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## BisGMA/TEGDMA dental composite containing high aspect-ratio hydroxyapatite nanofibers

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### Abstract

**Objectives**—The objectives of this study are to investigate the properties of high aspect-ratio hydroxyapatite (HAP) nanofibers and the reinforcing effect of such fibers on bisphenol A glycidyl methacrylate (BisGMA)/triethylene glycol dimethacrylate (TEGDMA) dental resins (without silica microparticle filler) and dental composites (with silica microparticle filler) with various mass fractions (loading rates).

**Methods**—HAP nanofibers were synthesized using a wet-chemical method and characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), and thermal gravimetric analysis (TGA). Biaxial flexural strength (BFS) of the HAP nanofibers reinforced dental resins without any microsized filler and dental composites with silica microparticle filler was tested and analysis of variance (ANOVA) was used for the statistically analysis of acquired data. The morphology of fracture surface of tested dental composite samples was examined by SEM.

**Results**—The HAP nanofibers with aspect-ratios of 600 to 800 can be successfully fabricated with a simple wet-chemical method in aqueous solution. Impregnation of small mass fractions of the HAP nanofibers (5 wt% or 10 wt%) into the BisGMA/TEGDMA dental resins or impregnation of small mass fractions of the HAP nanofibers (2 wt% or 3 wt%) into the dental composites can substantially improve the biaxial flexural strength of the resulting dental resins and composites. A percolation threshold of HAP nanofibers, beyond which more nanofibers will no longer further increase the mechanical properties of dental composites containing HAP nanofibers, was observed for the dental composites with or without silica microparticle filler. Our mechanical testing and fractographic analysis indicated that the relatively good dispersion of HAP nanofibers at low mass fraction is the key reason for the significantly improved biaxial flexural strength, while higher mass fraction of HAP nanofibers tends to lead to bundles that cannot effectively reinforce the dental resins or composites and may even serve as defects and thus degrade the resulting dental resin and composite mechanical properties.

**Significance**—The incorporation of small mass fraction of HAP nanofibers with good dispersion can improve the mechanical property of dental resins and dental composites.

### Keywords

Dental materials; Fiber reinforced composite; BisGMA; TEGDMA; Hydroxyapatite nanofibers

## 1. Introduction

Dental composite resins have been used as popular materials to restore teeth since their introduction about 50 years ago [1,2]. Compared to dental amalgams, they have less safety concern and possess better esthetic property. Based on the report in 2005, the composites were used in more than 95% of all anterior tooth direct restorations and about 50% of all posterior tooth direct restorations [2]. Despite the significant improvement of resin-based composite, restorative composites still suffer from two key shortcomings: deficiencies of mechanical strength and high polymerization shrinkage, which are responsible for the shorter median survival lifespan of resin-based composites (5–7 years) in comparison with amalgam (13 years) [2–5]. Dental composites are typically composed of four major components: organic polymer matrix (BisGMA, TEGDMA, urethane dimethacrylate (UDMA), etc.), inorganic filler particles, coupling agents, and the initiator–accelerator system. During the past decade, more efforts have been focused on dental nanocomposite, with a hope that contemporary nanocomposites with ceramic nanofillers should offer increased esthetics, strength, and durability [6–13]. However, research to date shows that most nanofillers provide only incremental improvements in the mechanical properties [12,14,15] with a few exceptions [8–10].

Variety of calcium phosphates (CaPs), such as HAP [16–18], amorphous calcium phosphates (ACP) [19–24], tetracalcium phosphate (TTCP) [25] and dicalcium phosphate anhydrous (DCPA) [26–28] have been studied as fillers to make mineral releasing dental composites. Skrtic et al. conducted pioneering research to investigate the physicochemical properties of dental composites containing unhybridized and hybridized amorphous calcium phosphates (ACP) [19–24]. Their research demonstrated that hybridization of ACP fillers using agents, such as tetraethoxysilane (TEOS) or  $ZrOCl_2$  solution, improved the mechanical properties, e.g. biaxial flexural strength, of the composites containing ACP fillers. However, the addition of both hybridized and unhybridized ACP fillers generally degraded the biaxial flexural strength of the resin materials [22,23,29]. It was hypothesized that the strength degradation compared to unfilled resin is attributed to poor dispersion and insufficient interaction between ACP and resin. Such hypothesis has been supported by mechanical testing of dental composites containing particles with different sizes [29]. Both nanosized and microsized HAP particles were also studied as dental fillers and the mechanical tests indicated that microsized instead of nanosized HAP was favored in terms of mechanical properties [16–18]. Xu et al. reported that 20% DCPA (dicalcium phosphate anhydrous) nanoparticles with silicon carbide (SiC) whiskers of average 0.9  $\mu\text{m}$  in diameter and 14  $\mu\text{m}$  in length improved the flexural strength of associated dental composites from  $103 \pm 32$  MPa to  $167 \pm 23$  MPa [27]. In summary, except for the positive results from Xu's work where the reinforcement is most likely attributed to silicon carbide whiskers, most of other dental composites using CaP based nanoparticles did not have improved mechanical properties.

