



Strong and bioactive dental resin composite containing poly(Bis-GMA) grafted hydroxyapatite whiskers and silica nanoparticles



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ABSTRACT

Novel light-curable bioactive dental resin composite with enhanced physical and mechanical properties was prepared by combining poly(Bis-GMA)-grafted silanized hydroxyapatite whisker (PGSHW) with silanized silica ($s\text{-SiO}_2$) nanoparticles in a bisphenol A glycidyl methacrylate (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA) based dental resin matrix. The effect of PGSHW/ $s\text{-SiO}_2$ mass ratios on properties of the resin composites was investigated. The grafted poly(Bis-GMA) on silanized hydroxyapatite whisker (HW) optimized the PGSHW–matrix interfacial properties and improved the reinforcing efficiency of PGSHW in the composites. The addition of $s\text{-SiO}_2$ effectively increased the degree of conversion and filler packing density of the resin composites. Mechanical test showed that PGSHW/ $s\text{-SiO}_2$ (mass ratio 2:4) hybrid fillers significantly improved flexural strength, flexural modulus, compressive strength and work of fracture of the resin composite, which were 39.1%, 61.1%, 50.1%, and 85.9% higher than those of the resin composite with single PGSHW filler, respectively. Besides, *in vitro* bioactivity test indicated that resin composites containing PGSHW had superior apatite forming ability. In conclusion, PGSHW/ $s\text{-SiO}_2$ (2:4) filled resin composite was developed with significantly improved mechanical properties and desirable bioactivity, a combination not available in current HA filled dental resin composite, which may be a promising material to reduce the occurrence of both restoration fracture and secondary caries.

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1. Introduction

Restoration fracture and secondary caries of dental restorative resin composites remain the two most common problems in clinical application [1,2]. Bioactivity is an intensively studied feature in orthopedic biomaterials research. However, it has received relatively little attention in restorative dentistry, and so far no truly bioactive dental material has been commercially available [3]. From a caries-preventive point of view, remineralization of dental resin composite will not only improve marginal adaptation between restorations and teeth, but will also delay bacterial accumulation and penetration, halting a potentially recurring caries-active process [4]. Increasing attention has been paid recently on the exploration of calcium phosphate filled dental resin composites which have superior remineralization effect [3–6]. Unfortunately, most of these bioactive materials either have insufficient mechanical properties or hardly meet the requirements of clinical application such as optical properties and curing methods.

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Hydroxyapatite (HA), as a form of calcium phosphate, is the major and essential component of teeth. HA has several promising advantages including superior biocompatibility and bioactivity, intrinsic radio-opaque property, enhanced polishability and wear performance (similar hardness to that of teeth) [7], making it an excellent bionic filler. Particulate HA was first used as filler for dental resin composite [7–10], but it did not provide satisfactory strengthening effects. Recently, HA whisker (HW) [11–13] and nanofibers [14] as novel dental fillers exhibited better reinforcing performances. However, these fillers with high aspect ratios (with or without silane treatment) tended to aggregate in resin matrix due to the unfavorable filler–matrix interfacial properties, causing poor filler dispersion and decreased strength of the composites; furthermore, the mixing methods (e.g. dispersing filler in solution) and curing methods (e.g. heat curing) limited the clinical applications of HW or HA nanofibers filled resin composites. In addition, evaluation on the comprehensive performances of these resin composites was inadequate, and extensive studies should be undertaken to understand and further improve the performance of HA based dental resin composite.

Nanotechnology and hybrid filling technique significantly improved aesthetics, wear resistance and mechanical properties

of dental resin composites [15]. Nevertheless, to our best knowledge, most studies on HA filled dental composite merely used single HA filler. Only Chen [14] attempted to improve flexural strength of the composite using HA nanofibers and SiO₂ nanoparticles. However, the HA nanofibers were used without surface modification and fabrication of the composite in solvent was less effective; thus, poor filler dispersion and undesirable filler–matrix interfacial properties limited the improvement of the strength. In our previous work, we first reported that the grafted poly (Bis-GMA) (graft ratio 8.5 wt%) on silanized HW enhanced PGSHW–matrix interfacial compatibility and bonding of PGSHW filled resin composite [16], leading to a better dispersion of PGSHW in resin matrix and an improvement of mechanical strength of the composite. In this present work, based on hybrid filling method, PGSHW and s-SiO₂ nanoparticles with a lower refractive index were combined to develop stress-bearing and bioactive dental resin composite for the two intractable problems of restoration fracture and secondary caries. And the effect of PGSHW/s-SiO₂ mass ratio on physical and mechanical properties, in vitro bioactivity of the composite was investigated.

2. Materials and methods

2.1. Materials

Bis-GMA and TEGDMA were purchased from Sigma–Aldrich. Camphorquinone (CQ), ethyl-4-dimethylaminobenzoate (4-EDMAB), and 3-(methacloxypropyl) trimethoxysilane (γ -MPS) were purchased from J & k Scientific. Propylamine and cyclohexane were purchased from Sinopharm Chemical Reagent Co., Ltd. All materials were of analytical grade and used as received without further purification.

