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ORIGINAL RESEARCH

Synthesis of dental resins using diatomite and nano-sized SiO₂ and TiO₂

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Abstract The mechanical properties of dental composites were improved by porous diatomite and nano-sized silica (OX-50) used as co-fillers. The resin composites, filled with silanized OX-50 and silanized diatomite (40:60 wt/wt), presented the best flexural strength (133.1 MPa), elastic modulus (9.5 GPa) and Vickers microhardness (104.0 HV). Besides these, TiO₂ nanoparticles were introduced to tune the dental resin composites colours which were valued by the CIE-Lab system. The colour parameters (L^* , a^* , b^*) showed that the colour changes of resin composites could be perceived obviously, when 300–400 nm TiO₂ particles were introduced as fillers. The resin composite, filled with 0.5 wt% TiO₂, exhibited both clear discolouration ($\Delta E^* = 3.22$) and high mechanical strength. Using scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX), the titanium elemental mapping results indicated that the TiO₂ particles were distributed evenly in the prepared dental composites.

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1. Introduction

Dental resin composites have been widely used for restoring dental caries and other defects instead of conventional amalgam alloys, owing to their advantages such as excellent aesthetic quality, mechanical properties, biocompatibility, and easy handling [1–3]. Dental restorative composites are ordinarily composed of resin matrix, inorganic fillers and initiating agents. Triethylene glycol dimethacrylate (TEGDMA) and bisphenol A diglycidyl dimethacrylate (Bis-GMA) or some Bis-GMA analogue are commonly used as main components of the organic part. The inorganic particles are utilised in order to improve the abrasion [4], aesthetic and radiopacity properties of the resin materials. Although a wide variety of fillers [5–8] have been introduced into composites to improve

the toughness, strength [4] and durability of the dental composites, the composite is still not enough to be used in heavy-load and large area restorations [6]. So far lots of fillers have been used to solve this problem, for example porous glass-ceramic [3], mesoporous and nonporous fillers [7] and diatomite.

The compatibility and bond between the fillers and resin matrix are essential to the mechanical properties of dental composites. Porous inorganic particles were used as fillers so that the monomers could fill into pore channels to form composites containing interpenetrating polymer network. The obtained interpenetrating polymer network should provide a good bonding to enhance the mechanical properties of dental composites. Wang et al. [3] studied the mechanical properties of dental resin composites filled with porous diatomite and nanosized silica particles (OX-50). The porous structure of diatomite could significantly improve the mechanical properties of resin composites. However, the aesthetic quality of the resin composites still needs to be improved. The properties of resin materials must be close to the dental tissues due to its usage as a substitute of the lost dental tissue, enamel and dentin. For a certain resin, acceptable optical and aesthetics properties are also the important performance index in the clinical applications. TiO₂ nanoparticles are usually preferred in dentistry due to their pleasing colour and high biocompatibility [9].

The dental resins using diatomite, nano-sized SiO₂ and TiO₂, were synthesised in the present investigation, and the experimental results showed that the flexural strength and elastic modulus of the as-prepared dental composites were obviously improved compared with the previous studies [3,5]. Furthermore, TiO₂ particles in the range of 300–400 nm were first used as fillers to tune the colour and optical properties of the dental materials. The colour changes and mechanical properties of the composites were also investigated.

2. Experimental

2.1. Starting materials

The Bis-GMA, TEGDMA, camphorquinone (CQ), ethyl 4-dimethylamino benzoate (4-EDMAB), and 3-methacryloxypropyltrimethoxysilane (γ -MPS) were obtained from Aldrich Chemical Co. (Milwaukee, USA) and used as received. Cyclohexane, *n*-propylamine, anhydrous ethanol, TiO₂ were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Raw 2000 mesh diatomite particles were supplied by Shengzhou Xinglong Products of Diatomite Co., Ltd. in Zhejiang province (China). Aerosil OX-50 fumed amorphous silica was obtained from Evonik Degussa China Co. Ltd. Shanghai Branch, (Shanghai, China). The average particle diameter of Aerosil OX-50 (nanosized silica) was 40 nm with special surface area of 50 m²/g.

