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Mechanical properties of dental resin/composite containing urchin-like hydroxyapatite

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ABSTRACT

Objectives. To investigate the reinforcing effect of urchin-like hydroxyapatite (UHA) in bisphenol A glycidyl methacrylate (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA) dental resin (without silica nanoparticles) and dental composites (with silica nanoparticles), and explore the effect of HA filler morphologies and loadings on the mechanical properties.

Methods. UHA was synthesized by a facile method of microwave irradiation and studied by X-ray diffraction (XRD), scanning electron microscope (SEM), and thermogravimetric analysis (TGA). Mechanical properties of the dental resin composites containing silanized UHA were tested by a universal mechanical testing machine. Analysis of variance was used for the statistical analysis of the acquired data. The fracture morphologies of tested composites were observed by SEM. Composites with silanized irregular particulate hydroxyapatite (IPHA) and hydroxyapatite whisker (HW) were prepared for comparative studies.

Results. Impregnation of lower loadings (5 wt% and 10 wt%) of silanized UHA into dental resin (without silica nanoparticles) substantially improved the mechanical properties; higher UHA loadings (20 wt% and 30 wt%) of impregnation continuously improved the flexural modulus and microhardness, while the strength would no longer be increased. Compared with silanized IPHA and HW, silanized UHA consisting of rods extending radially from center were embedded into the matrix closely and well dispersed in the composite, increasing filler-matrix interfacial contact area and combination. At higher filler loadings, UHA interlaced together tightly without affecting the mobility of monomer inside, which might bear higher loads during fracture of the composite, leading to higher strengths than those of dental resins with IPHA and HW. Besides, impregnation of silanized UHA into dental composites (with silica nanoparticles) significantly improved the strength and modulus.

Significance. UHA could serve as novel reinforcing HA filler to improve the mechanical properties of dental resin and dental composite.

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1. Introduction

Dental resin composites have been widely used instead of amalgam alloys and considered as versatile and reliable materials for different types of caries [1]. Most dental resin composites consist of the matrix and filler. The matrix is typically derived from the monomer system that includes a free radical initiating system and the filler is utilized to reinforce the softer organic matrix [2]. Since the introduction of dental resin composites in 1960s, extensive research has been attempted to develop materials with acceptable physical and mechanical properties. Owing to the development of nanotechnology and hybrid filling techniques, wear-resistant property, esthetic quality, and longevity of dental resin composites have been dramatically improved [3]. However, some problems remain, which include the adverse effects of polymerization shrinkage [4,5], and inadequate mechanical properties of the composites in posterior restorations during service [6,7]. Current researches demonstrated that most nanoparticle fillers did not yet provide anticipated reinforcing effects to significantly improve mechanical properties of the dental composites [3,8,9]. Therefore, fillers that could transfer and bear larger load have attracted numerous attention recently, such as Si_3N_4, SiC whisker, tetrapod whisker, inorganic fiber, halloysite nanotubes, and polymer fibers [10–13], and dental composites reinforced by these fillers show remarkably enhanced mechanical properties due to the diverse strengthening and toughening mechanisms of the fillers, which provide an effective and promising approach to fabricate strong dental composites.

Hydroxyapatite (HA) is the main component of the mineral part in bone tissue, tooth enamel and dentin. Synthetic HA has excellent biocompatibility and bioactivity, which is widely used as a material for human hard tissue regeneration. Besides, HA is also a promising material to reinforce biomedical composites, and it has drawn extensive attention in the development of biomaterials. Recently, different types of HA, such as particle, nanorod, whisker, and nanofiber, were employed to prepare bionic dental resin composite, and much basic work has been investigated for mechanical properties, service behaviors, stability, and biological properties. Unfortunately, dental composites using HA particles or nanorods possess lower flexural strength and modulus [14–17]. Hydroxyapatite whisker (HW) or nanofiber could improve the mechanical properties, while higher filler loading tends to result in aggregations that influence filler dispersion in the composite and serve as mechanical defects, which decrease the mechanical properties of the dental resin composite consequently [7,18,19]. Therefore, how to fabricate strong and bionic HA filled dental resin composite has gained more attention.

Inspired by the retention ability of the sea urchin spines on the seafloor, here, we report a novel dental resin composite which was embedded and enhanced by silanized urchin-like hydroxyapatite (UHA). UHA is bioactive filler with hierarchical structure, which has a globular appearance and consists of rods extending radially from the center like urchin. With the unique structure that combines features of globular and whisker, UHA is supposed to disperse easily in the matrix compared with nanorod, whisker or fiber-like HA, meanwhile, the radiate rods of UHA could embed and interlock with the matrix to result in efficient strengthening and toughening mechanisms compared with particulate HA. Moreover, the complicated morphology and large surface area of UHA could increase the contact area between filler and matrix, enhancing the interfacial combination. Thus, it is expected that UHA could enhance the mechanical properties of dental resin composites more efficiently [20]. In the past decade, polymers reinforced by filler with similar structure showed significantly improved mechanical properties [11,21–23]. However, to the best of our knowledge, no work has been reported about the preparation of dental resin composite enhanced by urchin-like hydroxyapatite. Herein, to explore the reinforcing effect of UHA, we prepared and characterized dental resin/composite filled with silanized UHA. In this study, UHA was synthesized by microwave irradiation and modified by 3-methacyloxypropyltrimethoxysilane (γ-MPS) to improve the compatibility and interfacial binding between UHA and resin matrix. Meanwhile, silanized IPHA and HW were employed to compare the reinforcing performance with UHA. The effect of UHA loading on mechanical properties of the dental resin/composite was also discussed with a view to developing strong, bioactive and reliable dental restorative resin composites.