SiO₂ nanoparticles (Aerosil OX50, average size 40 nm, Degussa, Germany) were modified with γ -MPS [17]. PGSHW was synthesized by graft polymerization of Bis-GMA onto silanized HW in 1,2-dichloroethane for 1 h as previously reported [16], and the graft ratio of PGSHW was 8.5 wt%. Morphology of PGSHW was examined by field emission scanning electron microscope (SEM, S-4800, Hitachi, Japan).

2.2. Preparation of dental resin composite

As Fig. 1 shows, PGSHW/s-SiO₂ hybrid fillers (total filler loading 60 wt%) were premixed with a resin matrix (40 wt% of resin composite) containing monomers (Bis-GMA/TEGDMA, 49.5/49.5, wt%) and initiators (CQ/4-EDMAB, 0.2/0.8, wt%) by hand spatulation. Once the filler was wetted with matrix completely, the composite was moved onto a three roll mixer (EXAKT 80E, Exakt Apparatebau GmbH & Co., Germany) to blend thoroughly [16]. PGSHW/s-SiO₂

mass ratios were 56.1:0, 40:20, 30:30, 20:40, 10:50, and 0:60. The maximum PGSHW loading was 56.1 wt%. If excess PGSHW was added, the composite paste would change into fragmentary pieces and hardly be cured into a monolithic material. The composite with single filler of PGSHW or s-SiO₂ served as controls. All the uncured composites were placed in a vacuum chamber for 8 h to remove air bubbles and then maintained in the refrigerator (4 °C).

2.3. Characterization

2.3.1. Degree of conversion (DC)

DC was measured using a Fourier transform infrared spectroscopy (FTIR, attenuated total reflection, resolution 4 cm⁻¹, 10 scans). Three specimens were used for each ratio of each material. Each specimen was light cured with a LED curing unit (SLC-VIII B, 1000 mW/cm², 430–490 nm, Hangzhou Sifang Medical Apparatus Co., Ltd., China) for 60 s. The spectra of each specimen before and after curing were recorded. DC was calculated from the ratio of absorbance intensities (peak height) of aliphatic C=C peak at 1637 cm⁻¹ and aromatic C=C peak at 1608 cm⁻¹ [16], as follows:

$$DC (\%) = \left[1 - \frac{(A_{1637}/A_{1608})_{\text{cured}}}{(A_{1637}/A_{1608})_{\text{uncured}}} \right] \times 100 \quad (1)$$

where $(A_{1637}/A_{1608})_{\text{cured}}$ stands for the ratio of the absorbance intensities of peaks at 1637 cm⁻¹ and 1608 cm⁻¹ of cured specimens, and $(A_{1637}/A_{1608})_{\text{uncured}}$ is the ratio of the absorbance intensities of peaks at 1637 cm⁻¹ and 1608 cm⁻¹ of uncured specimens.

2.3.2. Depth of cure

Depth of cure was tested according to ISO 4049-2009. The composite paste was filled into a mold (4 mm in diameter and 10 mm in thickness) and light-cured for 20 s. The specimen was taken out of the mold and the uncured material was removed with a plastics spatula. The height of the cylinder of cured resin composite was measured using a caliper (± 0.01 mm). The experiment was repeated three times for each composite.

2.3.3. Mechanical properties and morphology of fracture surface

Flexural and compressive properties were tested using a universal testing machine (Instron 5900, USA). The dimensions of the specimens and test parameters were according to ANSI/ADA Specification No.27-2009 (ISO 4049-2009). The composite paste was filled in molds and light-cured for 60 s on both sides. Rectangular-shaped (25 mm \times 2 mm \times 2 mm) and cylinder-shaped (4 mm in diameter and 6 mm in thickness) specimens were prepared for three-point bending test (span distance 20 mm, cross-head speed 0.75 mm/min, $n=6$) and compressive test (loading rate 1 mm/min, $n=6$), respectively. The obtained specimens were polished using sandpaper (grit number 2500 #)

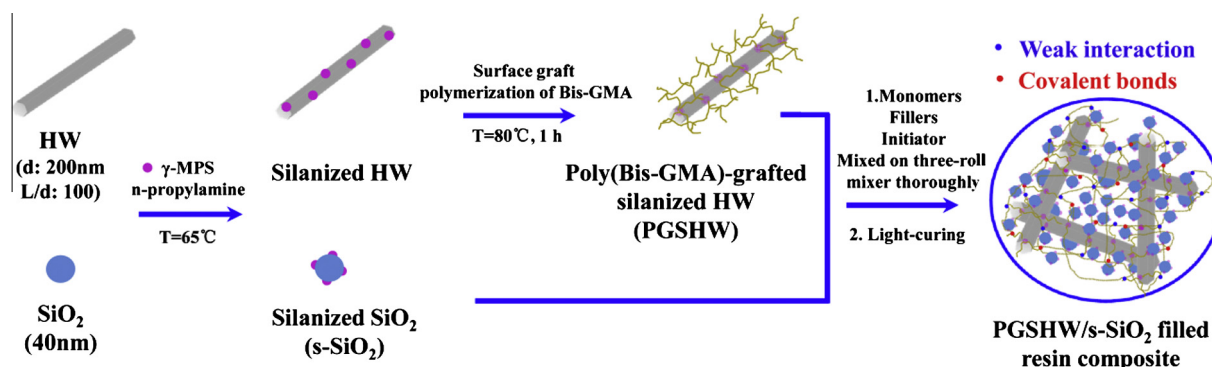


Fig. 1. Schematic representation of the preparation of strong and bioactive dental resin composite with PGSHW/s-SiO₂ hybrid fillers.