2.2. Silanization of inorganic particles

In order to enhance the interfacial adhesion between resin matrix and inorganic particles, the hydrophilic surface of the inorganic particles was treated with γ -MPS using a previous procedure [10]. The silica powder 5.0 g, γ -MPS 0.55 g, cyclohexane 100 ml and *n*-propylamine 0.1 g were stirred at 30 °C

for 30 min, then kept at 60 °C for another 30 min. The mixture was placed in a rotary evaporator (RE301 Shanghai Kexing Equipment Co., Ltd., Shanghai, China) at 60 °C for the removal of the solvent and volatile byproducts. The powder was heated at 100 °C for 1 h in the rotary evaporator and finally dried at 80 °C in a vacuum oven for 20 h.

2.3. Preparation of composites

The silanized silica powders were manually premixed by hand spatulation with the resin monomer. The monomer system which was used for all specimens consisted of 50 wt% Bis-GMA and 50 wt% TEGDMA. Camphorquinone (0.2 wt%) and 4-EDMAB (0.8 wt%) were used as a photoinitiator system. After the powders were completely wetted with the resin matrix, the composite pastes were thoroughly blended into a three-roll extruder (EXAKT 80E, Exakt Apparatebau GmbH & Co., Norderstedt, Germany) at room temperature. The mass ratios of 2000 mesh diatomite and OX-50 were 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, and the mass fraction of the inorganic fillers were 60.8 wt%, 61.3 wt%, 64.3 wt%, 64.6 wt%, 66.0 wt%, 67.7 wt% and 64.5 wt%, respectively. The composites mixtures were placed in silicon rubber moulds and light-cured using a LED curing unit (SLC-VIII B Hangzhou Sifang Medical Apparatus Co., Ltd., Zhejiang, China) for 120 s. After curing, the specimens were stored at room temperature for 3–4 days and then polished using progressively finer silicon carbide papers (grit numbers of 800#, 1000# and 2000#) for mechanical testing.

2.4. Characterisation

The silanized inorganic particles were characterised by a Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). TGA curves of the composites were collected using a Netzsch TG 209 F1 Analyser. The samples were heated from 30 to 800 °C with a temperature ramp rate 20 °C/min and air as sample purge gas (15 ml/min).

Colour was evaluated according to the 1976 Supplementary Standard Observer CIE $L^*a^*b^*$ system. In the three-dimensional colour space, CIE L^* is a measure of the lightness of an objective, CIE a^* is a measure of redness ($+a^*$) or greenness ($-a^*$), CIE b^* is a measure of yellowness ($+b^*$) or blueness ($-b^*$) [11]. The colour of the composites was measured using a spectrophotometer (Hunter Lab, Colour Quest XE) with D65 illumination and 10° standard observation angle were selected.

Flexural strength and elastic modulus were measured by the three-point bend test in a universal testing machine (WDW-300, Changchun Kexin Equipment Co., Ltd., Changchun, China) with 20 mm span and 0.75 mm/min crosshead speed. Vickers microhardness was evaluated using a pyramid diamond point (MHV-2000) by applying a 200 g load for 10 s. For each group material, at least six samples were prepared according to ISO 4049.

Light transmission at wavelength from 200 to 800 nm was measured using a UV-vis spectrophotometer (Lambda 950, Perkin Elmer, USA). The uncured resin composites were placed on a microscope glass slide, then the composites' surfaces were covered with another glass slide. We controlled 0.25 mm thickness of samples with a micrometer accurate to

0.01 mm. After that, the samples were cured at the top and bottom surfaces for 60 s.

The titanium elemental mapping of dental composites was carried out using scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX).

