



# Effect of hydroxyapatite whisker surface graft polymerization on water sorption, solubility and bioactivity of the dental resin composite



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## ABSTRACT

The aim of this study was to investigate the effect of poly bisphenol A glycidyl methacrylate (poly(Bis-GMA)) grafted hydroxyapatite whisker (PGHW) on water sorption, solubility and bioactivity of the dental resin composite. PGHW with different graft ratios was synthesized, by controlling grafting time, and filled into a dental resin matrix respectively. Fracture surface of the resin composites showed that PGHW–matrix interfacial compatibility and bonding were enhanced, and lower amounts of poly(Bis-GMA) on PGHW-1h (graft ratio: 8.5 wt.%) could facilitate the dispersion of PGHW-1h in the composite. The PGHW-1h filled resin composite absorbed the lowest amount of water (27.16  $\mu\text{g}/\text{mm}^3$ , 7 d), whereas the untreated hydroxyapatite whisker (HW) filled resin composite absorbed the highest. PGHW with higher graft ratios induced the decrease of the monomer conversion in the resulting composite, therefore, the PGHW-18h (graft ratio: 32.8 wt.%) filled resin composite had the highest solubility. In vitro bioactivity of the studied resin composites in simulated body fluid (SBF) showed that a dense and continuous apatite layer was formed on the surface of the resin composite, and the surface graft polymerization on the whisker did not significantly affect the apatite forming ability of the resin composite. It was revealed that graft polymerization of an appropriate amount of Bis-GMA onto HW could be an effective method to improve the interfacial properties and stability in water of the dental resin composite without compromising the bioactivity.

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## 1. Introduction

Dental resin composites have been widely used to repair decayed or damaged teeth due to their superior esthetics, acceptable mechanical properties, ease of use and the ability to bond to tooth tissues. Typically, the composite mainly consists of a photopolymerizable organic resin matrix and inorganic reinforcing fillers. During the development of dental resin composites, the main focus has been on the fillers. An ideal replacement for tooth tissues may be a material with similar physico-chemical and physico-mechanical characteristics to those of the natural substance it must replace [1]. Hydroxyapatite is the main mineral part in human tooth, thus synthetic hydroxyapatite seems to be a good choice as the inorganic filler for fabricating bionic dental restorative materials [2]. In the past decades, hydroxyapatites of different morphologies (e.g. particle, nanorod, whisker) were studied as dental fillers, and hydroxyapatite whisker (HW), that had similar structure to enamel rods [3], showed superior reinforcing effects, which would make it a promising filler for a bionic dental resin composite with higher reliability.

The physico-mechanical properties and longevity of HW filled resin composite are greatly associated with whisker–matrix interfacial bonding quality. Silanization was proven to have beneficial effects on interfacial optimization, such as slowing the degradation process of filler

debonding from the resin matrix, and improving distribution and stress transition from the flexible organic matrix to the stiffer inorganic filler [4,5]. Nevertheless, the effect was not evidently observed for silanized HW filled dental resin composite [6]. Recently, we synthesized novel poly(Bis-GMA) grafted HW (PGHW) which effectively enhanced the whisker–matrix interfacial compatibility and bonding by functional polymer grafting on the surface of HW [7]. Compared with HW and silanized HW (SHW), the PGHW filled resin composite showed improved mechanical properties and decreased volume shrinkage. It was reported that strong filler–matrix bonding and hydrophobic silane on the filler surface would reduce water sorption of the resin composite [5,8,9]. Hence, the hydrophobic poly(Bis-GMA) on PGHW introduced more incorporable groups to interact with resin's polymer network [7], which would be expected to enhance interfacial properties and improve the stability of the PGHW filled resin composite in an aqueous environment. However, to the best of our knowledge, relevant researches of dental resin composites with surface modified HW are rarely reported. Much work still remains to be done, such as long-term service behavior under simulated oral environment, absorption/solubility tests, bioactivity, biological evaluation, etc.

