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Surface modification of quartz fibres for dental composites through a sol-gel process

Yazi Wang [a], Renlin Wang [a,c], Eric Habib [b], Ruili Wang [b], Qinghong Zhang [a], Bin Sun [a,*], Meifang Zhu [a,*]

[a] State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of Material Science and Engineering, Donghua University, Shanghai 201620, PR China
[b] Department of Chemistry, Université de Montréal, CP 6128, Succ. Centre-ville, Montreal, Quebec, Canada
[c] Yanfeng Plastic Omnium Automotive Exterior Systems Co., Ltd., Shanghai 201805, PR China

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ABSTRACT

In this study, quartz fibres (QFs) surface modification using a sol-gel method was proposed and dental posts reinforced with modified QFs were produced. A silica sol (SS) was prepared using tetraethoxysilane (TEOS) and 3-methacryloxypropyltrimethoxysilane (γ-MPS) as precursors. The amount of γ-MPS in the sol-gel system was varied from 0 to 24 wt.% with a constant molar ratio of TEOS, ethanol, deionized water, and HCl. Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), and contact angle (CA) measurements were used to characterize the modified QFs, which confirmed that SS had successfully coated the surface of QFs. SEM images showed good interfacial bonding between the modified QFs and the resin matrix. The results of three-point bending tests of the fibre reinforced composite (FRC) posts showed that the QFs modified by SS with 12 wt.% γ-MPS presented the best mechanical properties, demonstrating improvements of 108.3% and 89.6% for the flexural strength and flexural modulus, respectively, compared with untreated QFs. Furthermore, the sorption and solubility of the prepared dental posts were also studied by immersing the posts in artificial saliva (AS) for 4 weeks, and yielded favourable results. This sol-gel surface modification method promises to resolve interfacial bonding issues of fibres with the resin matrix, and produce FRC posts with excellent properties.

1. Introduction

Endodontically treated teeth suffering from a severe loss of structural integrity become easier to fracture than healthy teeth [1]. Over the past decades, posts made of metals have been used to restore defective teeth. However, traditional metal posts can cause root fractures due to the mismatch of elastic modulus between restorative materials and dentin. Metal posts also have other disadvantages such as potential allergic reactions, and risks of corrosion [2]. Fibre-reinforced composite (FRC) posts were introduced by Duret in 1990 and have gradually replaced metal posts [3]. These are typically fabricated by embedding oriented reinforcing fibres (carbon fibres, glass fibres, quartz fibres, etc.) in the resin matrix. Compared to traditional metal posts, FRC posts exhibit elastic properties closer to that of dentine, hence decreasing the occurrence of root fracture by distributing stresses more uniformly in the tooth. In particular, quartz and glass fibre posts have recently been popular in clinical application due to good aesthetics, excellent mechanical properties, and advantageous biocompatibility [4].

For composite materials, the interfacial adhesion between reinforcing fibres and resin matrix is vital to the mechanical properties and long-term durability of the FRC posts [5]. Surface modification with coupling agents has been a common method to enhance the interfacial continuity, allowing a good stress transfer from matrix to reinforcement [6,7]. 3-methacryloxypropyltrimethoxysilane (γ-MPS) is the most common coupling agent used in dental composites and its amount has a significant influence on the matrix-reinforcement interfacial properties [8]. Excess use of coupling agents can result in the formation of multilayer silane structures on the fibres where much of the coupling agents is loosely attached to the surface without covalent bonding, decreasing the interfacial strength within the composites [9]. However, current efforts are still not sufficient with respect to enhancing the bonding of fibres to the resin matrix. Debonding occurs easily in practical application, and the service life of FRC posts is reduced because of the complex conditions of the oral environment, such as cyclic loads, pH fluctuation, temperature variation, and saliva [10]. Hence, the development of novel surface treatment techniques and the synthesis of novel coupling agents are required to address these problems [11].

In this study, quartz fibres (QFs) were selected as reinforcements and modified using a sol-gel technique. A silica sol (SS) was firstly prepared using tetraethoxysilane (TEOS) and γ-MPS as precursors,

* Corresponding authors.
E-mail addresses: sunbin@dhu.edu.cn (B. Sun), zhumf@dhu.edu.cn (M. Zhu).

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followed by coating QFs with the prepared SS. Compared with previous surface modifications directly employing coupling agents [12], the potential advantages of SS coating mainly include: (1) the SS anchored on the surface of fibres act as a tight "bridge" between fibres and γ-MPS which is linked to the —Si—O—Si— network of SS with covalent bonds; and (2) the envelope of SS may facilitate the contact of γ-MPS with QFs and enhance the grafting ratio of QFs. This may be useful for improving the compatibility and bonding strength between QFs and resin matrix. The modified QFs were then assembled into FRC posts and their mechanical properties were measured. Considering the aqueous environment in the oral cavity can cause fibre-matrix debonding upon hydrolysis of the silane coupling agent, therefore the performances of these FRC posts were also investigated after immersion in artificial saliva.