before test. Flexural strength, flexural modulus, work-of-fracture (the energy required to fracture the specimen, obtained from the area under the strain–stress curve divided by the specimen's cross-sectional area), and compressive strength were measured [18].

SEM was used to examine the morphology of fracture surface of the specimen after three-point bending test.

2.3.4. Water sorption and solubility of resin composite

Water sorption and solubility of the resin composite were characterized according to the method described in the literature [19]. For each resin composite, sixteen disc specimens (15 mm in diameter and 1 mm in thickness) were prepared and irradiated for 60 s on each side. The mass of the specimen (m_0) was weighed using a Mettler AL204 (accuracy: ± 0.0001) balance and then soaked in distilled water at 37 °C. At each interval time (1 d, 7 d, 14 d, or 30 d), four specimens were removed, mopped dry and weighed until a constant weight was attained (m_1). Then the specimens were dried in an oven at 60 °C for 24 h and weighed (m_2). Water sorption and solubility were calculated from the equations:

$$\begin{aligned} \text{WI}(\%) &= [(m_1 - m_0)/m_0] \times 100 \\ \text{SL}(\%) &= [(m_0 - m_2)/m_0] \times 100 \\ \text{WS}(\%) &= \text{WI}(\%) + \text{SL}(\%) \end{aligned} \quad (2)$$

where WI represents an apparent water sorption value because the unreacted monomer is simultaneously extracted, leading to a decrease of weight, SL is the amount of unreacted monomers extracted by water (also known as solubility), and WS stands for the actual water sorption value.

2.3.5. In vitro bioactivity

Apatite forming ability of the resin composite was evaluated in simulated body fluid (SBF). Disc specimens (10 mm in diameter and 1 mm in thickness) were soaked in 20 mL SBF at 37 °C for 1 d and 30 d. SBF was renewed once a week. After being soaked, the specimens were removed from SBF, gently rinsed with deionized water several times, and dried in an oven at 60 °C for 24 h. The surface morphological change and chemical composition change were examined by SEM equipped with an energy dispersive X-ray spectroscopy (EDS, Quantax 400, Bruker, Germany).

3. Results and discussion

3.1. Morphology of whisker and preparation of PGSHW/s-SiO₂ filled resin composite

Fig. 2 shows the SEM micrographs of the synthesized HW and PGSHW. As shown in a low magnification SEM image (Fig. 2a), the untreated HW was whisker-like with diameters ranging from 100 to 400 nm (average aspect ratio 100). A higher magnification SEM image (Fig. 2b) revealed that the untreated HW had a smooth surface. After graft polymerization of Bis-GMA on silanized HW for 1 h, an apparent coating of poly(Bis-GMA) was observed on the surface of PGSHW (Fig. 2c). Compared to the untreated HW, PGSHW had a rougher surface that would increase PGSHW–matrix interfacial friction force. As discussed in our previous work, the graft ratio of poly(Bis-GMA) on PGSHW was 8.5 wt%, and the grafted poly(Bis-GMA) could act as a functional transition layer between whisker and dental matrix, enhancing interfacial adhesion and stress transferring.

The as-fabricated PGSHW, s-SiO₂ and dental matrix were thoroughly mixed with the three roll mixer as shown in Fig. 1. The obtained composite paste was stored in an opaque box to avoid light. During the photopolymerization, the initiators in the composite paste are activated by blue light (wavelength 410–500 nm) to produce free radicals that initiate the cross-linking polymerization of monomers (Bis-GMA and TEGDMA). Due to C=C bonds and more O-H bonds from the grafted poly(Bis-GMA) layer of PGSHW [16] and C=C bonds from SiO₂ modified with γ -MPS [17], PGSHW and s-SiO₂ would be cross-linked with the matrix through hydrogen bonds and covalent bonds, promoting to form a tightly bonded resin composite with enhanced organic–inorganic interfacial properties (Fig. 1).