3. Results and discussion

3.1. Silanization of inorganic particles

In order to improve the interfacial adhesion between inorganic fillers and resin matrix, the inorganic particles are usually treated with silane coupling agent (γ -MPS). Fig. 1 exhibits the FTIR spectra of the untreated 2000 mesh diatomite, silanized 2000 mesh diatomite, untreated OX-50 and silanized OX-50. These inorganic particles exhibit strong absorbing bands at 3432 and 1628 cm^{-1} , corresponding to the O–H stretching vibration and O–H distorting vibration, respectively. The particles show an intense absorption bands at 1100 cm^{-1} , indicating the formation of Si–O–Si. The silanized inorganic particles exhibit an absorption peak at 1708 cm^{-1} , which is due to the C=O stretching vibration.

Fig. 2 shows the TGA curves of the silanized diatomite and silanized OX-50. It shows a two-step weight loss, the first stage including a low amount of weight loss at $T < 200^\circ\text{C}$ is due to water and the unreacted γ -MPS. The second stage (200–800 $^\circ\text{C}$) is due to the decomposition of γ -MPS binding onto silica spheres chemically. Therefore, weight loss between 200–800 $^\circ\text{C}$ presents the silane grafting ratios of silanized silica. The grafted γ -MPS on the diatomite and OX-50 were approximately 4.98 wt% and 3.43 wt%, respectively.

3.2. Mechanical and optical properties

The mechanical properties of dental resin composites containing different mass ratios of silanized fillers are shown in Fig. 3. The flexural strength and Vickers microhardness were gradually enhanced with the increasing amount of nano-sized silica (OX-50) in resins. The best mechanical properties of the resin composites were at the mass ratio of 40:60. The high flexural strength and elastic modulus can be attributed to the good interlocking between fillers and resin matrix. The resin matrix can penetrate into the pores of the diatomite so that the composite can be formed an interpenetrating polymer network during the polymerisation process. When the mass fraction of the silanized OX-50 was more than 40 wt% with respect to the

silanized OX-50, the mechanical properties of the composites showed the downward trend. This may be explained by the fact that an incomplete penetration of resins into the pores of diatomite. And therefore, empty pores were acted as voids in the system, which resulted in weak points in the composite structure [4,5].

In order to further improve the performance of the dental composites, TiO_2 particles with 300–400 nm were introduced. The mechanical properties of dental resin composites with different mass ratios of TiO_2 are listed in Table 1. When the mass fraction of TiO_2 was more than 0.5 wt%, elastic modulus of specimen decreased while vickers microhardness increased. Fig. 4 shows the light transmission of dental resin composites with addition of different mass ratios of TiO_2 , there was a trend for the transmittance to increase with the wavelength

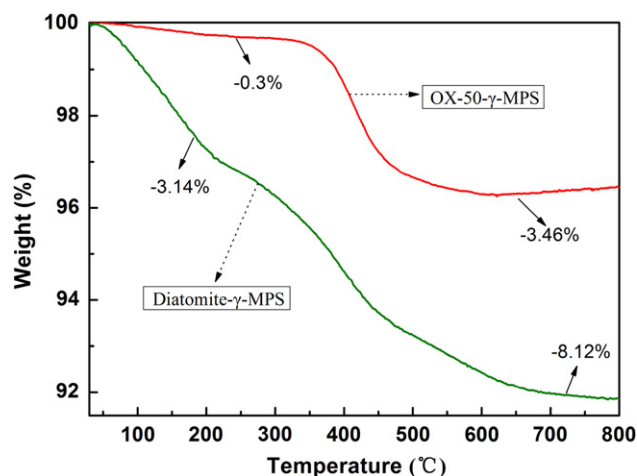


Fig. 2. TGA curve of silanized 2000 mesh diatomite and OX-50.

Table 1 The mechanical properties of dental resin composites with different mass ratios of TiO_2 addition.

