, it can be confirmed that there is PEEK in the sample. Absorption peaks at 964.50 cm⁻¹ and 1035.84 cm⁻¹ are corresponding to the key band of PO₄³⁻; absorption peaks at 564.74 cm⁻¹ and 603.75 cm⁻¹ belong to the bending vibration peaks of PO₄³⁻. From the analysis above, it can be confirmed that there is HA in the sample. No appearance of obvious shifting or new peaks, which indicates that the original HA and PEEK matrix is physically combined, which is propitious to maintain the original biological characteristics of HA and PEEK.

Figure 5 is the XRD diffraction of PEEK/nHA. In it, the peaks at 18.9°, 20.9°, 22.9°, 28.9° are the characteristic diffraction peaks of PEEK; the peaks at 25.8°, 31.5°, 32.9°, 34.4°, 46.9° are the
characteristic diffraction peaks of HA. No new diffraction peaks appearance in the pattern further illustrated that the HA and PEEK matrix were physically combined.

![Figure 5. XRD diffraction of PEEK/nHA.](image)

3.2.2. Thermal property of PEEK/nHA. Good thermal stability is required when biological composite material PEEK/nHA as bone tissue substitute material. In long-term organism environment and molding process it can keep its heat-resisting, thermostability and property stable. TG and DSC test results of PEEK/nHA composites are shown in table 2. It can be seen that the decomposition temperature and the maximum weight loss rate of the composites gradually increase with the increase of HA content, but the decomposition temperature decreased slightly when the addition of hydroxyapatite exceeds 30%, which showed that the thermal stability of the composite is better than that of PEEK. Melting point of PEEK matrix in PEEK/nHA composite is lower than pure PEEK, while the crystallization temperature didn’t change basically. Synthesizing the TG and DSC analysis, it can be proved that the PEEK/nHA composite material has good thermal stability.

| Sample number         | m_{nHA}/m_{PEEK} | T_m\(^a\)/℃ | T_c\(^b\)/℃ | T_{max}\(^c\)/℃ | T_{5}\(^d\)/℃ | T_{10}\(^d\)/℃ | T_{20}\(^d\)/℃ |
|-----------------------|------------------|-------------|------------|-----------------|--------------|-------------|-------------|
| PEEK/nHA(0)           | 0                | 341.9       | 281.2      | 583.1           | 572.1        | 579.1       | 587.2       |
| PEEK/nHA(10)          | 10               | 337.7       | 283.3      | 592.9           | 570.9        | 581.9       | 592.4       |
| PEEK/nHA(20)          | 20               | 337.7       | 281.3      | 595.1           | 572.2        | 583.0       | 593.2       |
| PEEK/nHA(30)          | 30               | 337.6       | 279.9      | 594.1           | 575.1        | 585.3       | 595.8       |
| PEEK/nHA(40)          | 40               | 339.1       | 279.2      | 593.4           | 569.6        | 582.9       | 594.9       |

\(^a\) Melting point.
\(^b\) Crystallization temperature.
\(^c\) Temperature in maximum weight loss rate.
\(^d\) Temperature when weight loss rate on TG curve was 5%, 10% and 20%, respectively.

3.2.3. Mechanical properties. As scaffold for scleros tissues, material should maintain its shape within a period of time in order to ensure that it can withstand proper external forces in the process of new bone formation, so mechanical property of material is one of the important factors. The compressive strength values of PEEK/nHA composites with different nHA contents are listed in table 3. It can be seen from table 3, compressive strength of material decreased with the increase of...
Hydroxyapatite addition but decreased slightly. When mass fraction of HA is 40%, the compressive strength of PEEK/nHA is more than 235MPa, which indicated that PEEK/nHA has good compression performance and can meet the requirements of mechanical strength for bone tissue engineering.

**Table 3. Mechanical property of PEEK/nHA.**

| Sample        | Compressive strength(MPa) |
|---------------|---------------------------|
| PEEK/nHA(30)  | 236.8                     |
| PEEK/nHA(40)  | 235.9                     |

4. Conclusions

Acicular nanohydroxyapatite with particle size under 100nm was prepared by chemical precipitation method; PEEK/nHA composite material was prepared by solution blending and vacuum sintering method. The composite material has good thermal stability and compressive property, which is potential to be used as scaffold material in bone repair and bone tissue engineering.

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