Dental resin composites are constantly exposed to an aqueous environment, and their water sorption, solubility, and bioactivity are of great importance for dental clinical applications. The water absorbed into the polymer matrix may decrease the longevity of the resin composite by silane hydrolysis and microcrack formation, causing filler–matrix

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debonding [10]. During the light curing process of dental resin composite, the molecules of monomers would be converted to polymer by free radical polymerization in the presence of photoinitiators. Several factors may influence the degree of conversion including the type of filler and monomer, the concentration of photoinitiators, the features of the light-curing unit, and the shade of the resin composite, leading to the conversion ranging from 55 to 85% [11–13]. When insufficient conversion occurs, the unreacted monomers are released to the oral environment, and this may contribute to cytotoxicity of the resin composite, stimulate the growth of bacteria around the restoration, and cause allergic reactions in some patients [14,15]. In addition, resin composites containing calcium phosphate have been proven to release Ca and PO<sub>4</sub> ions and remineralize tooth lesions in vitro [16–18], which provides a promising self-healing method by decreasing gaps between restorative composite and tooth, creating a stable interface, and combating secondary caries [19]. Therefore, it is essential to investigate the behavior of HW filled dental resin composites in an aqueous environment. Herein, this work was carried out as a further investigation of PGHW filled dental resin composites, aiming at determining water sorption, solubility, and bioactivity of resin composites with PGHW and investigating the effect of surface graft polymerization of HW and the graft ratios on these properties.

## 2. Materials and methods

### 2.1. Preparation of the resin composites

Bis-GMA and triethylene glycol dimethacrylate (TEGDMA) were obtained from Sigma-Aldrich. Camphorquinone (CQ) and ethyl-4-dimethylaminobenzoate (4EDMAB) were obtained from J&K Scientific. HW, SHW, and PGHW were prepared as we previously reported [7], and it should be noted that PGHW synthesized in different graft polymerization periods (1 h, 3 h, 7 h, and 18 h) is labeled as PGHW-1h, PGHW-3h, PGHW-7h, and PGHW-18h, respectively. Each filler was mixed with a dental resin matrix containing monomers (Bis-GMA/TEGDMA, 49.5/49.5, wt.%) and initiators (CQ/4-EDMAB, 0.2/0.8, wt.%) by a three-roll extruder (EXAKT 80E, Exakt Apparatebau GmbH & Co., Norderstedt, Germany), and the filler loading was 48 wt.% [7]. All uncured composites were placed in an oven under vacuum at room temperature for 8 h to remove air bubbles and then maintained in a refrigerator (4 °C).

Morphology of the obtained PGHW was observed using field emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan). The graft ratios of PGHW were measured using thermogravimetric analysis (TGA, STA409PC, NETZSCH, Germany) [7]. The monomer conversions of the resulting resin composites were analyzed by Fourier transform infrared spectroscopy (FTIR, Nicolet Nexus 670, Thermo Fisher, USA, attenuated total reflection (ATR) mode, resolution 4 cm<sup>-1</sup>, 10 scans, 4000–650 cm<sup>-1</sup>) following the reported method [7]. In short, a thin layer of the composite paste was placed on the diamond of ATR unit and cured with a LED lamp (Blue light, 430–490 nm, 1000 mW/cm<sup>2</sup>, SLC-VIII B Hangzhou Sifang Medical Apparatus Co., Ltd., China) for 60 s. The ratios of the infrared spectra of aliphatic (1637 cm<sup>-1</sup>) to aromatic (1608 cm<sup>-1</sup>) C=C double bonds in cured and uncured resin composites were used to calculate the monomer conversion. Three replicates for each resin composite were made.

### 2.2. Water sorption and solubility of the resin composites

Water sorption and solubility of the resin composite were determined according to the method described in literature [20]. The unpolymerized material was filled into a rubber mold (15 mm in diameter and 1 mm in thickness) and irradiated for 60 s on each side with a LED curing unit. Then the cured composite specimen was carefully removed and polished using sandpaper (grid number: 1500 #). Sixteen specimen discs were prepared for each composite.

All the specimens were dried in an oven at 60 °C for 48 h and then stored in the desiccator. The specimen mass was weighed to an accuracy of ±0.0001 g repeatedly using a Mettler AL204 balance until a constant mass ( $m_0$ ) was obtained. Subsequently, the discs were soaked in deionized water at 37 °C. After each fixed time interval (1, 7, 14, and 30 days), four specimens were removed, blotted dry on filter paper to remove excess water and weighed ( $m_1$ ). Then the specimens were dried in an oven at 60 °C for 7 days and transferred to the desiccator. The specimen mass was weighed to an accuracy of ±0.0001 repeatedly until a constant mass ( $m_2$ ) was obtained. Water sorption and solubility were calculated using the following formulas:

$$\begin{aligned} \text{WI}(\%) &= 100 \frac{m_1 - m_0}{m_0} & \text{SL}(\%) &= 100 \frac{m_0 - m_2}{m_0} \\ \text{WS}(\%) &= \text{WI}(\%) + \text{SL}(\%) \end{aligned}$$

where WI represents an apparent value for absorbed water because the unreacted monomer is simultaneously extracted, SL is the amount of unreacted monomers extracted by water (also known as solubility), and WS stands for the amount of absorbed water. Also the absorbed amount of water was calculated in μg/mm<sup>3</sup> using the equation:

$$\text{WS}(\mu\text{g}/\text{mm}^3) = \text{WI}(\mu\text{g}/\text{mm}^3) + \text{SL}(\mu\text{g}/\text{mm}^3)$$

where  $\text{WI}(\mu\text{g}/\text{mm}^3) = 10^3((m_1 - m_0)/V)$ ,  $\text{SL}(\mu\text{g}/\text{mm}^3) = 10^3((m_0 - m_2)/V)$ , and V the volume of discs in cubic centimeters was measured by a density tester (ULTRA PYCNOMETER 1000, Quanta Chrome Instruments, USA, flow time 1 min, 10 cycles).

### 2.3. Morphology

Morphology of the fracture surface of the non-soaked specimen disc after bending was observed using FE-SEM.

### 2.4. Behavior in SBF

The apatite forming ability of the obtained composites was tested in SBF using similar methods, as previously reported [21]. The composition (g/L) of SBF is as follows: NaCl 6.6682, NaHCO<sub>3</sub> 2.2682, KCl 0.2237, K<sub>2</sub>HPO<sub>4</sub>·3H<sub>2</sub>O 0.2283, MgCl<sub>2</sub>·6H<sub>2</sub>O 0.3060, CaCl<sub>2</sub> 0.2771, and Na<sub>2</sub>SO<sub>4</sub> 0.0711. The pH of SBF was adjusted to 7.4 with HCl solution. Four disc-specimens of 10 mm diameter × 1 mm thickness were prepared for each composite: three specimens were soaked in 20 mL SBF at 37 °C for 1, 14 and 30 days, respectively, and the SBF was renewed once a week; the non-soaked one was used as a control. The surface morphological changes and element quantification were performed by FE-SEM (SU8010, Hitachi, Japan) equipped with an energy dispersive X-ray spectroscopy (EDS, INCA X-Max 50, Oxford Instruments).

## 3. Results and discussion

### 3.1. Morphology and graft ratio of HW, SHW, and PGHW

Fig. 1 is the schematic representation of the synthesis of PGHW and PGHW morphology change with the reaction time. As previously reported [7], the surface of HW and SHW was clean, and no obvious change was observed after silanization. By contrast, PGHW-1h showed apparent polymeric coatings on the surface after 1 h graft polymerization, and most whiskers were separate. However, with the increase of the reaction time, the coating became rougher with more irregular bulges on the surface, bonding whiskers together to form aggregations with internal voids; moreover, the graft ratio of PGHW was also increased as shown in Table 1.

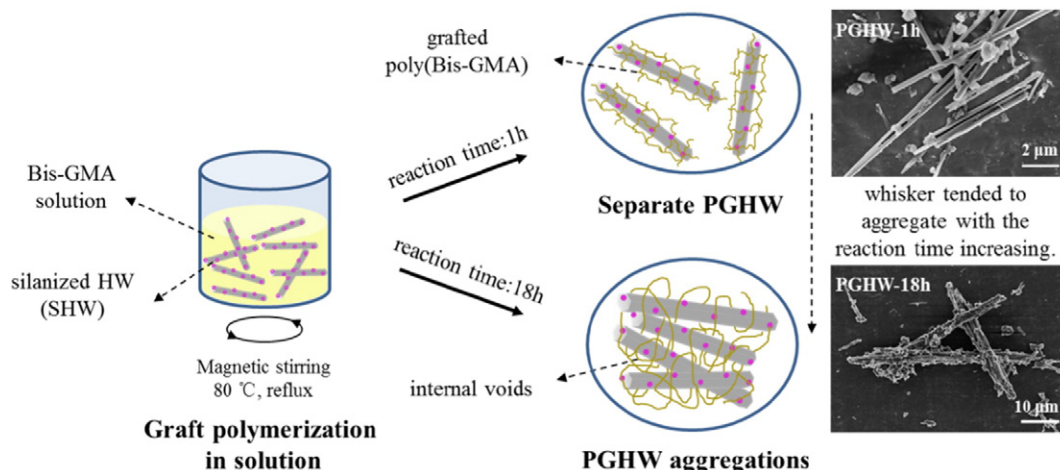


Fig. 1. Schematic representation of the synthesis of PGHW and PGHW morphology change with the graft polymerization time.