2. Materials and methods

2.1. Materials

Bis-GMA and TEGDMA were obtained from Sigma-Aldrich (USA). Camphorquinone (CQ), γ-MPS, and ethyl-4-dimethylaminobenzoate (4-EDMAB) were obtained from J&K Scientific (China). Propylamine, cyclohexane, calcium nitrate, sodium dihydrogen phosphate dehydrate, gelatin, urea, calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) and dibasic anhydrous sodium phosphate (Na_2HPO_4), ethylenediaminetetracetic acid disodium salt (EDTA), sodium hydroxide (NaOH) were all obtained from Sinopharm Chemical Reagent Co., Ltd. (China). Irregular particulate HA (IPHA) was obtained from Emperor Nano Material Co., Ltd. (Nanjing, China). Silica nanoparticles (Aerosil OX50, average size 40 nm) were purchased from Shanghai Haiyi Co. Ltd. (China). All materials were of analytical grade and used as received without further purification. HW was prepared as previously reported [24].

The synthesis procedure of UHA was modified from a method reported by Liu [25]. Briefly, 200 mL of a mixed solution of $Ca(NO_3)_2{\cdot}4H_2O$ (0.4 M) and EDTA (0.4 M) was introduced into 200 mL of Na_2HPO_4 (0.24 M) solution. The pH of solution was adjusted to 13 by adding NaOH solution. The obtained solution was put into a household type microwave oven of 700 W power with a refluxing system and the reaction was performed at 105 °C under ambient air for 30 min. After cooling to room temperature, the precipitate was filtered, washed with deionized water, and dried in oven under vacuum at 70 °C for 2 h.

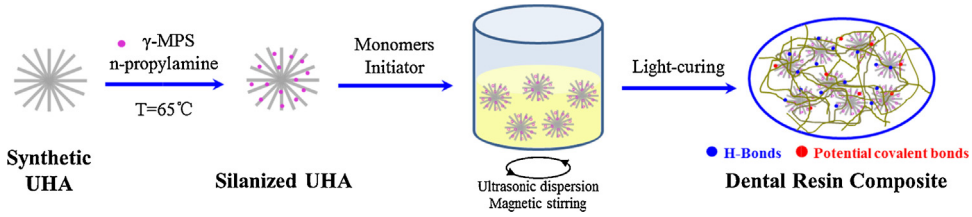

Fig. 1 – The schematic representation of the preparation of novel dental resin composite with silanized UHA.

2.2. *Silanization*

UHA, IPHA, HW, and silica were silanized respectively following the method as reported [24]. Filler (5.0 g), cyclohexane (500 mL), propylamine (0.2 g) and γ-MPS (0.5 g) were stirred in a 1 L three-neck flask at room temperature for 30 min and then heated at 65 °C for 90 min. The mixture was evaporated on a rotary evaporator at 60 °C to remove the volatile substances and then heated at 95 °C for 2 h. Finally, the product was dried in oven under vacuum at 85 °C for 18 h.

2.3. *Preparation of dental resin composites*

As illustrated in Fig. 1, resin matrix containing monomers (Bis-GMA/TEGDMA, 49.5/49.5, wt%) and initiators (CQ/4-EDMAB, 0.2/0.8, wt%) was uniformly mixed with a magnetic stirrer in a 20 mL flat bottom bottle, and then the silanized UHA was slowly added into the matrix while continuously stirring. After mixing thoroughly, the mixture with different filler mass fractions (5 wt%, 10 wt%, 20 wt%, and 30 wt%) was dispersed by ultrasonic method for 15 min and stirred (1000 rpm) for 12 h subsequently. The unfilled resin (0 wt%) and composites containing silanized IPHA and HW served as controls. Silanized UHA and silica (the weight percent ratio of UHA/silica in the composite: 0/60, 5/55, 10/50, 30/30) were mixed with the resin matrix (40 wt% of the composite) using a three-roller mixer (EXAKT 80E, Exakt Apparatebau GmbH & Co., Germany, for fabrication of viscous composite with a higher filler loading) according to the reported method [24]. All the obtained uncured composites were placed in oven under vacuum at room temperature for 8 h to remove air bubbles. Afterwards, the composite was added carefully to the rectangular (25 mm × 2 mm × 2 mm) and circle shaped (Φ 4 mm × 6 mm, Φ 6 mm × 4 mm) silicon rubber molds covered by glass slides. Then, the samples were light-cured by a curing unit (Blue light, 470 nm, SLC-VIII B Hangzhou Sifang Medical Apparatus Co., Ltd., Zhejiang, China) for 60 s on each side. All specimens were polished using a sand paper with a grit number of 1500 #.

2.4. *Characterization and evaluation*

2.4.1. *X-ray diffraction*

X-ray diffraction (XRD) pattern of UHA was collected on a X-ray difractometer (XRD, D/Max-2550 PC, RIGAKU, Japan) using Ni-filtered Cu Kα1 radiation (λ = 0.154 nm) in the 2θ range 10–80° at a voltage of 40 kV and a current of 200 mA.

2.4.2. *Fourier transform infrared spectroscopy (FTIR) analysis*

The FTIR analysis was conducted with a method of attenuated total reflection in a FTIR spectrometer (Nicolet Nexus 670, Thermo Fisher, USA). Spectra were collected over 4000–650 cm^{-1} region and were acquired with a resolution of 4 cm^{-1} and a total of 10 scans per spectrum.

2.4.3. *Thermogravimetric analysis*

The amount of grafted γ-MPS on filler was determined by thermogravimetric analysis (TGA). Weight changes as a function of time and temperature were evaluated during a thermal program from 50 to 600 °C at a heating rate of 10 °C/min in nitrogen atmosphere. The measurement was performed on a thermal gravimetric analyzer (STA409PC, NETZSCH, Germany) using 5–10 mg of each sample.

2.4.4. *Morphology*

Field emission scanning electron microscope (S-4800, Hitachi, Japan) and back-scattered scanning electron microscope (Quanta-250, FEI Company, Czech Republic) were employed to observe the morphology and size of UHA and the fracture surface of dental resins/composites after three-point bending test.