Resin	Flexural strength (MPa)	Elastic modulus (GPa)	Vickers microhardness (HV)
0% TiO_2	133.1	9.5	104.0
0.5% TiO_2	120.1	10.1	105.4
1% TiO_2	119.6	7.8	106.2
2% TiO_2	104.2	7.5	112.5

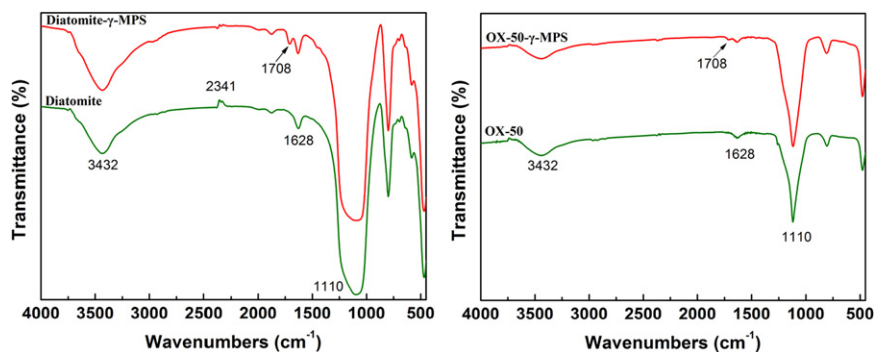


Fig. 1. FTIR spectra of the untreated 2000 mesh diatomite, silanized 2000 mesh diatomite, untreated OX-50 and silanized OX-50.

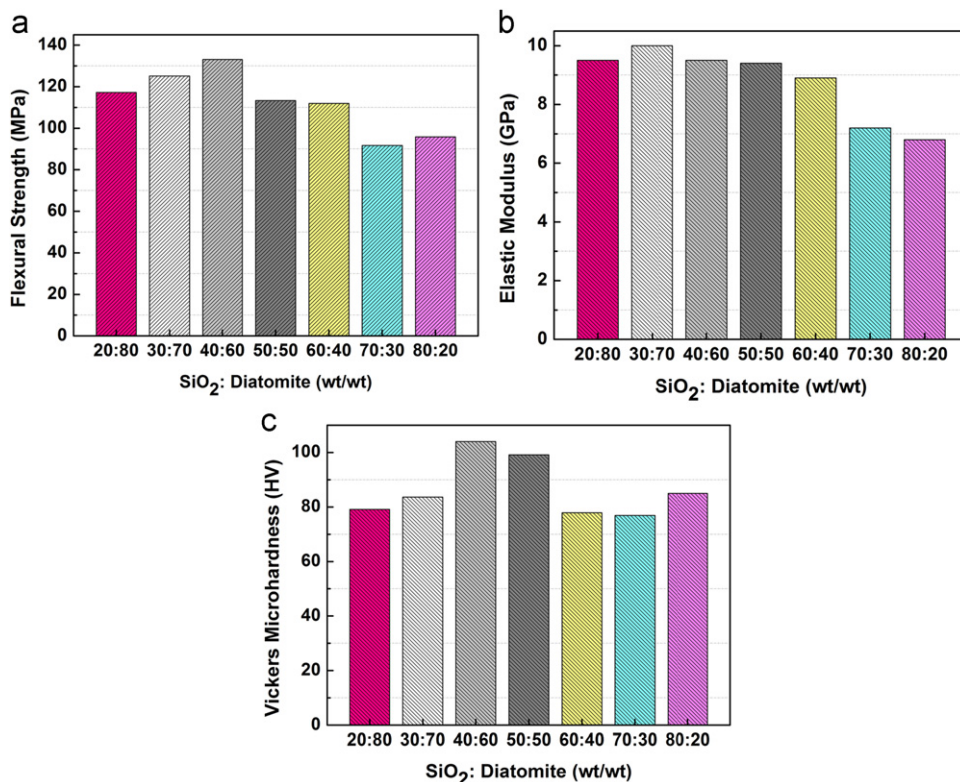


Fig. 3. Mechanical properties of dental resin composites added silanized 2000 mesh diatomite and OX-50 with different mass ratios (20:80, 30:70, 40:60, 50:50, 60:40, 70:30 and 80:20, respectively): (a) flexural strength; (b) elastic modulus; (c) Vickers microhardness.