From the point of view of composite mechanics, fibers are the preferred reinforced materials compared to particles since fibers can provide larger load transfer and they can also facilitate some well-known toughening mechanisms, such as fiber bridging and fiber pullout. Reinforcement with high-strength inorganic fibers indeed demonstrates significant improvement on the mechanical properties of dental composite [8,26,30–35]. Particularly, Xu et al. showed that the impregnation of extremely strong  $Si_3N_4$  or SiC whiskers with silica nanobeads could result in two-fold increase in composite strength and toughness [26,33,35]. Fong et al. reported that the addition of 5 wt% relative low-strength polymer (Nylon 6) nanofibers could also lead to 36% and 26% increase in flexural strength and modulus, respectively [8]. Beyond the benefits of strengthening effects, it has been reported that fibers can reduce the polymerization shrinkage as well [36,37]. As a result, we

anticipated that the addition of HAP nanofibers could substantially improve the properties, especially mechanical properties, of dental composites, which might eventually extend the lifespan of the restoration.

The aim of this study was to investigate the reinforcement of BisGMA/TEGDMA dental resins (without any silica particles) and composites (with conventional glass fillers) with various mass fractions of HAP nanofibers. The novel HAP nanofibers were synthesized by a wet chemical method and characterized by the X-ray diffraction (XRD), thermogravimetry analysis (TGA) and scanning electron microscopy (SEM). We hypothesize that HAP nanofibers with diameter of around 100 nm should have a very high tensile strength estimated using a ceramic fiber strength model based on Griffith criterion and proposed by Gao [38], and the high aspect-ratio HAP nanofibers can also provide high load transfer from dental resin matrix to strong nanofibers and eventually result in dramatic improvement of the dental nanocomposite mechanical properties. To test this hypothesis, photo-cured BisGMA/TEGDMA dental resins/composites filled with different mass fractions of HAP nanofibers were systematically fabricated. The biaxial flexural strength was then tested, and analysis of variance (ANOVA) was used for the statistical analysis of the acquired data. The morphology of HAP nanofibers and the fracture surface of dental resins and composites were examined by scanning electron microscopy (SEM).

## 2. Materials and methods

### 2.1. Materials

Camphorquinone (CQ), ethyl 4-dimethylamino-benzoate (EDMAB), calcium nitrate, sodium dihydrogen phosphate dehydrate, gelatin, urea, and acetone were all purchased from Sigma-Aldrich Company (St. Louis, MO, USA) without further purification. BisGMA, TEGDMA, and the 0.7  $\mu\text{m}$  size silica particles with 2 wt% silane (V-117-2207) were provided by Esstech, Inc. (Essington, PA, USA).

### 2.2. Synthesis of HAP nanofibers

The HAP nanofibers synthesis procedure is modified from a method reported by Zhan et al. [39]. In a typical synthetic process, calcium nitrate (0.02 mol/L), sodium dihydrogen phosphate dehydrate (0.02 mol/L), gelatin (0.4 g/L), and urea (0.04 mol/L) were dissolved and mixed in an aqueous solution at the room temperature. Then, this mixed solution was heated to 95 °C and kept at such temperature for 72 h. Finally, the product was filtered, washed with deionized water, and dried at the room temperature.

### 2.3. Dental composite preparation

The organic matrix contained 49.5 wt% BisGMA and 49.5 wt% diluent comonomer TEGDMA. CQ (0.5 wt%) and EDMAB (0.5 wt%) were added as the initiator and co-initiator, respectively. Various mass fractions of HAP nanofibers were added into the vial to mix with the dental resins (without silica particles) and composites (with silica microparticles and the total inorganic filler mass fraction was 60 wt%) systems. Several drops of acetone were added to reduce the viscosity of mixture and the resin and filler were mixed with the magnetic stir for about 24 h in order to evaporate the acetone. The initiator and co-initiator (CQ and EDMAB) were added into the monomer solution after covering the whole vial with an aluminum foil to prevent the photo-curing. After mixing thoroughly with the initiator and the solution, the high viscosity solution can be added carefully to the circle shaped Teflon mold (diameter 12 mm, thickness 1.5 mm) covered by glass slide. Then, the samples were photo-cured by Triad 2000 (Dentsply, York, PA, USA) for 2 min on each side.