2.4.5. *Mechanical properties*

Flexural strength, flexural modulus, compressive strength, and diametral tensile strength of the resin composites were measured using a universal mechanical testing machine (Instron 5900, USA) according to the reported methods [24,26,27]. Six rectangular bar specimens

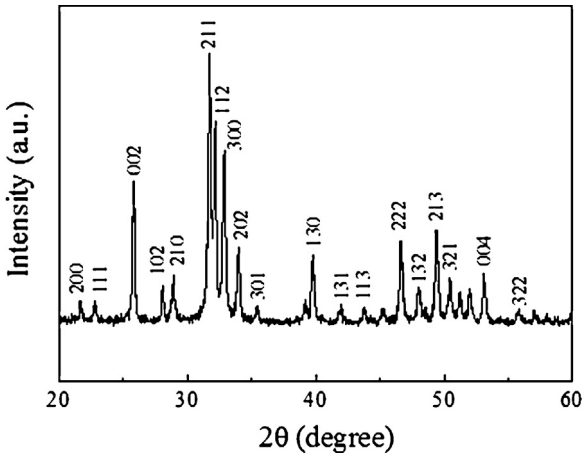

Fig. 2 – XRD pattern of the synthetic UHA.

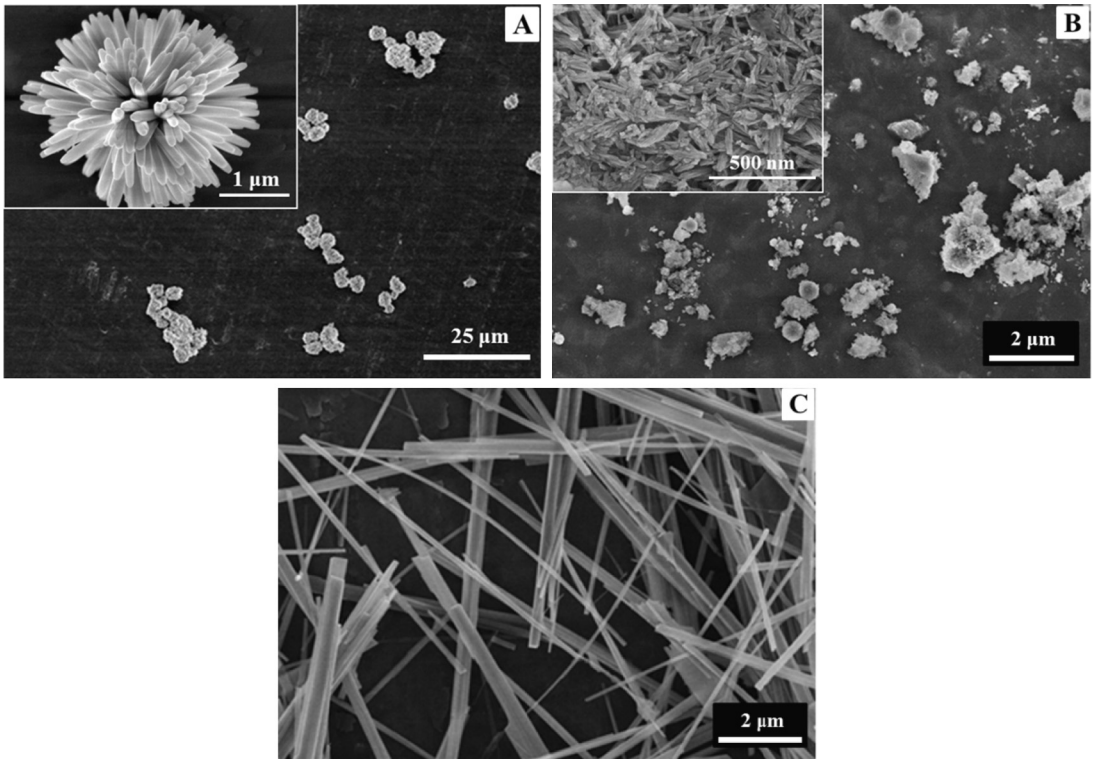

Fig. 3 – Representative SEM images of (A) UHA, (B) IPHA, and (C) HW.

(25 mm × 2 mm × 2 mm) were prepared for the three-point bending test (span 20 mm, crosshead speed 0.75 mm/min). In the compressive test, six cylinder specimens (Φ 4 mm × 6 mm) and six disk specimens (Φ 6 mm × 4 mm) were prepared for measuring the compressive strength (loading rate 1 mm/min) and the diametral tensile strength (crosshead speed 1.0 mm/min), respectively. Vickers microhardness was determined on six disk-shaped specimens (Φ 6 mm × 4 mm) under a load of 50 g for 10 s using a micro hardness tester (HXD-1000TMC/LCD, Shanghai Taiming Optical Instrument Co., Ltd., China).

2.4.6. *Statistical analysis*

The acquired data of mechanical properties were analyzed with one-way analysis of variance using SPSS software (version 17, Chicago, IL). Significant differences were determined using the Tukey's test. References to significant differences were based on a probability of $P < 0.05$ unless otherwise stated.

3. Results and discussion

3.1. *Characterization of UHA*

XRD analysis was used to characterize the crystal structure of the products. Fig. 2 shows the XRD pattern of the synthetic UHA. All the diffraction peaks marked in the pattern can be indexed and are consistent with HA phase (ICDD 09-432). Furthermore, sharp and narrow diffraction peaks are examined, which imply that UHA has a highly crystalline structure [25].

