Composites Science and Technology 101 (2014) 86–93

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: www.elsevier.com/locate/compscitech

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

Fengwei Liu, Xiaoze Jiang, Qinghong Zhang, Meifang Zhu *

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 201620, PR China

ARTICLE INFO

Article history:
Received 13 June 2014
Received in revised form 2 July 2014
Accepted 3 July 2014
Available online 10 July 2014

Keywords:
A. Hybrid composites
B. Interface
B. Mechanical properties

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-SiO_2) nanoparticles in a bisphenol A glycidyl methacrylate (Bis-GMA)/triethylene glycol dimethacrylate (TEGDMA) based dental resin matrix. The effect of PGSHW/s-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-SiO_2 effectively increased the degree of conversion and filler packing density of the resin composites. Mechanical test showed that PGSHW/s-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-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.

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.

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

* Corresponding author. Tel.: +86 21 67792434; fax: +86 21 67792855.
E-mail address: zhumf@dhu.edu.cn (M. Zhu).

http://dx.doi.org/10.1016/j.compscitech.2014.07.001
0266-3538/

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 SiO_2 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-SiO_2 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-SiO_2 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-(methacyloxypropyl) 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.

SiO_2 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-SiO_2 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-SiO_2 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-SiO_2 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/cm^2, 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:

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

where $(A_{1637}/A_{1608})_{cured}$ stands for the ratio of the absorbance intensities of peaks at 1637 cm^{-1} and 1608 cm^{-1} of cured specimens, and $(A_{1637}/A_{1608})_{uncured}$ 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 × 2 mm × 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 #)

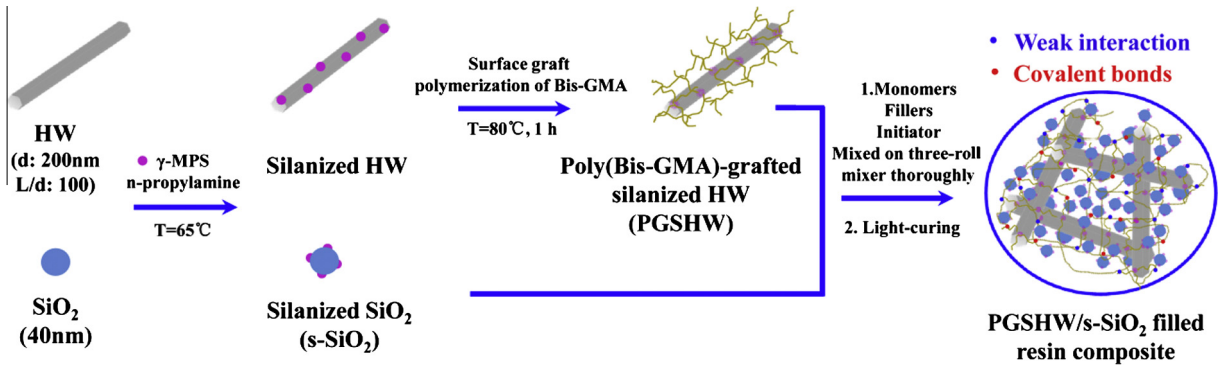

Fig. 1. Schematic representation of the preparation of strong and bioactive dental resin composite with PGSHW/s-SiO_2 hybrid fillers.