### 3.2. Degree of conversion

An adequate degree of conversion is critical to guarantee the structural integrity, strength, and biocompatibility of the dental resin composite. Generally, the monomer conversion is affected by the type of filler (shade, size, dispersion, refractive index) and monomer (concentration, reactivity, mobility), the concentration of photoinitiators, the features of the light-curing unit (light density and spectrum, curing time), etc. [11].

In this work, a higher amount of poly(Bis-GMA) on the surface of PGHW resulted in the decrease of monomer conversion of the studied resin composites (Table 1). The reasons might be that, at the same mass filler loading, PGHW with a higher amount of poly(Bis-GMA) possessed a higher volume fraction in the composite compared with HW and SHW due to the lower density of the poly(Bis-GMA) layer than inorganic whisker [7,10], therefore, the mobility of monomers was limited and the concentration of C=C double bonds in the composite was decreased, leading to a reduced monomer reaction rate. Besides, the blue-light propagation and initiation efficiency of initiators in the PGHW filled composites would be decreased because the poly(Bis-GMA) layer and whisker both had higher refractive indexes, which also affected the photo-polymerization [2,7,22]. Therefore, the HW filled resin composite had the highest monomer conversion while the conversion of the PGHW-18h filled resin composite was the lowest. These results indicated that more monomers remained unreacted in PGHW filled resin composites and would probably release to the aqueous environment under the action of water [23,24].

### 3.3. Behavior in water

Low absorption and solubility of dental resin composite are of great importance for clinical applications. Clinically acceptable composites

Table 1

Graft ratio of the whisker and degree of conversion (S.D.) of monomers in the resin composites with HW, SHW, and PGHW [7].

Filler in composite resin	Graft ratio of whisker (wt.%)	Degree of conversion (%)
HW	–	57.3 (1.0)
SHW	6.6 <sup>a</sup>	56.2 (1.2)
PGHW-1h	8.5 <sup>b</sup>	53.2 (1.1)
PGHW-3h	16.8 <sup>b</sup>	49.9 (1.2)
PGHW-7h	28.3 <sup>b</sup>	47.4 (1.0)
PGHW-18h	32.8 <sup>b</sup>	47.2 (0.9)

<sup>a</sup> Amount of silane ( $\gamma$ -MPS) grafted on the surface of SHW.

<sup>b</sup> Amount of poly(Bis-GMA) grafted on the surface of PGHW, amount of  $\gamma$ -MPS has been deducted.

should have relatively low values of water sorption and solubility (2–3 wt.%) [25]. And the international standard ISO 4049-2009 suggests that the water sorption and solubility of polymer based restorative materials should not be more than 40.0  $\mu\text{g}/\text{mm}^3$  and 7.5  $\mu\text{g}/\text{mm}^3$  after soaking in water for 7 days respectively. It is known that absorption and solubility of resin composites are affected by factors such as polymer (monomer, degree of conversion, hydrophobic–hydrophilic properties), the filler (morphology, size, dispersion in the matrix, fraction), and the properties of the filler–matrix interface [1,5,10,25–27]. In this work, mass fractions of monomer and filler in the composites were fixed. The effect of whisker surface modification on absorption/solubility of the composites was investigated.