## 2.4. Characterization

**2.4.1. X-ray diffraction**—Power X-ray diffraction (XRD) experiments were performed on a Scintag Pad V X-ray diffractometer with Cu K $\alpha$  radiation (1.54 Å) and a Ni filter. Scans of bulk powder were run at 40 kV and 35 mA.

**2.4.2. Thermal gravimetric analysis (TGA)**—The amount of organic layer on HAP nanofiber was determined by thermal gravimetric analysis (TGA) using Perkin-Elmer DSC-7 Differential Scanning Calorimeter (Waltham, MA, USA). TGA measurements were performed from room temperature to 900 °C at a heating rate of 5 °C/min. The amount of organic layer on the HAP surface was determined by comparing the weight loss percentage during heating measured using TGA with previously reported TGA data of HAP nanoparticles synthesized by wet-chemical methods [40–43].

**2.4.3. Heat treatment**—The HAP nanofibers were heat treated at 400 °C, 600 °C, 800 °C, 1000 °C, 1200 °C, and 1400 °C in air using a box furnace for about 24 h (Carbolite RHF 16/15, Pacific Combustion, Torrance, CA, USA), respectively.

**2.4.4. Morphology**—Scanning electron microscope (Quanta 600 FESEM, FEI, Japan) and digital camera (Canon PowerShot SD780, Canon, Japan) were employed to characterize the morphology and size of the HAP nanofibers and the fracture surface of as-fabricated dental resins and composites.

**2.4.5. Biaxial flexural strength (BFS)**—Biaxial flexural strength of the dental resin and composite samples was measured using a SMS TA.HDPlus Texture Analyzer (Texture Technologies, Scarsdale, NY, USA) [23,44]. The Analyzer recorded the applied load as a function of time. The BFS was calculated according to Timoshenko and Woinowsky-Kreiger (Eq. (1)) [45].

$$\sigma = \frac{P}{h^2} \left\{ (1+V) \left[ 0.485 \ln \left( \frac{a}{h} \right) + 0.52 \right] + 0.48 \right\} \quad (1)$$

where  $\sigma$  was the maximum tensile strength,  $P$  was the measured fracture load,  $a$  was the radius of the knife-edge support,  $h$  was the mean specimen thickness measured from fragments at the point of fracture with a screw-gage micrometer accurate to 10  $\mu$ m and  $\nu$  was the Poisson's ratio. In comparison with the three point flexural test, the biaxial flexural test is known to be more clinically relevant. In addition, disc specimens are photo-cured in one-shot, eliminating an overlapping photo-curing technique associated with bar-shaped specimens, which might reduce the reliability of strength data [45].

## 3. Results

### 3.1. Synthesis and characterization of HAP nanofibers

Fig. 1 shows the XRD pattern of as-fabricated HAP nanofibers. The HAP nanofibers have the characteristic peaks at  $2\theta$  regions of 26°, 29°, 32–34°, 40°, 46–54°, which are consistent with the HAP phase (ICDD 09-432). The digital image (Fig. 2a) shows that the obtained product is white color and the cotton-like. As shown in a low magnification SEM image (Fig. 2b), the product consists of bundles of HAP nanofibers and the average lengths of such bundles are 60–80  $\mu$ m. A higher magnification SEM image (Fig. 2c) revealed that the average diameter of as-fabricated HAP fibers is about 100 nm.

Heat treatment and thermal analysis were conducted to examine the HAP nanofibers. SEM images of as-fabricated HAP nanofibers heated in atmosphere at different temperatures for

about 24 h are shown in Fig. 3. After the heat treatment, the 400 °C sample is brown, which is speculated to be due to a very thin graphite layer on the surface of nanofibers. Samples treated at higher temperatures are white, because the graphite layer disappears due to oxidization at higher temperatures. No structural change was observed with SEM when the heating temperature is below or equal to 400 °C as shown in Fig. 3a. Fig. 3b and c depict the morphological change due to heat treatment at 800 °C. The nanofibers were sintered together and formed long beads with rounded corners. The diameter of such beads is about 200–400 nm, about three times of original fiber diameter and the length typically ranges from 1 μm to 3 μm with some as long as 10 μm. At a higher temperature of 1400 °C (Fig. 3d), the beads are even shorter, typically ranging from 1 to 2 μm, and the diameter is also larger.