Fig. 3A shows the typical SEM image of the UHA structure prepared by microwave irradiation. The obtained product with a globular appearance has a good uniformity of size (diameter 2–3 μm). The morphology of UHA is in the form of rods of 100–200 nm width and of average 1 μm length extending radially from the center. Due to the unique spatial structure, a concentrated stress at the tip of each rod can be transferred to other rods, which causes stress distribution in the polymer matrix [28,29]. This might avoid crack and damage of the composites under external force, enhancing the mechanical properties of the composites consequently [30]. For comparison, two most-studied fillers with different morphologies were chosen: IPHA (Fig. 3B, consisting of needle-like HA) with similar shape and size ranging from sub-microns to 2 μm; Synthetic HW (Fig. 3C) with an aspect ratio of 100–200 and average diameter of 200 nm, which could provide similar reinforcing mechanisms as rods in the UHA structure.

3.2. *Mechanical properties of dental resin composites*

Strong mechanical properties of the resin composite are essential for the long-term clinic application of dental restoratives. To evaluate the reinforcing effect of UHA, flexural strength (S_F), flexural modulus (E_Y), compressive strength (S_C), Vickers microhardness (H_m), and diametral tensile strength (DTS) of the dental resins (without silica nanoparticles) filled with 5 wt%, 10 wt%, 20 wt%, and 30 wt% silanized UHA and the control samples (unfilled resin, dental resin filled with silanized IPHA and HW) were measured and the results are shown in Fig. 4.

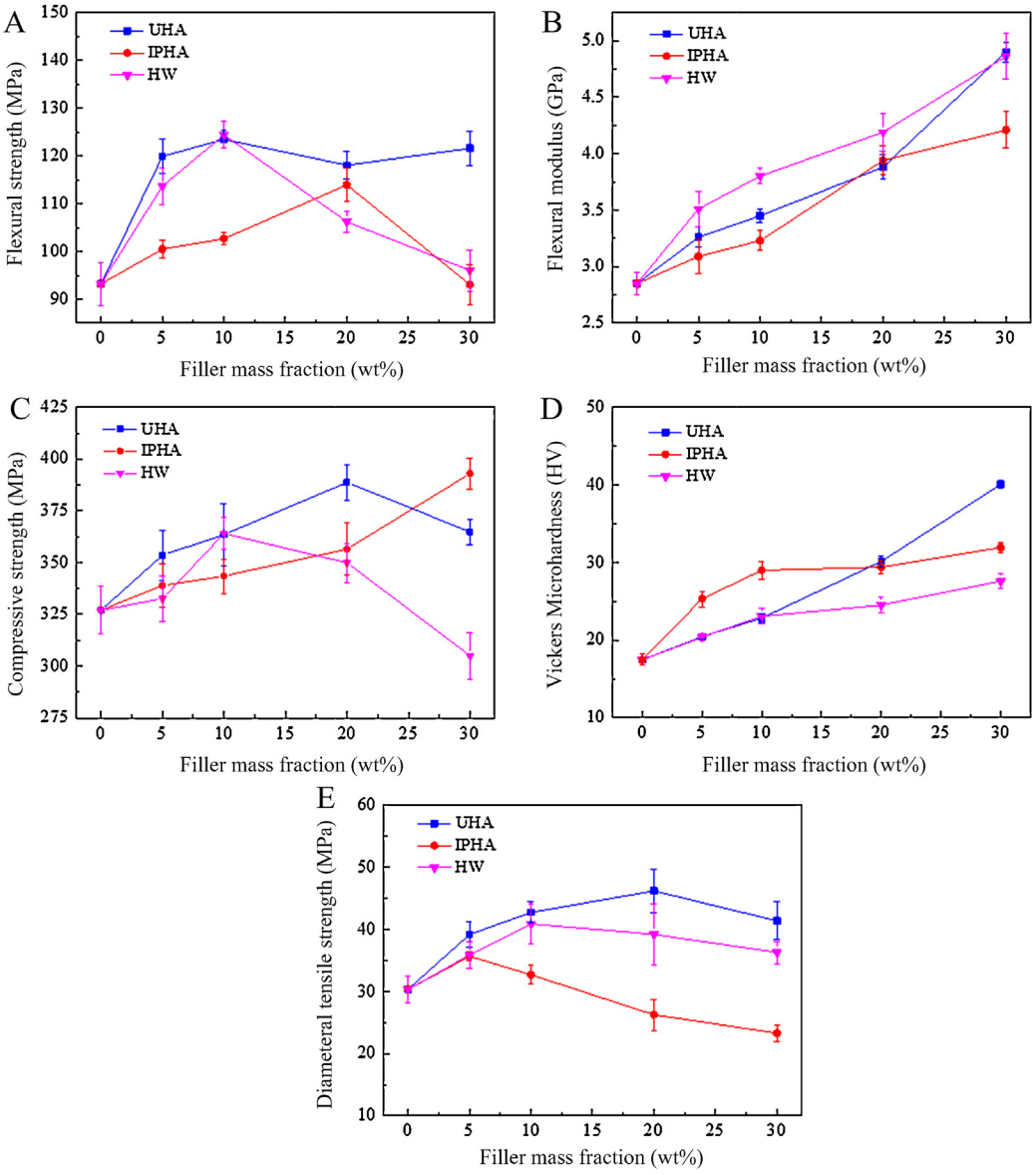

Fig. 4 – The flexural strength (A), flexural modulus (B), compressive strength (C), Vickers microhardness (D), and diametral tensile strength (E) of the dental resins filled with silanized UHA, IPHA, and HW.