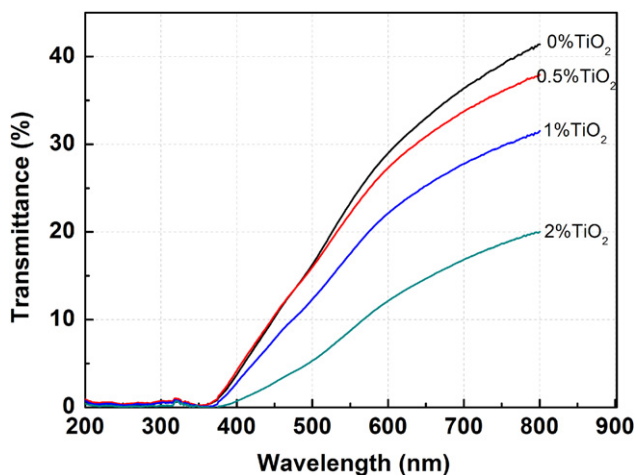


Fig. 4. Light transmission of dental resin composites with addition of different contents of TiO₂.

from 200 to 800 nm. It can be seen that the flexural strength and light transmission of the samples presented a decreased trend with increasing amount of TiO₂.

3.3. Energy dispersive X-ray analysis

The cross-section morphologies of the resin composites with different contents of TiO₂ are characterised using SEM as shown in Fig. 5a–d. It can be found that with increasing the

amount of TiO₂ in resins, the fracture surface of specimen changed a little. It is obviously that TiO₂ has no influence on the interfacial properties of the composites. Fig. 6a, b shows the SEM-EDX photomicrograph of titanium elemental map on the fracture surfaces of the dental composites with 1 and 2 wt% of TiO₂ loadings. The finite orange dots in Fig. 6 are corresponding to the X-ray signal of titanium elements in the dental composites. The SEM-EDX titanium mapping results indicated the homogeneous dispersion of TiO₂ in the prepared dental composites. When TiO₂ addition was equal to or less than 0.5 wt%, the ingredient of Ti in the composites was not easily measured due to the little content. Therefore Fig. 6 only shows the Ti distribution of resin composites with 1 and 2 wt% TiO₂ additions, respectively.

3.4. Colour change

Colour plays an important role in obtaining optimum aesthetics. The CIE $L^*a^*b^*$ colour system used in this study is a recommended method for dental purposes, and it characterises colour based on human perception [12]. Changes in colour (ΔE^*) of the resin composites before and after adding different contents of TiO₂, and other colour coordinates (L^* , a^* , b^*) are listed in Table 2. Colour difference (ΔE^*) was calculated as

$$\Delta E^* = [(L_1^* - L_0^*)^2 + (a_1^* - a_0^*)^2 + (b_1^* - b_0^*)^2]^{1/2}$$

There are many studies on the perceptible/acceptable limit of colour difference (ΔE^*). Human eyes cannot detect ΔE^* values of less than 1.5, although this value is measured with the help of spectrophotometer. A colour difference value of