As shown in the TGA curve (Fig. 4), the weight of HAP nanofiber sample reached the stable stage at about 870 °C and the weight loss of HAP nanofibers is about 4.4 wt%. According to the TGA data from other researchers [40–43], the weight loss of pure HAP nanoparticles synthesized by wet-chemical method (similar to our method for synthesizing HAP nanofibers) generally ranged from less than 1 wt% to about 3.4 wt%. As a result, we speculated the mass fraction of gelatin layer on the HAP nanofibers should be around 1–3.4 wt%.

### 3.2. Mechanical properties of HAP nanofibers reinforced dental resins/composites

Biaxial flexural strength (BFS) of BisGMA/TEGDMA dental resins containing various mass fractions of HAP nanofibers was tested and the results are shown in Table 1. The control samples were made of pure resins. Each datum in the plots provides the mean value of six measurements with standard deviation.

As shown in Table 1, the values of biaxial flexural strength (BFS) were significantly increased ( $P < 0.05$ ) by the impregnation of small contents (5 wt% and 10 wt%) of HAP nanofibers into the dental resins. The BFS of unfilled dental resins was  $100.3 \pm 2.4$  MPa. The dental resins filled with 5 wt% and 10 wt% HAP nanofibers had the BFS at  $112.6 \pm 5.9$  MPa and  $122.3 \pm 4.4$  MPa, respectively. The BFS was improved by 22.2% with 10 wt% of HAP nanofibers. However, further increasing the mass fractions of the nanosized HAP fibers did not increase the mechanical properties. On the contrary, the BFS decreased substantially compared with the control with higher loading rate of HAP nanofibers. Table 1 also revealed that both the BFS of dental resins filled with 20 wt% HAP nanofibers ( $80.4 \pm 5.7$  MPa) and 40 wt% HAP nanofibers ( $41.7 \pm 10.4$  MPa) were significantly lower than the control ( $P < 0.05$ ).

Fig. 5 shows the SEM pictures of the fracture surface of dental resins and dental composites containing various mass fractions of HAP nanofibers. Compared to Fig. 5a (unfilled resin), HAP nanofibers and their bundles were observed in other three samples (Fig. 5b–d). As shown in Fig. 5b (filled with 5 wt% of HAP nanofibers), there are many white spots observed on the fracture surface. Such small white spots are generally well dispersed HAP nanofibers. In Fig. 5c and d, besides the well dispersed HAP nanofibers, HAP bundles were also observed and the bundle density is higher in 20 wt% sample (Fig. 5d) than in the 10 wt% sample (Fig. 5c).

Biaxial flexural strength testing results of BisGMA/TEGDMA dental resins filled with various mass fractions of HAP nanofibers and 0.7 μm size silica particles are shown in Table 2. After incorporating a small mass fraction HAP nanofibers into dental composites (2 wt%, 3 wt%, 5 wt%, and 7 wt%), the values of BFS were significant greater ( $P < 0.05$ ) than the control (60 wt% silica). 10 wt% HAP nanofibers incorporated dental composites have no significant difference ( $P < 0.05$ ) with the control in terms of biaxial flexural strength. The

dental composite containing 3 wt% HAP nanofibers and 57 wt% silica microparticles has a BFS with the maximum value  $124.2 \pm 3.5$  MPa, which is 29.2% higher in comparison with the control.

Fig. 6 shows the SEM images of fracture surface of dental composites containing silica particles (control) and dental composites containing both silica particles and HAP nanofibers. With silica particles, formation of bundles and aggregates tends to happen at lower mass fractions of HAP nanofibers.

#### 4. Discussion

XRD spectrum (Fig. 1) and SEM images (Fig. 2) showed that the HAP nanofibers with aspect-ratios of 600 to 800 could be successfully fabricated with a simple, clean and biocompatible wet-chemical method in aqueous solution. Zhan et al. investigated the formation process of HAP nanofibers [39] and claimed that the gelatin molecules can be strongly adsorbed on the octacalcium phosphate (OCP) and suppress the growth of OCP in b-axial direction. Hence, rod-like crystals are generated instead of typical ribbon like OCP crystals. With the increase in pH value caused by the decomposition of urea, the OCP nanofibers will transform into HAP nanofibers after 72 h. It can be inferred that there is a thin gelatin layer on the HAP nanofiber surface. In this study, heat treatment results (Fig. 3) confirmed that there is an organic layer, most likely gelatin, on the surface of as-fabricated HAP nanofibers, which turns to graphite around 400 °C and is burned off at 600 °C; the heat treatment at or higher than 800 °C destroys HAP nanofibers original microstructures to form crystal with larger diameters. The structural change at high temperatures is mainly driven by the reduction of surface free energy of HAP crystals as bigger crystal size leads to a larger volume/surface ratio. TGA test (Fig. 4) revealed the weight loss of HAP nanofibers is about 4.4 wt% and the amount of gelatin layer ranges from 1 to 3.4 wt%.