The addition of silanized UHA substantially increases the values of S_F, E_Y, S_C, H_m, and DTS compared with the unfilled resin ($P < 0.05$). The values of S_F, E_Y, S_C, H_m, and DTS of the unfilled resin were (93.2 ± 4.6) MPa, (2.8 ± 0.1) GPa, (326.9 ± 11.6) MPa, (17.4 ± 0.7) HV, and (30.3 ± 2.2) MPa, respectively. For the dental resin filled with 10 wt% UHA, the values of S_F, S_C, and DTS were (123.5 ± 1.8) MPa, (363.5 ± 14.9) MPa, and (42.7 ± 1.7) MPa, respectively. Thus, S_F was improved by 32.5%, S_C was improved by 11.2%, and DTS was improved by 40.8%. For the composite with 20 wt% UHA, the values of S_F, S_C, and DTS were increased to (118.0 ± 2.9) MPa, (388.7 ± 8.4) MPa, and (46.2 ± 3.5) MPa; and the improvements were 26.6%, 18.9%, and 52.2%, respectively. However, higher UHA loading (30 wt%) wound no longer increase the strength. E_Y and H_m of UHA filled composites increased significantly ($P < 0.05$) with the increase of UHA loading (Fig. 4B and D). The values of E_Y and H_m were (4.9 ± 0.1) GPa and (40.1 ± 0.6) HV when UHA loading was 30 wt%, and the respective improvements were 75.0% and 130.5%. These results indicated that UHA improved the mechanical properties of the dental resin effectively. The following were the suggested reasons: (1) UHA was strongly embedded into the matrix, which strengthened the resin and resulted in an increase of the strength; (2) the modulus of UHA was higher than that of the resin matrix, leading to the substantial increase of flexural modulus; and (3) with the increase of filler loading, the packing density of UHA in the resin and the density of the composite were improved, enhancing the values of H_m. Furthermore, the trend of strength improvements implied that the reinforcing effect of UHA could be weakened when filler loading was higher, which might be possibly due to the undesirable distribution of UHA.

As illustrated in Fig. 4, UHA showed better reinforcing effect on dental resin than IPHA and HW, especially for the strength (S_F, S_C, and DTS) enhancement at higher filler loadings ($P < 0.05$). The strength of dental resin containing 20 wt% or 30 wt% UHA still remained at higher values, implying the different strengthening effect of UHA from HA whisker and nanofiber [18,19]. Besides, at higher loadings (e.g., 30 wt%), E_Y and H_m of the UHA filled dental resin showed more significant increasing trends than IPHA and HW filled dental resins. These results indicated that UHA with radial rods had advantages to enhance dental resin compared with IPHA and HW, probably due to the unique morphology. The complicated structure and large surface area of UHA might facilitate forming an interlocked and enhanced interface between UHA and matrix. As a consequence, the stress could be more efficiently transferred between the matrix and UHA, improving the material's resistance to fracture [31].

Furthermore, compared with silica (60 wt%) filled dental composite, impregnation of silanized UHA into dental composites (with silica nanoparticles) significantly enhanced the mechanical properties as shown in Fig. 5 ($P < 0.05$), giving 50.3%, 40.0%, and 13.1% improvement in S_F, E_Y, and S_C, respectively, when 10 wt% silanized UHA was added. These results further proved the favorable reinforcing efficiency of UHA on dental composite as discussed above. In addition, E_Y and S_C of UHA filled dental composite (with silica nanoparticles) were 177.0% and 16.5% higher than E_Y and S_C of UHA filled dental resin (without silica nanoparticles) when the UHA loading was 10 wt% (Fig. 5B and C); this might be resulted from the improvement of filler packing density by silica nanoparticles, as well as the difference in the fabrication methods between UHA filled dental resin (without silica nanoparticles) and dental composite (with silica nanoparticles).

3.3. *Surface morphology of fractured composites*

The fracture surfaces of the composite samples after three-point bending test were examined by SEM. Representative images of the dental resins (without silica nanoparticles) with different silanized UHA loadings are shown in Fig. 6. The flat fracture surface of the unfilled resin sample (Fig. 6A) indicated little resistance of the sample to the applied force. In comparison, the fracture surfaces of dental resin filled with UHA (Fig. 6B–E) were rough with numerous curved and stretched steps, which implied that UHA could deflect the cracks and the composites had higher fracture energy than the unfilled resin [21]. As shown in Fig. 6B–E, UHA embedded in the matrix were identifiable, and a good dispersion of UHA could be observed even at a higher UHA loading. This was one critical factor in maximizing the mechanical properties of the composites. As the filler loading increased, UHA interlaced together and packed tightly (Fig. 6F), which affected the uniform dispersion of UHA and the distribution of stress under load. However, unlike IPHA and HW dense aggregations (Fig. 7E and F), the UHA aggregation with mutual support of crisscrossing rods was supposed to bear higher loads during bending and tensile processes of the composite. The inside of the aggregation could be fully wetted by monomers because enough space among the interlaced rods facilitated the mobility of monomers, and the matrix could glue the aggregation