3.2. DC and depth of cure of PGSHW/s-SiO₂ filled resin composite

It is known that properties of the dental resin composite are directly related to the organic and inorganic components [20,21] as well as the DC. Insufficient DC would cause problems such as unfavorable physical and mechanical properties, biocompatibility,

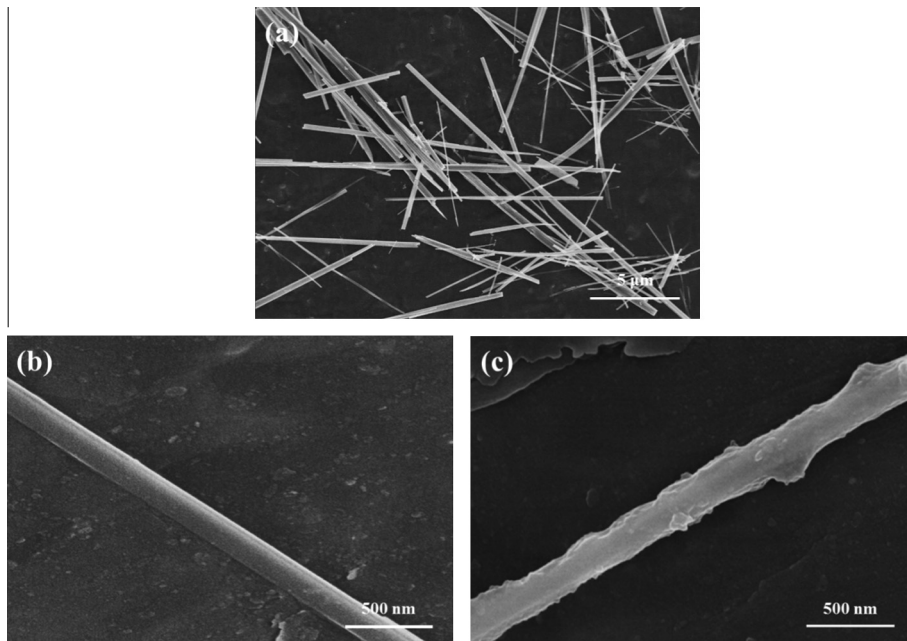


Fig. 2. SEM images of the synthesized HW with different magnifications (a, 5000 \times) and (b, 50000 \times), and PGSHW (c, 50000 \times).

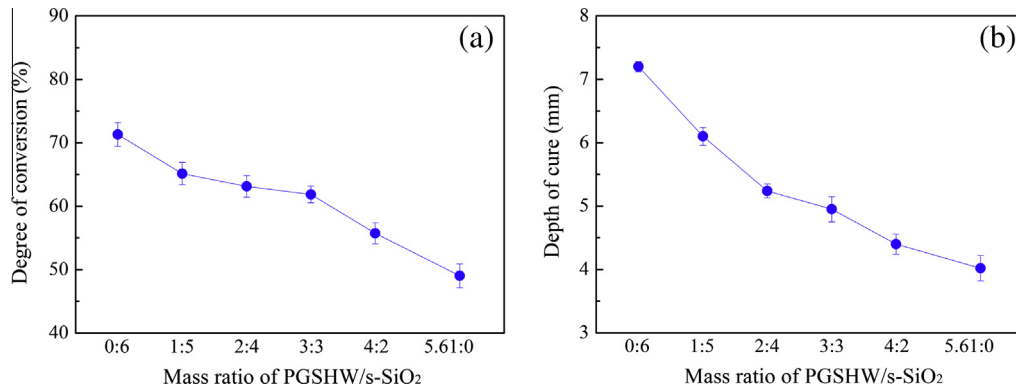


Fig. 3. Degree of conversion (a) and depth of cure (b) of PGSHW/s-SiO₂ filled resin composites.

etc. [22]. Several factors may affect the DC, including composition of the resin composite (monomer reactivity and content, filler size and shape, initiator concentration, etc.) and features of light-curing unit (such as light spectrum, power density, and curing time).

Fig. 3a shows the effect of PGSHW/s-SiO₂ mass ratio on DC of the resin composites. The DC values of the resin composites with s-SiO₂, PGSHW/s-SiO₂ (1:5, 2:4, 3:3, 4:2) hybrid fillers, and PGSHW were 71.3%, 65.1%, 63.1%, 61.9%, 55.7%, and 49.0%, respectively. The composite with single PGSHW filler had the lowest DC value, which was lower than those of most reported dental resin composites (55–75%) [23]. The DC value was evidently increased to 71.3% when s-SiO₂ mass fraction was increased. It might be because the refractive index of PGSHW (poly(Bis-GMA) 1.54, HW 1.62) [9,24] is higher than that of s-SiO₂ (1.46) [25], and thus the resulting light refraction might decrease light transmittance in the composite and reduce the photopolymerization efficiency. On the other hand, filler size might also have effect on DC. As the filler size approaches the wavelength of the activating light, light scattering in the resin composite is increased, and this scattering would reduce the amount of light that is transmitted through the composite [26]. Ruyter and Oysæd have suggested that scattering is maximized as the filler size is half wavelength of the activating light (approximately 0.23 μm) [27]. Since PGSHW has an average diameter of 200 nm, it is apparent that the whisker would enhance scattering and adversely reduce light transmittance, leading to the lower DC consequently.

Good curing properties of dental resin composite are closely related to the success of clinical restoration, especially when the cavity is large and deep. As Fig. 3b shows, depth of cure of the composite is dramatically increased with the increase of s-SiO₂ mass fraction from 4.02 mm to 7.20 mm, and the values of PGSHW/s-SiO₂ (2:4) filled resin composite was 5.24 mm, which was 30.3% higher than that of the single PGSHW filled resin composite. These results might be attributed to the improved light transmittance of the composite as discussed above. Thereby higher DC would contribute to more extensive polymerization and crosslinking, resulting in better curing of the resin composite [28].