The mass fraction of HAP nanofibers in dental composites plays a critical role in determining the mechanical properties. Results in Table 1 indicated that incorporating small mass fraction of HAP nanofibers into the dental resins significantly improved the mechanical properties and the critical mass fraction (percolation threshold) should be around 10%. The SEM images of representative fracture surface of the dental composites were shown in Fig. 5. The unfilled resins (Fig. 5a) fractured as a typical ductile resin, and the fracture surface was smooth with oriental fracture lines. In comparison with the pure resin samples, the fracture surfaces of HAP nanofibers reinforced resins (Fig. 5b–d) were very rough with no clearly identifiable fracture lines. In addition, the distribution of HAP nanofibers can also be observed by the SEM. The impregnation of the HAP nanofibers into BisGMA/TEGDMA dental resins may lead to double-edged effects: the reinforcing effect due to the well dispersed HAP nanofibers and the weakening effect due to the formation of HAP nanofibers bundles/agglomerates. The HAP nanofibers can be uniformly distributed in the dental resins at a low loading rate (Fig. 5b), which results in the improvement on mechanical properties. As the HAP nanofiber mass fraction increased to 10 wt%, a small portion of HAP nanofibers started to form bundles and most of HAP nanofibers might still be well distributed in the resin matrix (Fig. 5c). When the HAP nanofiber mass fraction increased to 20 wt%, more bundles were formed in the dental resin matrix (Fig. 5d), which can act as the mechanical weak point in the dental resins and lead to the much lower BFS value at 20 wt% mass fraction.

The resin shrinkage during curing can generate residual stress and has been considered a critical challenge for resin based dental composites for restoration applications. As the polymerization shrinkage of BisGMA and TEGDMA are 6.1% and 14.3%, respectively [46], in commercial dental composites at least 60 wt% inorganic fillers have to be

incorporated into the dental resins to lower the total shrinkage rate to about 2% so as to improve the marginal adaption and avoid micro-leakage [2]. The results in Table 1 indicated that it is impossible to achieve a high mass fraction of inorganic components with HAP nanofibers alone, as even 20 wt% mass fraction of HAP nanofibers already reduce the strength of the resin. Moreover, the dental composites are really difficult to handle with very high viscosity and relatively large volume at a high HAP nanofiber mass fraction. In order to meet the low shrinkage requirement and make the materials easy to handle, adding other inorganic fillers, such as silica particles, besides the HAP nanofibers into dental composites become a viable solution. In this study, commercial 0.7  $\mu\text{m}$  sized silica particles with 2 wt% silane were chosen as the filler to be added to the composite system and the dental composites containing 60 wt% inorganic fillers in total with various fractions HAP nanofibers were systematically fabricated and tested for BFS strength. The control sample was the resin with 60 wt% silica microparticles.

Results in Table 2 revealed that the mechanical property of dental composites embedding with silica particles and HAP nanofibers had a similar improvement trend as the dental resin filled with HAP nanofibers and the critical mass fraction (percolation threshold) was around 3 wt%, which was much lower than the HAP nanofibers reinforced dental resins. This phenomenon can also be well explained from the SEM images of fracture surface of dental composites (Fig. 6). Based on the SEM observation, the HAP nanofibers could be uniformly distributed in the matrix at a small mass fraction (2 wt%, Fig. 6b). As the HAP nanofibers mass fraction rise to 5 wt%, bundles could be observed, which were responsible for the reduction of biaxial flexural strength of dental composite, compared to composites containing 2 wt% and 3 wt% HAP nanofibers. When the HAP nanofibers mass fraction reached 10 wt%, most of fibers aggregated to form bundles, which resulted in a greater decrease of mechanical strength. These results and phenomena further supported the previous conclusion that the HAP nanofibers had both reinforcing and weakening effects depending on the mass fraction influenced distribution of HAP nanofibers. In addition, as revealed by the SEM images of fracture surface (Figs. 5 and 6), the HAP nanofibers in the composites filled with silica particles seemed to be easier to form larger bundles and aggregate at lower mass fraction.

With further analysis, it is worthy of pointing out that the percolation threshold of HAP nanofibers in dental resin samples corresponds well with the percolation threshold of HAP nanofibers in dental composite samples containing silica particles if we use weight ratio between HAP nanofibers and the resin. For dental composites containing silica particles, the percolation threshold is around 3 wt% (7.5 wt% of resin) between 2 and 5 wt% (5–12.5 wt% of resin), which matches well with dental resin samples with the percolation threshold around 10 wt% and between 5 and 20 wt%. Generally, nanocomposites have lower percolation threshold with smaller filler size. In the present study, the small diameter of HAP nanofibers is also one of reasons for the low percolation threshold. In order to further evaluate the potential of HAP nanofiber reinforced composites for dental restoration application, more experiments and analysis, such as mechanical tests after immersion in simulated oral environment, composite shrinkage tests, water absorption tests, and biocompatibility tests, should be conducted.