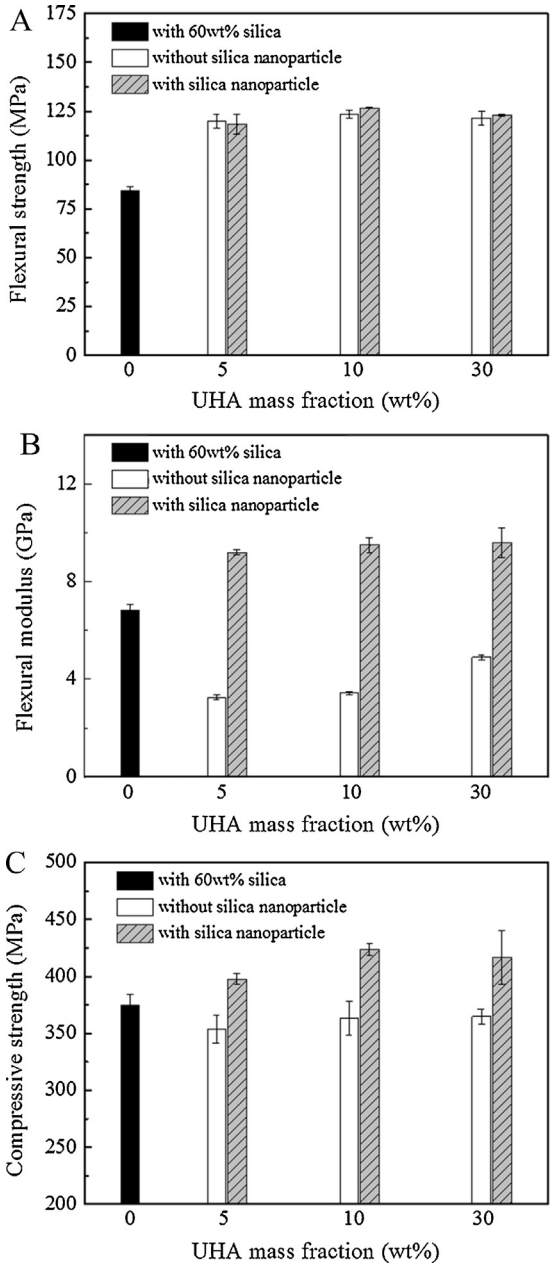

Fig. 5 – The flexural strength (A), flexural modulus (B), and compressive strength (C) of the dental resins/composites filled with different mass fractions of silanized UHA.

tightly after photo-polymerization. These might be reasons that the values of S_F and DTS were not decreased significantly at higher UHA loadings. The radiate rods of UHA, embedded in the matrix like a claw, could provide effective reinforcement through crack deflection, crack bridging, rod pullout and break. And these reinforcing and toughening mechanisms were clearly observed as pointed in Fig. 6F, indicating more energy could be consumed during the fracture of the composites [18,32].

Silanization has been proved a useful method to improve the compatibility and combination between filler and matrix. The synthetic UHA was modified by γ-MPS to enhance the

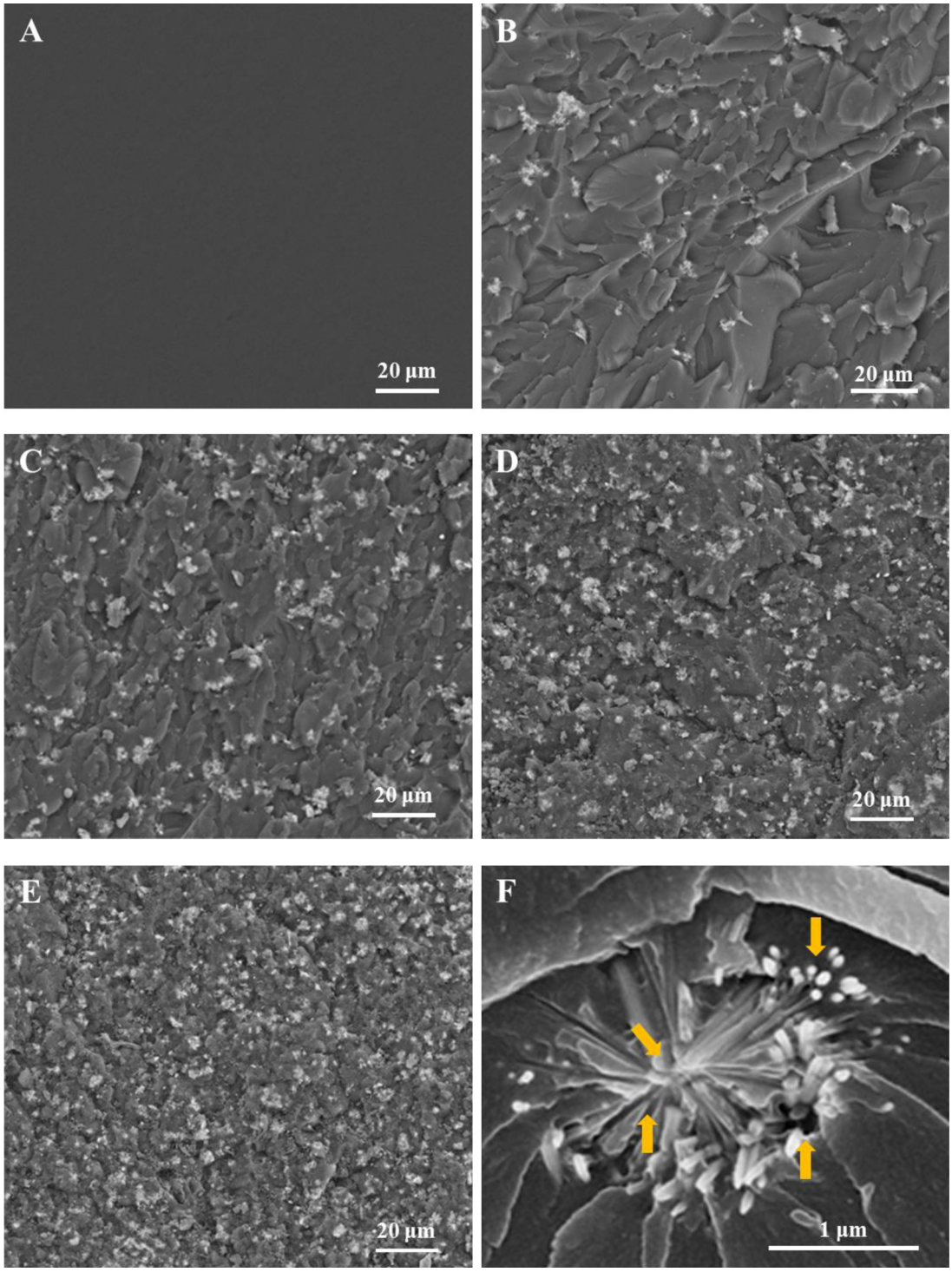

Fig. 6 – SEM images of fracture surfaces of (A) unfilled resin, and dental resins filled with different silanized UHA loadings: (B) 5 wt%, (C) 10 wt%, (D) 20 wt%, (E) 30 wt%, and (F) 20 wt%, higher magnification of UHA aggregation.

interface adhesion. As shown in Fig. 6F, the silanized UHA had a desirable bonding with the matrix, no appreciable gaps or voids appeared on the fracture surface. Besides, UHA with the unique spatial structure were easily inserted into the matrix, increasing the UHA–matrix contact area. Therefore, strong filler–matrix interfacial interactions were formed, and stress could be efficiently transferred between UHA and matrix, facilitating the improvement of mechanical properties, consequently.