As shown in Table 2 and Fig. 2A, both water sorption and solubility of six studied composites increase with the soaking time, and tend to reach saturation within 14 days, which was in agreement with the results reported by Santos et al. [10]. It was also observed that surface graft polymerization on the whisker had significant effect on absorption and solubility of the dental resin composites. During the same immersion time (1 d, 7 d, 14 d, or 30 d), with increasing graft ratio of the whisker, the rate of water sorption declined first and then increased (Table 2); the water sorption values of four PGHW filled resin composites are lower than those of HW or SHW filled resin composites (Fig. 2A), and the PGHW-1h filled resin composite shows the lowest value (27.16  $\mu\text{g}/\text{mm}^3$ , 7 d). Different factors could account for the variation of water sorption: FE-SEM images of the internal structure of the resin composites revealed the differences in whisker–matrix interface properties and whisker dispersion (Fig. 3). Whiskers in HW or SHW filled resin composites had smooth and clean surface, and the boundary between the whisker and the matrix was clearly evident with gaps and voids (Fig. 3A and B). In contrast, the surface of PGHW was rough with organic components, and the interface between the whisker and the matrix was fuzzy and closer (Fig. 3C and D). The grafted poly(Bis-GMA) layer on the surface of PGHW introduced more incorporable groups (hydroxyl groups, carbon–carbon double bonds) to interact with resin's polymer network by Van der Waal's force, hydrogen bonds, and covalent bonds [7,28], which contributed to forming tightly bonded whisker–matrix interface and resisting water diffusion in the resin composite consequently. Hence, the loose interface between the whisker (HW or SHW) and the matrix would accommodate additional amount of water and also provide the fastest paths for water migration into the interior resin composite [5,10]. On the other hand, PGHW-1h had a better dispersion in the matrix because the organic layer on the surface of the separate whisker improved the interfacial compatibility (Fig. 3C). By comparison, the untreated whisker tended to aggregate in the matrix because of its poor surface wettability (Fig. 3A), and

**Table 2**Water sorption (wt.%) and solubility (wt.%) of the studied composites after soaking in water ( $37 \pm 1$  °C) for different durations [means (S.D.)],  $n = 4$ .

Composite with	Sorption of water				Solubility			
	1 d	7 d	14 d	30 d	1 d	7 d	14 d	30 d
HW	1.69 (0.04)	2.98 (0.06)	3.85 (0.05)	4.03 (0.10)	0.22 (0.02)	0.56 (0.03)	0.80 (0.04)	1.02 (0.11)
SHW	1.59 (0.04)	2.73 (0.04)	3.84 (0.03)	3.80 (0.09)	0.19 (0.02)	0.63 (0.06)	0.82 (0.04)	0.83 (0.05)
PGHW-1h	1.10 (0.02)	2.33 (0.05)	3.33 (0.05)	3.40 (0.07)	0.24 (0.02)	0.60 (0.03)	0.87 (0.04)	0.88 (0.06)
PGHW-3h	1.18 (0.05)	2.24 (0.03)	3.53 (0.05)	3.61 (0.08)	0.29 (0.01)	0.65 (0.04)	0.90 (0.03)	0.94 (0.05)
PGHW-7h	1.32 (0.02)	2.49 (0.05)	3.65 (0.07)	3.77 (0.05)	0.34 (0.01)	0.67 (0.05)	0.92 (0.05)	0.97 (0.08)
PGHW-18h	1.21 (0.03)	2.60 (0.06)	3.74 (0.09)	3.86 (0.08)	0.35 (0.02)	0.71 (0.04)	0.95 (0.06)	0.99 (0.07)

PGHW also tended to form aggregations with internal voids after longer graft polymerization periods, especially PGHW-7h and PGHW-18h [7]. These aggregations would facilitate water diffusion owing to the voids inside and loose gaps that were easily formed between the aggregations and the matrix (Fig. 3A and D).