These results clearly proved that PGSHW/s-SiO₂ hybrid fillers effectively improved the DC and depth of cure of the resin composite compared to single PGSHW filler.

3.3. Mechanical properties of PGSHW/s-SiO₂ filled resin composite

Fracture of dental resin composite is one of the primary reasons for restoration failure. Superior mechanical properties are crucial to guarantee long-term clinical application of the materials [15]. Herein, hybrid filling technique was used to further improve

comprehensive mechanical properties of PGSHW filled resin composite.

As shown in Fig. 4, PGSHW/s-SiO₂ hybrid fillers significantly improved flexural strength (S_F), flexural modulus (E_Y), compressive strength (S_C), and work of fracture (WOF) of the resin composites compared to single PGSHW filler. At PGSHW/s-SiO₂ mass ratio of 2:4, the values of S_F , E_Y , S_C , and WOF were increased to (141.3 ± 5.2) MPa, (9.9 ± 0.3) GPa, (338.2 ± 11.3) MPa, and (2.4 ± 0.4) kJ/m², which were 39.1%, 61.1%, 50.1%, and 85.9% higher than those of the resin composite with single PGSHW filler, respectively. These results indicated that PGSHW/s-SiO₂ hybrid fillers (2:4) could substantially improve mechanical properties of the resin composite. The suggested reasons might be that PGSHW had a better dispersion at the mass ratio of 2:4 and provided intrinsic reinforcing and toughening effect. Meanwhile, the incorporation of appropriate amount of s-SiO₂ nanoparticles in the “soft” matrix was capable to improve the DC as discussed above and filler packing density of the composite, promoting the formation of denser polymer network and stronger material. Consequently, the fracture resistance of PGSHW/s-SiO₂ filled resin composite was enhanced. To the best of our knowledge, Chen et al. [14] reported untreated HA nanofibers/s-SiO₂ filled dental resin composites and studied their flexural strength. Comparatively, the highest S_F obtained in our work was 13.8% higher than the highest value (124.2 MPa) reported by Chen. For the composite with the same filler composition (HA/SiO₂ mass ratio 1:5, total filler loading 60 wt%), the S_F value (117.6 MPa) was 24.6% higher than that (94.4 MPa) given by Chen. These results might be attributed to functional modification on the surface of HW (for enhancing whisker–matrix interaction) and effective fabrication of composite paste using a three roll mixer (for improving filler dispersion). In addition, the mechanical properties of PGSHW/s-SiO₂ (2:4) filled resin composite matched commercial non-bioactive resin composites (S_F 100–140 MPa, E_Y 8–10 GPa) [15], and the S_F was superior to the value (minimum 80 MPa) required by ISO 4049–2009, indicating that the stress-bearing PGSHW/s-SiO₂ (2:4) filled resin composite was capable of resisting mechanical forces in clinical application. Future studies are needed to investigate the mechanical properties of PGSHW/s-SiO₂ (2:4) filled resin composite under simulated wet oral environment.

3.4. Surface morphology of fractured resin composites

Fig. 5 shows the SEM images of fracture surfaces of the resin composites with s-SiO₂, PGSHW/s-SiO₂ (2:4, 4:2) hybrid fillers, and PGSHW. The fracture surface of s-SiO₂ filled resin composite was smooth (Fig. 5a), while resin composites containing PGSHW have rougher and larger fracture surfaces (Fig. 5b–d), indicating that more energy was consumed during fracture [29]. The grafted