Mechanical properties of dental resins with different fillers differed obviously, which was associated with filler dispersion, morphology, and interfacial interaction, etc. At a lower filler loading, IPHA and HW dispersed well in the matrix (Fig. 7A and C), and the impregnation allowed the filler surface

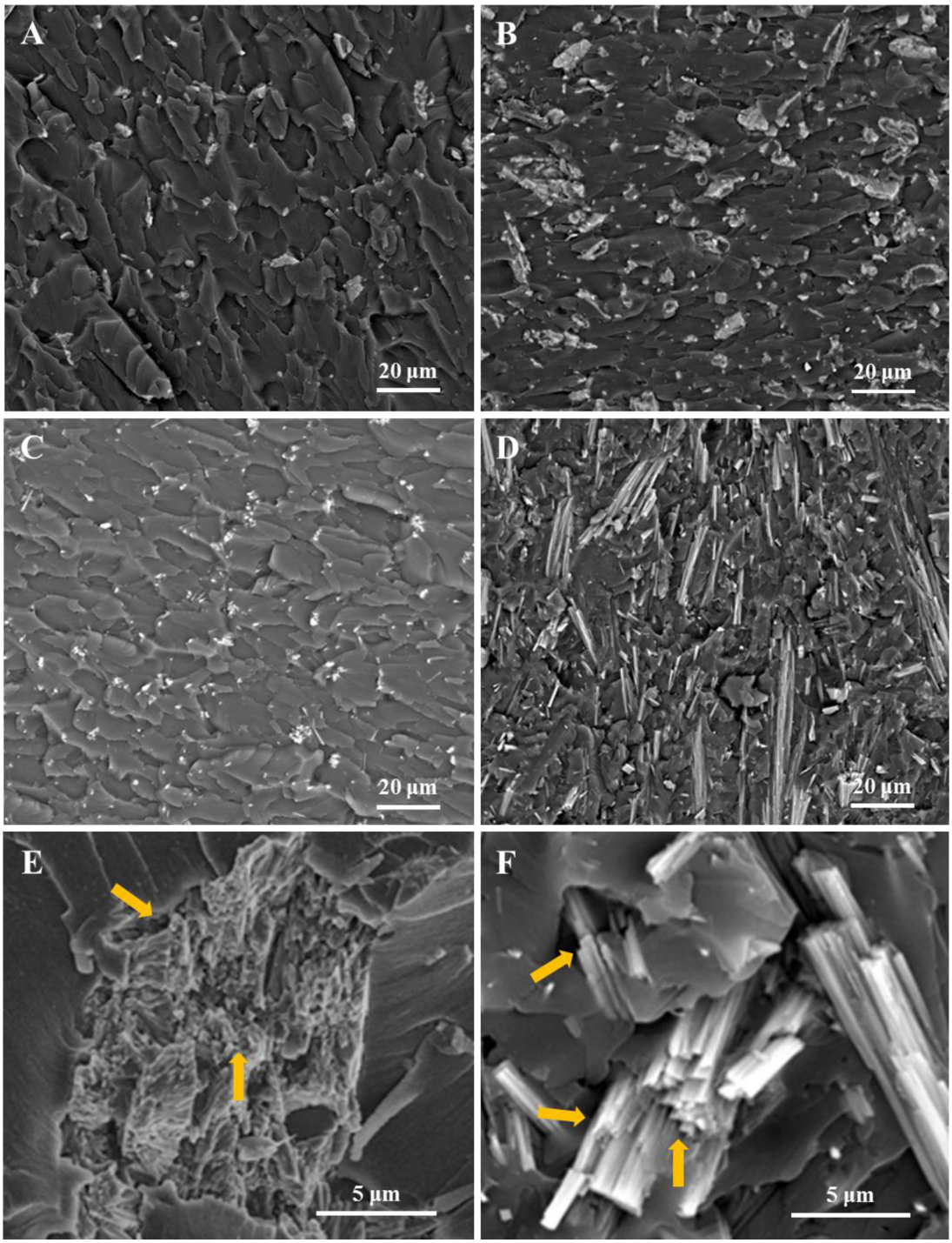

Fig. 7 – SEM images of fracture surfaces of the dental resins filled with silanized IPHA and HW. (A) 5 wt% silanized IPHA, (B) 20 wt% silanized IPHA, (C) 5 wt% silanized HW, (D) 20 wt% silanized HW, (E) IPHA aggregation in 20 wt% silanized IPHA filled composite, and (F) HW aggregation in 20 wt% silanized HW filled composite.

to contact with the resin, exerting different and profound reinforcing effects on mechanical properties of the composites: HW had obvious advantages in improving the modulus of the composite; IPHA had a better performance in hardness enhancement. At higher filler loadings, IPHA agglomerated seriously and exposed on the fracture surface (Fig. 7B). The IPHA aggregation had loose internal structure without being glued closely by matrix (Fig. 7E), and the gaps around IPHA also revealed the weak filler–matrix interactions, which would reduce the efficiency of stress transfer. Hence, mechanical defects easily formed and led to the worse mechanical properties, e.g., S_F, S_C, and DTS. For the composites filled with silanized HW, crack deflection, whisker pinning, pullout, and break were shown in Fig. 7D and F, and these contributed to

