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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 μg/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.

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 interface 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_4 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^{-1}, 10 scans, 4000–650 cm^{-1}) 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^2, SLC-VIII B Hangzhou Sifang Medical Apparatus Co., Ltd., China) for 60 s. The ratios of the infrared spectra of aliphatic (1637 cm^{-1}) to aromatic (1608 cm^{-1}) 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:

$$\mathrm{WI}(\%) = 100\frac{m_1-m_0}{m_0} \quad \mathrm{SL}(\%) = 100\frac{m_0-m_2}{m_0}$$
$$\mathrm{WS}(\%) = \mathrm{WI}(\%) + \mathrm{SL}(\%)$$

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 $\mu g/mm^3$ using the equation:

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

where $\mathrm{WI}(\mu g/mm^3) = 10^3((m_1 - m_0)/V)$, $\mathrm{SL}(\mu g/mm^3) = 10^3((m_0 - m_2)/V)$, 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, $NaHCO_3$ 2.2682, KCl 0.2237, $K_2HPO_4 \cdot 3H_2O$ 0.2283, $MgCl_2 \cdot 6H_2O$ 0.3060, $CaCl_2$ 0.2771, and Na_2SO_4 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.