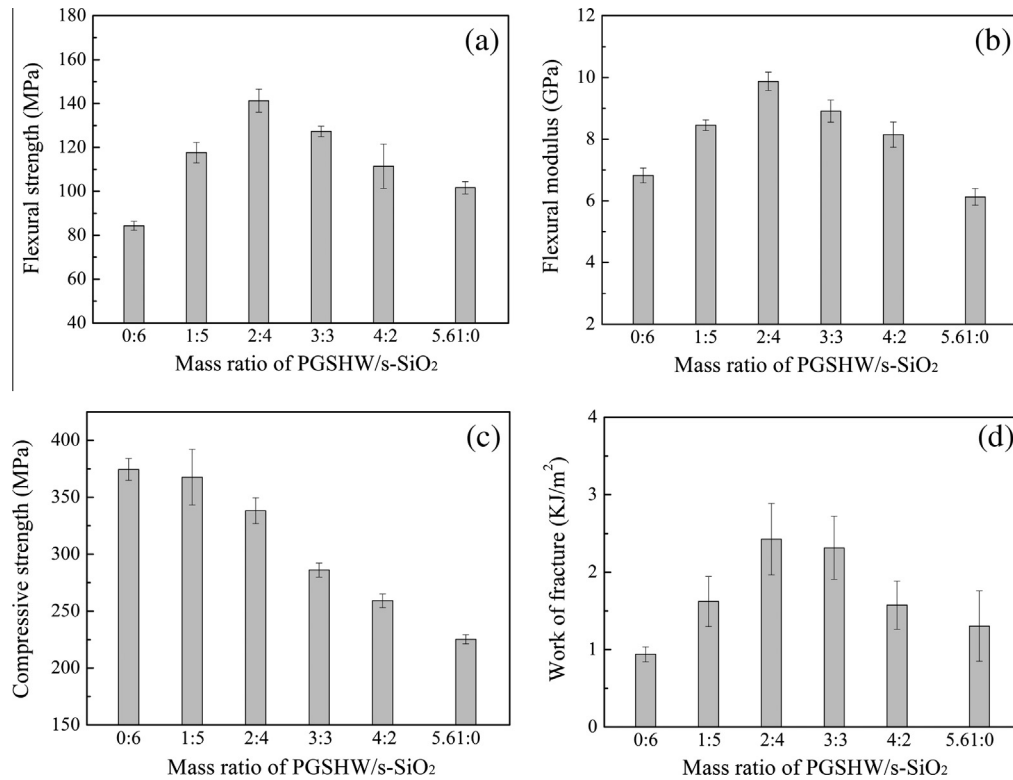


Fig. 4. Mechanical properties of PGSHW/s-SiO₂ filled resin composites: (a) flexural strength, (b) flexural modulus, (c) compressive strength, and (d) work of fracture.

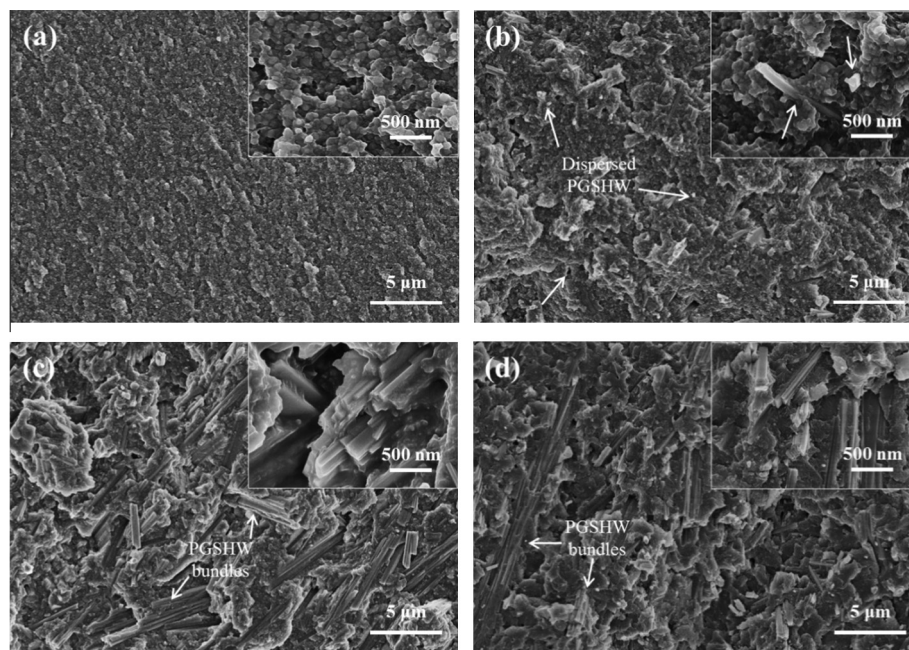


Fig. 5. SEM images of fracture surface of the resin composites with the filler of (a) s-SiO₂, (b) PGSHW/s-SiO₂ (2:4), (c) PGSHW/s-SiO₂ (4:2) and (d) PGSHW.

poly(Bis-GMA) on silanized HW acted as a functional transition layer between whisker and matrix, enhancing interfacial compatibility and bonding by hydrogen bonds and covalent bonds [16]. As a result, PGSHW embedded in the composite had a favorable combination with matrix, and the optimized interfacial adhesion allowed more effective stress transfer from the matrix to the reinforcement. Besides, typical whisker reinforcing and toughening mechanisms were observed (as pointed out in Fig. 5b), such as

whisker pulling-out, break, crack bridging and deflection [13], which would absorb more energy under applied stress and improve the ability of the resin composite to resist fracture. Furthermore, s-SiO₂ nanoparticles filling in the “soft” matrix between whiskers apparently increased the filler packing density (as shown in Fig. 5b and d), making the resin composite harder and stronger. All these factors contributed to enhancing the mechanical properties of PGSHW/s-SiO₂ filled resin composite.