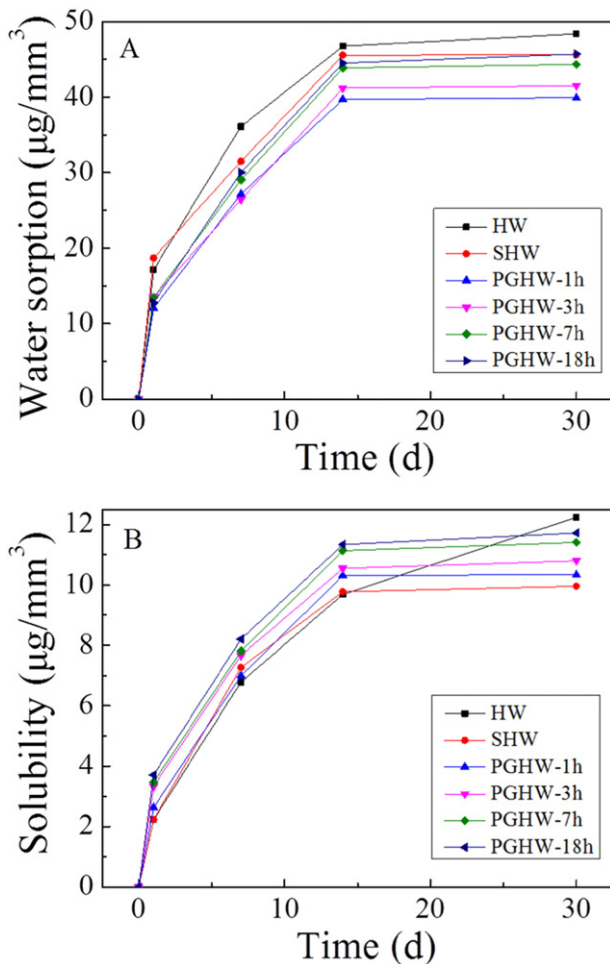
For the solubility of the studied resin composites (Table 2 and Fig. 2B), in the same immersion time, the values were generally increased with the graft ratio of the whisker. As discussed above, the poly(Bis-GMA) layer on the surface of the whisker had an adverse effect on degree of conversion of the resulting resin composites [7]. At a lower conversion, more Bis-GMA and TEGDMA monomers remained unreacted and tended to release from the composite under the action of water [15,24], thus, the PGHW-18h filled composite had a relatively high solubility (HW:  $6.78 \mu\text{g}/\text{mm}^3$ , 7 d; PGHW-1h:  $6.99 \mu\text{g}/\text{mm}^3$ , 7 d; PGHW-18h:  $8.21 \mu\text{g}/\text{mm}^3$ , 7 d). Meanwhile, the release of unreacted monomers provided vacated space to facilitate water diffusion, which

might be one possible reason for the higher values of water sorption of the PGHW-7h and PGHW-18h filled composites than PGHW-1h and PGHW-3h filled composites. After soaking for 30 days, the solubility of the HW filled resin composite was dramatically increased (Fig. 2B) and this might be attributed to the poor interfacial bonding (Fig. 3A) which caused a whisker–matrix debonding and a loss of material during the absorption process.

### 3.4. Bioactivity

Exchange of calcium and phosphorus ions at the interface between bioactive material and SBF results in the generation of a surface apatite layer, and this defines in vitro bioactivity of the material [19]. The mechanism has been discussed in detail elsewhere [29–31]. For the dental restorative resin composite, the formed apatite layer could narrow the composite–tooth gap caused by photopolymerization and decrease the chance of bacteria aggregation and secondary caries.

In this work, the effect of whisker surface modification on bioactivity of the resin composites was investigated by soaking the resin composites in SBF for different durations. Morphology of the PGHW-1h filled resin composite after soaking in SBF showed that small amounts of dispersed apatite particles formed after 1 day of exposure to SBF (Fig. 4B) compared with the specimen before immersion (Fig. 4A), and dense and thick layers were covered on the surface of the resin composites after 14 and 30 days (Fig. 4C and D). The layer showed a typical globular morphology. The globules stacked closely and formed a continuous layer over the surface. After soaking for 14 days, no obvious difference was observed between the surface morphology of resin composites with HW, SHW, PGHW-1h, and PGHW-18h (Fig. 5). Results of EDS dot-mapping of the surface of the resin composites show that the main elements are carbon, oxygen, calcium, and phosphorus (bottom column of Figs. 4 and 5). Carbon might be from the resin matrix or poly(Bis-GMA) grafted on the surface of the whisker. For the PGHW-1h filled resin composite before immersion (Fig. 4A), small amounts of calcium and phosphorus were detected and might be ascribed to the whisker nearby the detection dot. After immersion, dot mappings of the formed particles show significant intensities of calcium and phosphorus, which could be from the precipitated apatite layer. The Ca/P atomic ratios of the surface apatite were calculated by EDS analysis and ranged from 1.41 to 1.46, which were less than the stoichiometric ratio 1.67 [32] of hydroxyapatite. These results confirmed the presence of calcium and phosphorus in the surface layer and implied that the precipitated layer was calcium-deficient apatite incorporating other minor elements such as sodium and magnesium [33]. Moreover, surface graft polymerization on HW did not significantly affect the bioactivity of the resin composites. It was reported that the organic coating on the surface of hydroxyapatite did not affect the tendency of the mineral to take up calcium and phosphate from SBF, and the coating was assumed to be transparent for Ca and  $\text{PO}_4$  ion transport in an aqueous environment [18,34]. However, it is reasonably assumed that the kinetics of ions transport to the whisker surface might be interfered with by poly(Bis-GMA) layer grafted on the surface of PGHW, leading to lower Ca/P ratio and poor crystal structure of the formed apatite. Thus further study on the apatite forming mechanism was required in later work.