## 5. Conclusion

In this study, the HAP nanofibers with aspect-ratios of 600 to 800 can be successfully fabricated with a simple wet-chemical method in aqueous solution. Impregnation of small mass fractions of the HAP nanofibers into the BisGMA/TEGDMA dental resins (5 wt% or 10 wt%) or into composites (2 wt% or 3 wt%) can substantially improved the biaxial flexural strength, while larger mass fractions could not further increase or even reduce the

mechanical properties. According to the mechanical testing and fractographic analysis, the relatively good dispersion of HAP nanofibers at low mass fraction is a primary reason for the significantly improved biaxial flexural strength, while higher mass fraction of HAP nanofibers tends to result in bundles that cannot effectively reinforce the dental resins or composites and may even serve as defects and thus degrade the resulting dental resin and composite mechanical properties. In terms of HAP nanofiber to resin ratio, the testing results for HAP nanofiber reinforced resins and HAP nanofiber reinforced composites match well. Our result indicates HAP nanofiber, which has similar chemical composition with the tooth minerals, is a promising candidate as a reinforcing material for dental composites.

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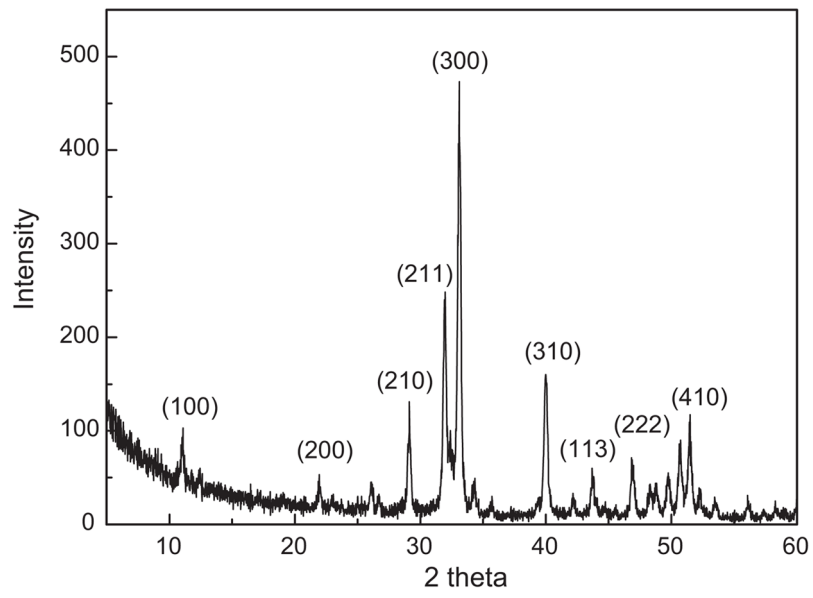
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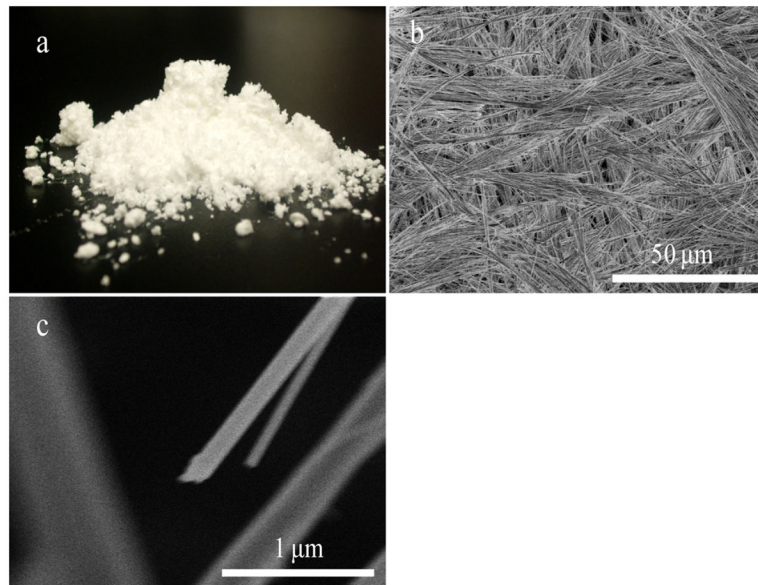