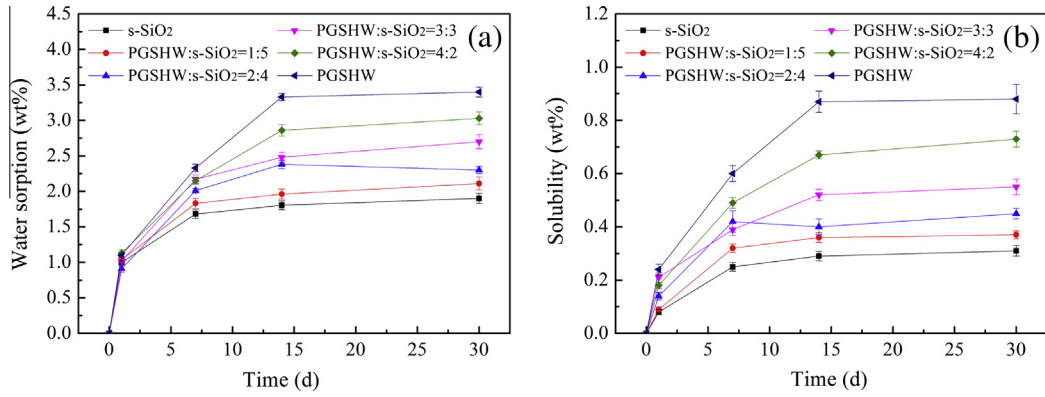


Fig. 6. Water sorption (a) and solubility (b) of the resin composites after storage in water (37 ± 1 °C) for different durations.

Lower fraction of PGSHW had a favorable dispersion in the composite (Fig. 5b) so that the whisker surface could fully contact with the resin matrix, exerting profound reinforcing effects on mechanical properties of the resin composites. However, with the increase of PGSHW mass fraction, PGSHW tended to aggregate in the composites (Fig. 5c and d), leading to loose boundaries and evident voids between aggregation and matrix. Therefore, mechanical defects and stress concentrations were formed easily and would decrease the mechanical properties of the resin composite.

3.5. Absorption/solubility properties of PGSHW/s-SiO₂ filled resin composite

Water sorption and solubility of resin composites reflect their stability under wet oral environment, and are affected by factors such as DC, hydrophobic-hydrophilic properties of components,

filler–matrix interface properties, filler loading, etc. [8,10,30,31]. The water absorbed in the composite may lead to the degradation of fillers, the weakening of polymer matrix, the debonding of filler–matrix interface, and the decreased physical and mechanical properties [10,32]. The unreacted monomers extracted by water may contribute to cytotoxicity of the resin composite, causing allergic reactions in some patients [33]. Hence, study and understanding of the absorption/solubility properties of the resin composite would be of great importance.

Fig. 6 shows water sorption and solubility of the studied resin composites after storage in water for 0 d, 1 d, 7 d, 14 d, and 30 d. As the time increased, both water sorption and solubility were increased, reaching saturation eventually. The saturation time was longer for the resin composites with PGSHW/s-SiO₂ (4:2) and PGSHW. Within the same immersion time, the water sorption and solubility were increased with the increase of PGSHW mass

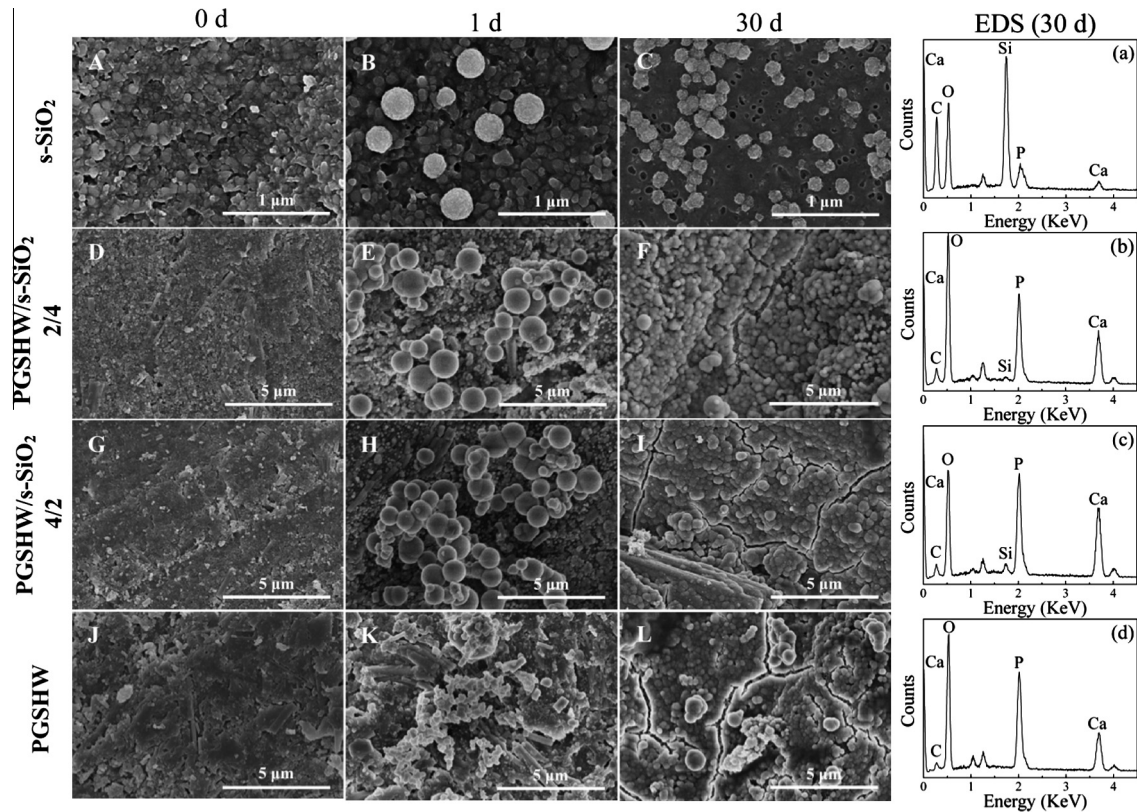


Fig. 7. SEM images and EDS profiles of the surface of the resin composites with s-SiO₂, PGSHW/s-SiO₂ (2:4, 4:2), and PGSHW after soaking in SBF for 0 d, 1 d, and 30 d.