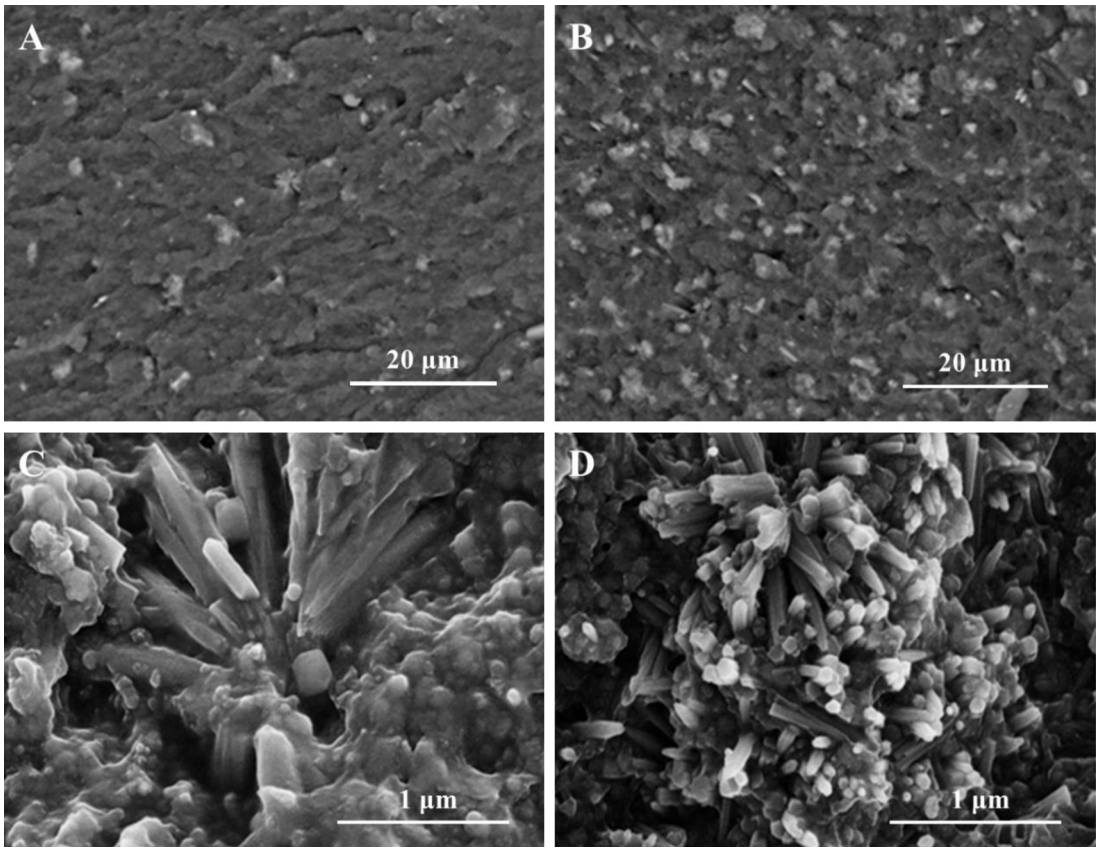

Fig. 8 – SEM images of fracture surfaces of dental composites with (A) 5 wt% UHA and 55 wt% silica filler, (B) 30 wt% UHA and 30 wt% silica filler, (C) 5 wt% UHA and 55 wt% silica filler, higher magnification, and (D) 30 wt% UHA and 30 wt% silica filler, higher magnification.

reinforcing the composite. However, the higher aspect-ratio HW was difficult to disperse in the matrix. Especially when the HW loading increased, the whisker tended to aggregate to form bundles and the gaps were observed around them (Fig. 7D and F), damaging the structure of matrix [18,19]. Besides, the inside of the dense bundles could not be fully wetted by monomers, leading to the formation of weak points in the aggregation. Thus, the mechanical properties were decreased eventually (Fig. 4A and C).

The fracture surface of silanized UHA filled dental composite (with silica nanoparticles) as shown in Fig. 8 further proved the reinforcing efficiency of UHA as described above. At the same UHA loading, similar dispersion was obtained in UHA filled dental resins (Fig. 6B and E) and dental composites (Fig. 8A and B). The possible stress concentration resulted from the undesirable UHA dispersion at higher loadings might be one factor to limit the strength improvement of the dental composite. In addition, silica nanoparticles (average size 40 nm) filling into the space among rods in UHA (Fig. 8C and D) indicated better incorporation of UHA and silica nanoparticles, which contributed to improving the filler packing density and enhancing the mechanical properties of the resulting composites.

This present study suggested that the easily prepared UHA could serve as more effective reinforcing filler for dental resins/composites compared with HA particulate and whisker, and the mechanical properties of the resulting composites could be further improved if more UHA could be added uniformly by appropriate methods. Moreover, it is worthy of pointing out that UHA with excellent biocompatibility and bioactivity has similar chemical composition with the tooth and bone minerals, which might have promising application in hard tissue restorations. For future research, more experiments and analysis such as shrinkage effect, absorption/solubility in solvents, mechanical properties under simulated oral environment, biological tests, should be conducted on UHA filled dental resin composites. Besides, hybrid filling technique (e.g., introducing different fillers, adjusting filler ratio and total filler loading) could also be employed for optimizing the properties of the composites.

4. Conclusion

The urchin-like hydroxyapatite was successfully synthesized by a simple method of microwave irradiation, and Bis-GMA/TEGDMA based dental resins with varied mass loadings of silanized UHA were fabricated. Compared with silanized IPHA and HW, silanized UHA with unique spatial structure were embedded into the matrix closely and dispersed (5–20 wt%) uniformly, which increased the interface contact area and combination between UHA and matrix effectively,

hence, the mechanical properties of the resulting composites were substantially improved. Specially, unlike IPHA and HW, UHA at higher filler loadings could interlace together tightly and form groups that could bear higher loads during fracture of the composite, leading to a higher mechanical strength than that of the dental resins with silanized IPHA and HW. Besides, the impregnation of silanized UHA into dental composite (with silica nanoparticles) significantly improved the mechanical properties, further demonstrating the reinforcing efficiency of UHA. Therefore, the novel urchin-like hydroxyapatite could be capable and promising filler for fabricating dental resin composites with improved mechanical properties and potential bioactivity.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.dental.2014.10.003.

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