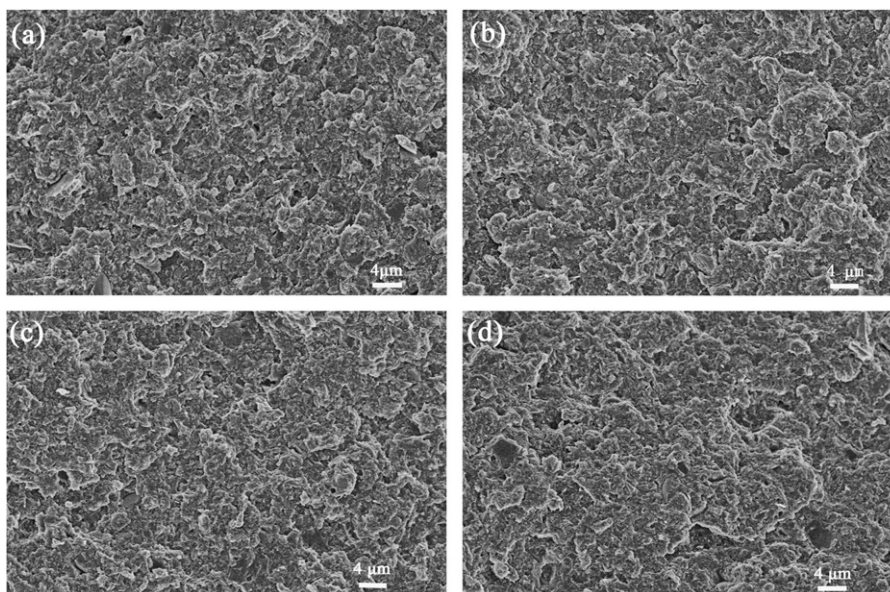


Fig. 5. FE-SEM images of the cross-section morphologies of the resin composites without (a) and with 0.5% (b), 1.0% (c) and 2 wt% (d) TiO₂ addition.

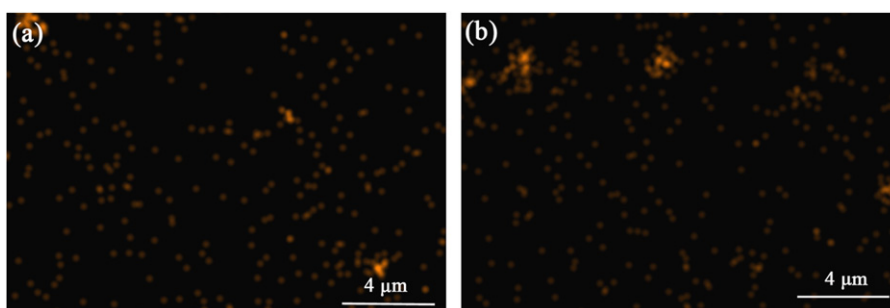


Fig. 6. SEM-EDX micrograph of titanium element map in resin composites with 1 wt% (a) and 2 wt% (b) TiO₂ addition.

Table 2 Colour values of dental resin composites with different mass ratios of TiO₂ addition.

Resin	L^*	a^*	b^*	ΔE^*
0% TiO ₂	71.44	4.97	15.40	
0.5% TiO ₂	74.53	4.06	15.53	3.22
1% TiO ₂	75.20	4.07	14.61	3.95
2% TiO ₂	76.83	3.63	12.90	6.09

more than 2 ΔE^* units was perceived by the 100% observers [13]. Therefore, ΔE^* values of all dental resin composites with adding different contents of TiO₂ could be visually perceived obviously. The above results indicated that the resin composite filled with 0.5 wt% TiO₂ exhibited clear discolouration ($\Delta E^* = 3.22$) and maintained higher mechanical strength.

4. Conclusions

Silanized nano-sized silica (OX-50) and porous diatomite at different mass ratios were used as co-fillers to reinforce dental composites. The resin composites, filled with silanized

OX-50 and silanized diatomite (40:60 wt/wt), presented the best flexural strength (133.1 MPa), elastic modulus (9.5 GPa) and Vickers microhardness (104.0 HV). For further modification of the clinical application of the composites, TiO₂ particles in the range of 300–400 nm were first used as fillers to tune the colour of the resin composite. The CIE-Lab colour parameters (L^* , a^* , b^*) showed that the colour changes of resin composites could be visually perceived obviously, when TiO₂ particles with size of 300–400 nm were introduced. It has high reference value in dental restorative applications.

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