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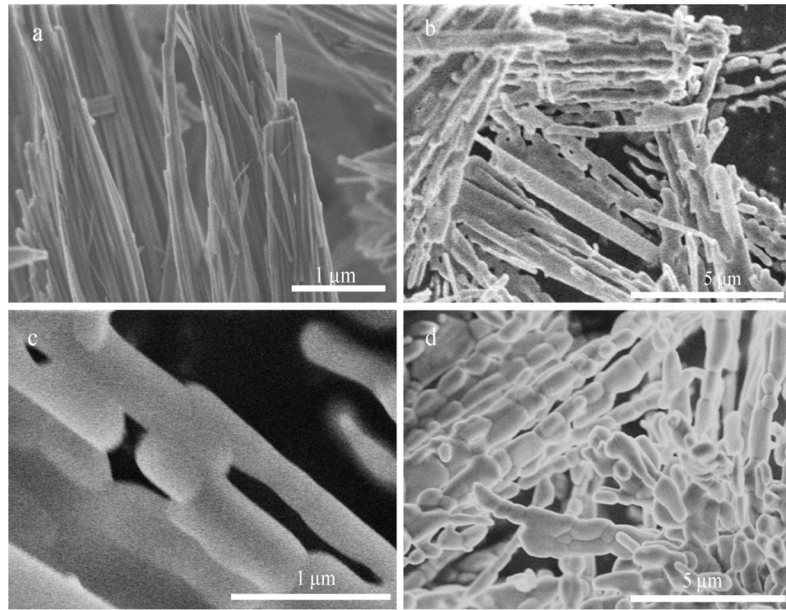
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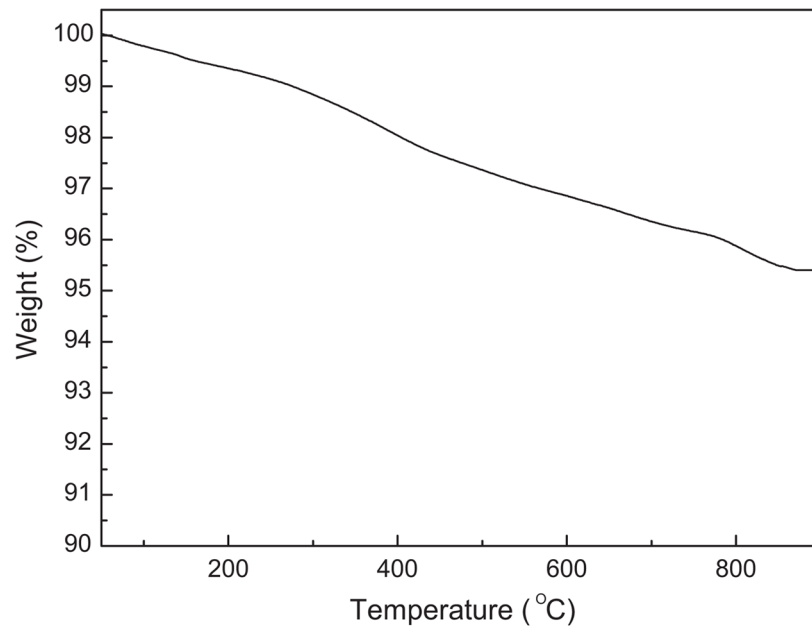
**Fig. 1.**  
X-ray diffraction spectrum of obtained nanofibers.



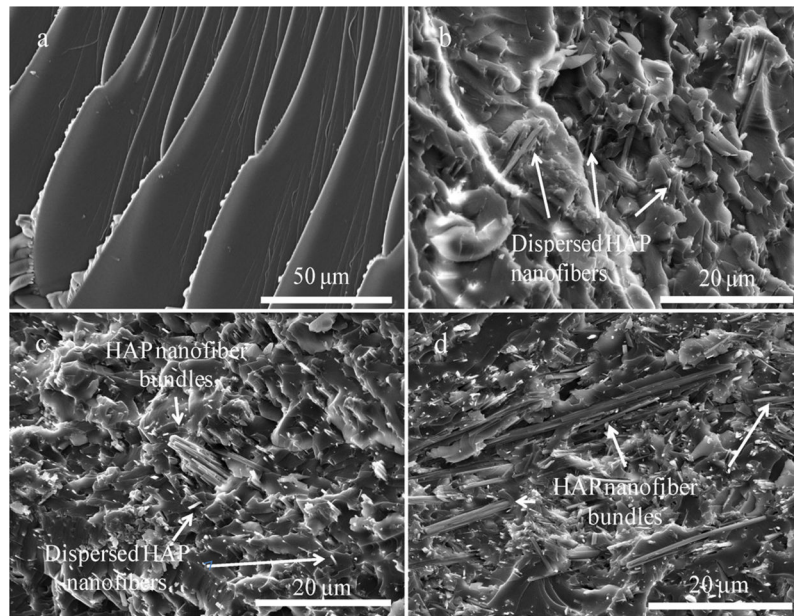
**Fig. 2.** Digital camera image (a) and SEM images of synthesized HAP nanofibers with the 1000× (b) and 5000× (c) magnification.