fraction. The resin composite with single *s*-SiO₂ filler had the lowest values of water sorption (1.90%, 30 d) and solubility (0.31%, 30 d), while the values of resin composite with single PGSHW filler were the highest (water sorption 3.40%, 30 d; solubility 0.88%, 30 d). The possible reasons might be that PGSHW with a high aspect ratio easily caused an inhomogeneous structure of the resin composite especially at higher PGSHW mass fractions, and therefore loose boundaries and evident voids around PGSHW aggregation (Fig. 5c and d) would accommodate additional amount of water and also provide the fastest paths for water diffusion towards the interior of the composite [30,10]. However, the addition of *s*-SiO₂ nanoparticles into the resin composite improved the filler packing density, which could restrain the water permeation in dental resin matrix and reduce the space for containing water, and therefore the water sorption values of PGSHW/*s*-SiO₂ filled resin composites were decreased (e.g. 2.30%, 30 d, PGSHW/*s*-SiO₂ mass ratio 2:4). On the other hand, the DC of PGSHW/*s*-SiO₂ filled resin composite is higher than that of the single PGSHW filled resin composite, and less unreacted monomers would release from the composite, leading to a lower solubility (e.g. 0.45%, 30 d, PGSHW/*s*-SiO₂ mass ratio 2:4). In addition, there was mutual influence between water sorption and solubility. The water permeating in the composite could extract unreacted monomers and degraded components, and the resulting voids would further facilitate water circulation. Finally, a balance was achieved after the interaction process. Since the resin composite with single PGSHW filler had the lowest DC, more unreacted monomers releasing from the composite might have led to longer saturation time.

3.6. *In vitro* bioactivity

In vitro bioactivity is defined as the ability of a material to form apatite layer on its surface when submerged in SBF [3]. Fig. 7 illustrates the surface morphological change and chemical composition change of the studied resin composites after storage in SBF for 0 d, 1 d, and 30 d. Apparent mineral precipitation was observed on the surfaces of the resin composites containing PGSHW filler after 1 d (Fig. 7E, H, and K), and after soaking for 30 d, the specimen surface was covered with a denser and continuous layer (Fig. 7F, I, and L). In contrast, the surface of the resin composite with single *s*-SiO₂ filler was merely covered with noncontinuous particles even after immersion for 30 d (Fig. 7C). It was implied that mass fraction of PGSHW did not have a significant influence on *in vitro* bioactivity of the resin composite, and the composite with single *s*-SiO₂ filler had relatively weaker remineralization effect. Results of EDS analysis of the formed layer on specimens after soaking for 30 d reveal that the main elements are oxygen, calcium, and phosphorus (Fig. 7a–d). Carbon and silicon could be from the resin matrix and *s*-SiO₂, respectively. The Ca/P atomic ratios of the formed layer were calculated by EDS analysis and ranged from 1.50 to 1.56. The values were less than the stoichiometric ratio 1.67 of HA, implying that the precipitated layer was calcium-deficient apatite [34,35]. These results proved that PGSHW/*s*-SiO₂ (2:4) filled resin composite possessed desirable *in vitro* bioactivity and may have the potential to improve marginal adaptation of restoration and remineralize restoration to inhibit the recurrence of secondary caries [4]. Further *in situ* studies on natural teeth are certainly needed to examine whether the apatite layer could be formed between PGSHW/*s*-SiO₂ (2:4) filled resin composite and teeth and the stability of the formed layer under simulated wet oral environment.

4. Conclusions

Novel bioactive dental resin composite with significantly enhanced mechanical properties were developed using hybrid

filling technique. The grafted poly(Bis-GMA) on the surface of silanized HW enhanced PGSHW–matrix interfacial compatibility and bonding, and the addition of lower mass fraction of PGSHW exerted profound reinforcing and toughening effects on mechanical properties of the resin composites. The introduction of *s*-SiO₂ nanoparticles increased light permeability and filler packing density, which effectively improved the DC, depth of cure, water sorption and solubility of single PGSHW filled resin composite. The obtained PGSHW/*s*-SiO₂ (mass ratio 2:4) filled resin composite had dramatically improved physical and mechanical properties as well as desirable *in vitro* bioactivity. Therefore, the hybrid filling technique could be viable approach to fabricate stress-bearing and bioactive dental resin composites containing bionic HA filler. These composites may be promising materials to reduce the occurrence of both restoration fracture and secondary caries.

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