2. Materials and methods

2.1. Materials

Bisphenol A glycerolate dimethacrylate (Bis-GMA), ethyl 4-dimethylamino benzoate (4-EDMAB, 99%), and camphorquinone (CQ, 97%) were obtained from Sigma-Aldrich, USA. Methyl methacrylate (MMA), γ-MPS, TEOS, hydrochloric acid (HCl, 37%), sulphuric acid (H_2SO_4), and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Unidirectional QF bundles (B type) with linear density of 72 tex were obtained from Hubei Feilihua Quartz Glass Co., Ltd., China. All reagents were used as received, without further purification.

2.2. Preparation of silica sol (SS) with different amounts of γ-MPS

In the preparation process of SS, the relative amounts of TEOS, ethanol, deionized water, and HCl were kept at a constant molar ratio of approximately 1:2.2:5.6:0.03. The amount of γ-MPS was varied from 0 to 24 wt.% of above mixture. Firstly, a solution of TEOS, ethanol, and γ-MPS was homogenized with magnetic stirring for 5 min, then HCl was added dropwise with stirring at room temperature. The solution was then heated in a water bath at 50 °C, and stirred for 2 h to obtain the SS.

2.3. Surface modification of QFs

A thin wetting agent layer is initially present on the surface of commercial QFs to reduce the friction between fibres, which first needed to be removed through acid etching. QFs were soaked in a sulfuric acid solution (30 wt.%) at 98 °C for 2 h, and then washed with deionized water to remove residual acid. The obtained QFs were dried in vacuum oven at 100 °C for 4 h.

The above QFs were further modified by the SS prepared in 2.2. Unidirectional fibres were soaked in SS for 2 h at room temperature, and shaken every 15 min to insure a good contact. After that, QFs were removed, washed with ethanol for 2 min, and finally dried in a vacuum oven at 100 °C for 4 h.

2.4. Preparation of FRC posts

Bis-GMA and MMA were first mixed with a mass ratio of 1:1 at room temperature, then 0.5 wt.% CQ and 0.5 wt.% 4-EDMAB were added and stirred uniformly. The bundles of modified QFs were immersed in Bis-GMA/MMA resin and kept in a vacuum oven at 60 °C for 2 h. After cooling to room temperature, the resin-impregnated oriented QFs bundles were placed into a mould using the pultrusion technique, and subsequently cured with a LED curing light with wavelength of 470 nm for 100 s. After demoulding, FRC post samples with a size of 25 mm × 2 mm × 2 mm were obtained.

2.5. Analysis and characterization

The surface morphology of QFs and fracture surface of FRC post samples were observed by scanning electron microscope (Hitachi, S-3000N, Japan). The QFs modified with SS were also characterized using FT-IR spectrometer (Thermo Fisher Scientific, Nicolet 8700, USA) with a spectral range of 500–4000 cm^{-1}. The weight changes of QFs with temperature were measured through thermal gravimetric analysis (TA, Q5000IR, USA) from 50 °C to 800 °C using a heating rate of 20 °C/min. The hydrophobicity of different QFs was evaluated by the contact angle (θ) measurements (OCA 40 Micro, China). A water droplet of 10 nl was placed at five different positions on the QFs and the average value was taken as the contact angle (θ). The mechanical properties of FRC posts were tested according to ISO 10477-2004. The universal testing machine (WDW-3020, China) was employed in three-point bending geometry, with a span distance of 20 mm and a loading rate of 1 mm/min.

2.6. Sorption and solubility test in artificial saliva (AS)

The preparation of AS was based on previous literature [13]. 8 samples of FRC posts made in 2.4 were randomly divided into two groups. One group was weighted (m_0) and then immersed in AS at 37 ± 1 °C. A regular time interval later (1, 2, 3 and 4 weeks), they were taken out, wiped off from excess liquid, weighed (m_w), and immersed in AS once again. After 4 weeks, all specimens were taken out and dried at 37 ± 1 °C until a constant mass (m_d) was obtained. The average weight of four specimens was used. The statistical significance was evaluated by one-way analysis of variance (ANOVA) using SPSS 13.0 software and $p < 0.05$ was considered statistically significant.

Sorption and solubility were calculated using the following formulas:

$$WI(\%) = 100\frac{m_w - m_0}{m_0}$$

$$SL(\%) = 100\frac{m_0 - m_d}{m_0}$$

$$WS(\%) = WI(\%) + SL(\%)$$

where *WI* represents an apparent value for absorbed water, *SL* is the amount of extracted unreacted monomers, and *WS* represents an actual value of absorbed water, taking the solvated monomers into consideration.

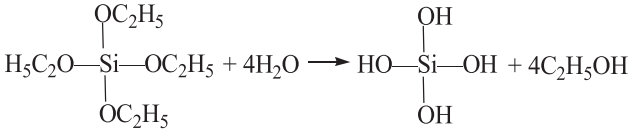
In addition, the mechanical properties of 4 specimens were tested after 4 weeks of immersion in AS. As a control, samples of the group that did not undergo the immersion in AS were directly tested with the three-point bending test.

3. Results and discussion

3.1. Modification mechanism

In the sol-gel process, TEOS is hydrolysed and then condensed to form an initial silica sol (SS) as shown in the following reactions [14,15]:

Hydrolysis:



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