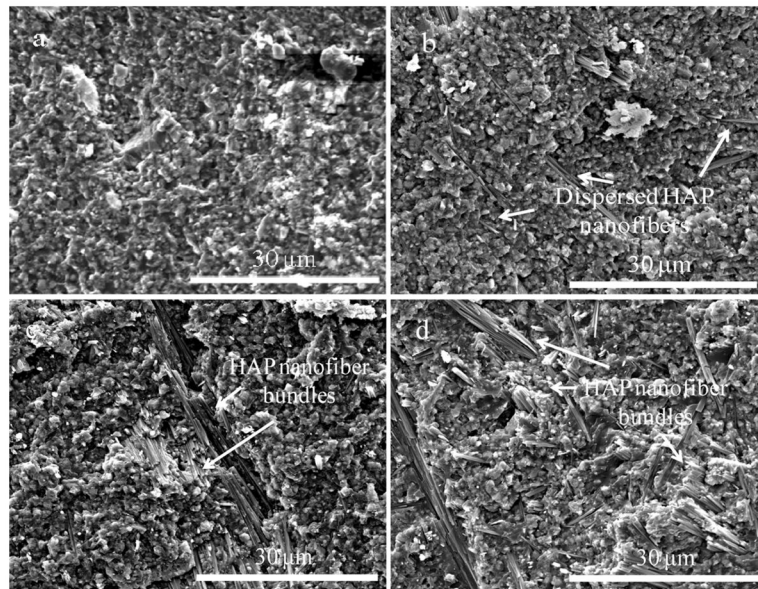
**Fig. 3.** SEM images of HAP nanofibers heated in atmosphere at different temperatures: (a) 400 °C, (b and c) 800 °C, and (d) 1400 °C.



**Fig. 4.**  
The TGA curve of HAP nanofibers.



**Fig. 5.** Representative SEM images of fracture surfaces of biaxial flexural test specimens: (a) unfilled BisGMA/TEGDMA, (b) BisGMA/TEGDMA filled with 5 wt% HAP nanofibers, (c) BisGMA/TEGDMA filled with 10 wt% HAP nanofibers, and (d) BisGMA/TEGDMA filled with 20 wt% HAP nanofibers.



**Fig. 6.** Representative scanning electron microscope images of fracture surface of biaxial flexural specimens: (a) BisGMA/TEGDMA filled with 60 wt% silica particles, (b) BisGMA/TEGDMA filled with 2 wt% HAP nanofibers and 58 wt% silica particles, (c) BisGMA/TEGDMA filled with 5 wt% HAP nanofibers and 55 wt% silica particles, and (d) BisGMA/TEGDMA filled with 10 wt% HAP nanofibers and 50 wt% silica particles.



**Table 1**

Biaxial flexural strength of BisGMA/TEGDMA dental resins filled with various mass fractions of HAP nanofibers, which were all photo-cured by Triad 2000 for 2 min on each side. The control is the dental resin without HAP nanofibers. Each datum is the mean value of six measurements with standard deviation (SD).

HAP mass fraction	Mean strength (MPa)	SD	ANOVA
0%	100.3	2.4	Control
5%	112.6	5.9	*
10%	122.3	4.4	*
20%	80.4	5.7	*
40%	41.7	10.4	*

\*  $P < 0.05$ .

**Table 2**

Biaxial flexural strength of BisGMA/TEGDMA dental composites filled with various mass fractions of HAP nanofibers and 0.7  $\mu\text{m}$  size silica particles (total mass fraction 60%), which were all photo-cured by Triad 2000 for 2 min on each side. The 60 wt% silica filled dental composite is used as control. Each datum is the mean value of six measurements with standard deviation (SD).

Filler mass fraction	Mean strength (MPa)	SD	ANOVA
60% silica	96.1	5.1	Control
2% HAP, 58% silica	109.9	9.6	*
3% HAP, 57% silica	124.2	3.5	*
5% HAP, 55% silica	114.6	6.3	*
7% HAP, 53% silica	108.6	4.2	*
10% HAP, 50% silica	94.4	11.2	

\*  $P < 0.05$ .