Novel acrylic resin denture base with enhanced mechanical properties by the incorporation of PMMA-modified hydroxyapatite

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Abstract A kind of novel acrylic resin denture base enhanced by PMMA-modified hydroxyapatite (M-HAP) was prepared and the modification effect of HAP on the mechanical properties of denture base material was investigated in the present study. HAP whiskers were prepared by hydrothermal homogeneous precipitation process and were silanized by the coupling agent, 3-methacryloxy propyl trimethoxyl silane (γ-MPS), to induce the vinyl groups onto its surface. Methyl methacrylate (MMA) were then modified outside the vinyl functionalized HAP via polymerization to build a similar chemical structure with the acrylic matrix. A novel acrylic resin denture base was obtained through self-curing process with the incorporation of this PMMA-modified HAP, and the content of which ranged from 0 wt% to 0.8 wt%. Thermal gravimetric analysis (TGA), fourier transform infrared spectroscopy (FT-IR), scanning electron microscope (SEM), and universal testing apparatus were used to characterize M-HAP and corresponding denture base. The results showed that PMMA were successfully grafted onto the surface of HAP whiskers with up to 15 wt% and the modification turned out to be useful for the dispersion and compatibility of whiskers in the acrylic resin matrix. The mechanical properties of the prepared denture base samples were enhanced greatly after incorporating with M-HAP fillers. The optimal incorporated content of M-HAP was also investigated.

1. Introduction

Since first polymerized by Walter Bauer in 1936, acrylic resin denture base gradually took the place of traditional metal base and became most commonly used denture base material in clinical fabrication [1,2]. It is a combination of advantages rather than one excellent aspect that accounts for its wide usage [3], including its popularity in satisfying aesthetic...
demands and clearly defined processing method in dentistry application. However, this material is not ideal in every respect [4], especially when meeting with mechanical requirements of prosthesis. Fracture of acrylic resin denture base happens frequently because of the fatigue and chemical degradation of base material [3], which is reflected by a large number of denture repairs annually [5].

Many attempts have been made to repair fractures of denture base for decades in order to improve its usability [6,7]. One method is to use fibers, such as glass, carbon/graphite and ultrahigh-modulus polyethylene fibers as reinforcement buried in the acrylic resin to reduce breakages [8,9]. However, fabrication of properly oriented fibers added in the resin is technically difficult and random dispersion would even result some defects [10]. Besides the fiber, many inorganic materials are of profound interest as reinforcement owing to their synergistically derived properties with organic matrix [11]. Chow [12] studied that essential requirement for obtaining reinforced acrylic resin material with desiring mechanical properties is good adhesion between reinforcements and acrylic matrix. Also clinical application of denture base not only requires excellent mechanical performance, but also expects good biocompatibility and biosafety, while some inorganic materials may cause irritation or even damage to gingival tissue and mouth mucosa in dentistry repair [13].

In this work, we used hydroxyapatite (HAP, Ca_{10}(PO_{4})_{6}(OH)_{2}) whiskers, which is natural biosafety material [14], to incorporate into acrylic resin denture base as reinforcing filler. Hydroxyapatite is widely used in ceramic for its excellent biocompatibility with tissues and skin [15]. In recent years, it was reported that HAP whiskers had been used in dental material as an effective filler to reinforce the polymer matrix [14,16,17]. In order to make HAP whiskers have better interaction to bond with acrylic resins, we designed the following surface modification route, as shown in Fig. 1. Mechanical properties were investigated to prove whether HAP is a promising reinforcement for polymeric resins.

2. Materials and experimental

The materials used in the present investigation were calcium nitrate, sodium dihydrogen phosphate dehydrate, gelatin, urea, methyl methacrylate (MMA, 98%), 3-methacryloxy propyl trimethoxysilane (γ-MPS, 99%), n-propylamine(C_{3}H_{7}N, 99%), benzoyl peroxide (BPO), cyclohexane (C_{6}H_{12}, 99%), acetone (C_{3}H_{6}O, 99%), dimethylbenzene (C_{8}H_{10}, 99%), which were all provided by Sinopharm Chemical Reagent Co., Ltd (SH, China) and directly used without the purification.

The surface modification process designed in the present investigation is shown in Fig. 1.

Synthesis procedure of M-HAP whiskers was modified according to the method reported by Zhan [18]. Calcium nitrate (0.02 mol), sodium dihydrogen phosphate dehydrate (0.02 mol), gelatin (0.4 g), and urea (0.04 mol) were dissolved in deionized water (1 L) at 25 °C. Then, this mixed solution was heated to 95 °C and kept for 72 h. Finally, the product was filtered, washed with 100 °C deionized water, and dried at the room temperature.

A representative procedure for the silanization of HAP is described by Franklin et al. [19]. HAP whiskers (1 g) was dispersed in the cyclohexane (100 mL) ultrasonically for 20 min and then 0.08 mL n-propylamine, 0.2 mL γ-MPS were subsequently added to silanized HAP under constant stirring for 30 min and then heated to 65 °C in water bath for another 90 min. Followed by vacuum filtration and washed 3 times by cyclohexane, the product was dried in the vacuum oven at 80 °C for 12 h.

After silanization 1 g HAP whiskers were dispersed in dimethylbenzene solution (30 mL), and 0.08 g BPO initiator and 8 mL methyl methacrylate were added into above dimethylbenzene solution under nitrogen atmosphere until totally dissolved. The mixed solution was kept stirring and heated to 80 °C in oil bath. After 10 h polymerization, the PMMA-modified HAP (M-HAP) were extracted using acetone at 75 °C for 48 h and dried in the vacuum oven at 80 °C for 12 h.