**Fig. 2.** (A) Water sorption ( $\mu\text{g}/\text{mm}^3$ ) and (B) solubility ( $\mu\text{g}/\text{mm}^3$ ) of the studied composites after soaking in water ( $37 \pm 1$  °C) for different durations.

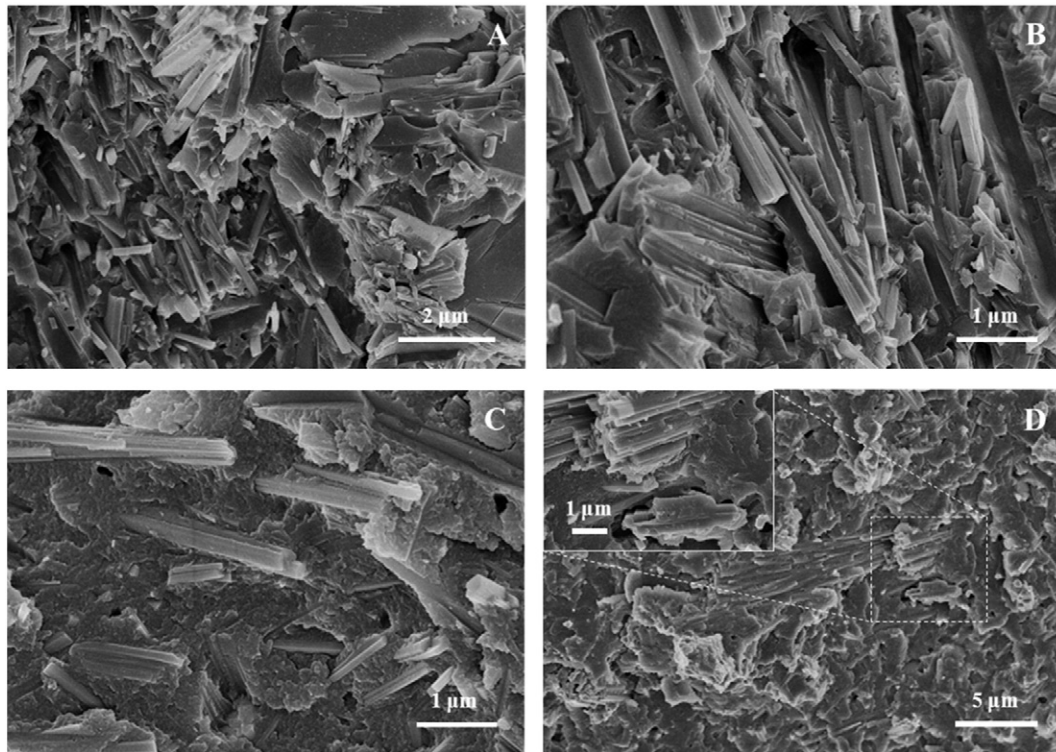


Fig. 3. FE-SEM images of the fracture surfaces of resin composites with (A) HW, (B) SHW, (C) PGHW-1h, and (D) PGHW-18h.

#### 4. Conclusions

Dental resin composites with HW, SHW and PGHW were fabricated to investigate the effects of whisker surface graft polymerization and graft ratio on absorption/solubility properties and in vitro bioactivity of the resin composites. Lower amount of poly(Bis-GMA) grafted on the surface of PGHW-1h provided incorporable groups to interact with resin network, which evidently improved the whisker–matrix interfacial properties and the filler dispersion in the matrix, reducing the space for water accommodation and resisting water diffusion consequently. Higher graft ratios of PGHW formed aggregations with voids inside during the graft polymerization and led to a decrease of monomer conversion of the resulting resin composites, which was an adverse factor for decreasing water sorption and solubility of the resin composites. In vitro bioactivity test demonstrated that the apatite forming

ability of PGHW filled resin composites was not significantly affected by surface graft polymerization on the whisker. Overall, the resin composite with PGHW-1h (graft ratio: 8.5 wt.%) had the lowest water sorption, less solubility, desirable bioactivity, as well as the lowest volume shrinkage and improved mechanical properties as previously reported. It was further demonstrated that grafting an appropriate amount of poly(Bis-GMA) (8.5 wt.% in this study) on the surface of the whisker could improve the physical and mechanical properties of the dental resin composite effectively. However, degree of conversion and mechanical properties of the resin composite with PGHW-1h still need to be further improved, which could possibly be realized by hybrid filler filling technique and filler loading adjustment. For reliability, evaluation of the PGHW filled dental resin composite, such as biological properties and simulated clinical restoration in isolated tooth, should be carried out in the future.

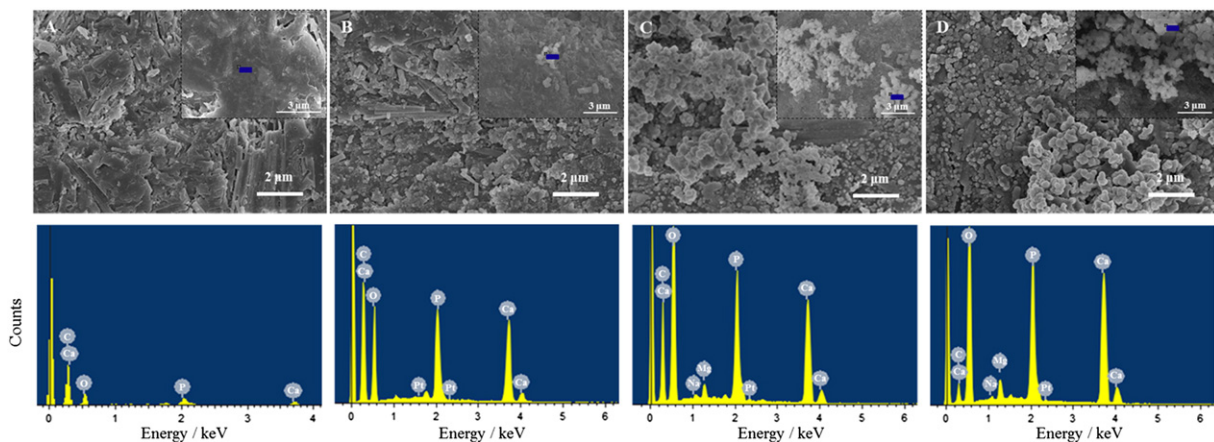
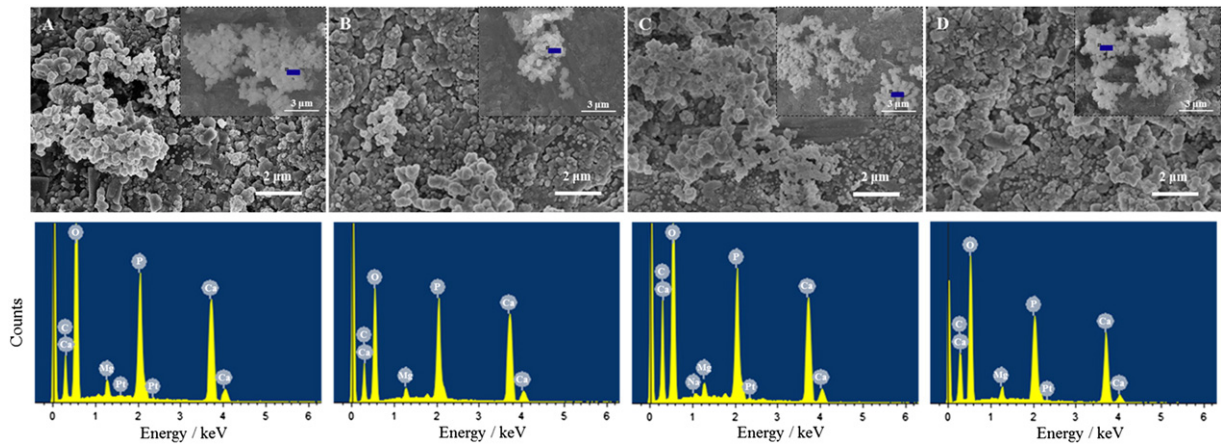


Fig. 4. FE-SEM images (top column) and EDS profiles (bottom column) of the surface of the composites with PGHW-1h immersed in SBF for (A) 0 day, (B) 1 day, (C) 14 days, and (D) 30 days.



**Fig. 5.** FE-SEM images (top column) and EDS profiles (bottom column) of the surface of the composites with (A) HW, (B) SHW, (C) PGHW-1h, and (D) PGHW-18h immersed in SBF for 14 days.

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