The self-curing denture base resin powder and liquid (Nissin Dental Product Co., Ltd.) were mixed according to the ratio (10 g/4.3 mL) and conditions specified in the instruction manual and polymerization procedure [20], incorporated with M-HAP whiskers ultrasonically dispersed in the liquid. The fabrication was conducted in vacuum and maintained at 60 °C for 30 min. Composite acrylic resins with the content of 0.0-0.8 wt% M-HAP whiskers were made into rectangle samples with the length of 64 mm, the width of 10 mm and the thickness of 3.3 mm. These standard samples were used to measure the flexural strength according to dentistry documents (ISO1567-1999).

The amount of PMMA content modified on the HAP whiskers was determined by Thermal gravimetric analysis (TGA) using Simultaneous Thermal Analysis System (Netzsch, STA409PC, Germany). Samples weighing from 5 mg to 10 mg were measured from 50 °C to 900 °C at a heating rate of 5 °C/min. The grafting ratio of PMMA polymer modified outside HAP was decided by the weight loss percentage [21].

The infrared spectra determining the chemical structure of investigated materials was recorded by Fourier transform infrared spectroscopy (FT-IR) Spectrometer (Thermo Fisher Scientific, Nicolet 8700, USA). Thirty-two scans were collected for each measurement over the spectral range of 400-4000 cm^{-1} with a resolution of 4 cm^{-1}.

Scanning electron microscope (Hitachi, S4800, Japan) was employed to characterize the size and morphology of the M-HAP whiskers, the dispersion and compatibility of M-HAP in the matrix via the fracture section of denture base samples.

Flexural strength and modulus of denture base samples were measured by Universal Testing Apparatus (WDW3020, China). According to dentistry documents (ISO1567-1999), the measurement used three point bending experiments with 50 mm testing length. The upper fixture loaded on the sample and shifted down at the rate of 5 mm/min until the sample fractures.
3. Results and Discussion

3.1. Characterization of M-HAP whiskers

The results of FTIR spectra of M-HAP and pure HAP (II) are shown in Fig. 2. According to Fig. 2a, the characteristic peak of HAP (PO$_4^{3-}$) is shown at 963 cm$^{-1}$, 1031 cm$^{-1}$ and 1091 cm$^{-1}$. M-HAP has got extra peaks of vinyl and carbonyl group detected at 1638 cm$^{-1}$ and 1718 cm$^{-1}$. Methyl and methylene groups at 1455 cm$^{-1}$ and 2954 cm$^{-1}$ also reveals that PMMA was successfully modified outside HAP whiskers. TGA data in Fig. 2b shows 3.4 wt% weight loss of pure HAP whiskers (II), while M-HAP whiskers have much more weight loss during 250$^\circ$C to 450$^\circ$C. Since the possible by-product was removed by extraction, we could make sure that PMMA polymer had been grafted successfully onto the surface of HAP by chemical bond. The curve reaches a stable stage at about 900$^\circ$C and the grafted ratio of PMMA content is 14.9 wt% in the M-HAP composites.

3.2. Mechanical performance of M-HAP reinforced denture bases

Fig. 3 represents mechanical properties of acrylic resin denture base that incorporated with both pure HAP and M-HAP fillers from 0 wt%, 0.2 wt%, 0.4 wt%, 0.6 wt% to 0.8 wt%, respectively. The histogram (Fig. 3a) indicates that the flexural strength decreased when added with more pure HAP. But the incorporation of M-HAP whiskers could enhance denture base and the flexural strength increased first and then decreased with constant addition of M-HAP. The best flexural strength was reached at 93.2 MPa, which is 32% higher than blank sample, with the optimal content of 0.6 wt% M-HAP. The trend of flexural modulus (Fig. 3b) is similar to flexural strength, which also shows the effect of the reinforcement by M-HAP. The best flexural modulus was reached at 1.92 GPa with 0.6 wt% M-HAP. It may be considered that the surface modification of M-HAP played an important role to endow good adhesion for HAP and acrylic resins and mechanical properties can be improved greatly by the incorporation of M-HAP whiskers.

3.3. The interface interaction between M-HAP and acrylic resins

Fig. 4 shows the morphology of HAP and M-HAP. HAP whiskers. It can be seen that the HAP and M-HAP. HAP whiskers have quite large aspect ratio at 60–80 and no adhesion could be found in Fig. 3a while whiskers seem to cohere together on small scale after grafted with PMMA (Fig. 3b).

FE-SEM was also used to check the fracture sections of denture base samples containing 0.6 wt% HAP and M-HAP, respectively, as shown in Fig. 5. Pure HAP whiskers were
embedded in the matrix and observed on the fracture surface as shown in (Fig. 5a and b), which have a relatively smooth fracture section and small voids near HAP existed in the form of lomerates. It manifests that the adhesion between pure HAP whiskers and acrylic resin was poor and turned out to be a brittle fracture. M-HAP whiskers had better compatibility with PMMA matrix and dispersed well after surface modification according to (Fig. 5c and d). It also explains why the mechanical properties were enhanced by M-HAP rather than pure HAP. Compared to (Fig. 5a), the fracture surface of the sample embedded with 0.6 wt% M-HAP became ductile fracture with many crack patterns when breaking off as shown in (Fig. 5c).

### 4. Conclusion

Biosafety acrylic resin denture base incorporated with PMMA-modified HAP whiskers filling in the matrix was successfully developed in the present study. PMMA chains were grafted on the surface of M-HAP whiskers, which contributes to better dispersion, adhesion, and compatibility with acrylic resin and results in the enhanced mechanical properties of prepared acrylic resin denture base. The performance of this denture base material in clinical application needs to be further studied.

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References