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Synthesis of wrinkled mesoporous silica and its reinforcing effect for dental resin composites

*Ruili Wang, Eric Habib, X.X. Zhu**

Département de Chimie, Université de Montréal, C.P. 6128, Succursale Centre-ville, Montreal, QC, H3C 3J7, Canada

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ABSTRACT

Objective. The aim of this work is to explore the reinforcing effect of wrinkled mesoporous silica (WMS), which should allow micromechanical resin matrix/filler interlocking in dental resin composites, and to investigate the effect of silica morphology, loading, and compositions on their mechanical properties.

Methods. WMS (average diameter of 496 nm) was prepared through the self-assembly method and characterized by the use of the electron microscopy, dynamic light scattering, and the N_2 adsorption–desorption measurements. The mechanical properties of resin composites containing silanized WMS and nonporous smaller silica were evaluated with a universal mechanical testing machine. Field-emission scanning electron microscopy was used to study the fracture morphology of dental composites. Resin composites including silanized silica particles (average diameter of 507 nm) served as the control group.

Results. Higher filler loading of silanized WMS substantially improved the mechanical properties of the neat resin matrix, over the composites loaded with regular silanized silica particles similar in size. The impregnation of smaller secondary silica particles with diameters of 90 and 190 nm, denoted respectively as Si90 and Si190, increased the filler loading of the bimodal WMS filler (WMS-Si90 or WMS-Si190) to 60 wt%, and the corresponding composites exhibited better mechanical properties than the control fillers made with regular silica particles. Among all composites, the optimal WMS-Si190- filled composite (mass ratio WMS:Si190 = 10:90, total filler loading 60 wt%) exhibited the best mechanical performance including flexural strength, flexural modulus, compressive strength and Vickers microhardness.

Significance. The incorporation of WMS and its mixed bimodal fillers with smaller silica particles led to the design and formulation of dental resin composites with superior mechanical properties.

1. Introduction

Dental resin-based composites have been widely used as hard tissue substitutes to restore dental caries and other defects since the early 1960s, thanks to their superior aesthetics and biocompatibility over dental amalgams [1–4]. These composites are primarily comprised of inorganic filler particles dispersed in a resin matrix which can be polymerized under a blue light irradiation. Despite recent advances in the optimization of monomer structures and filler compositions, the fracture of resin composite restorations is still one of the main

* *Corresponding author.*
E-mail address: julian.zhu@umontreal.ca (X.X. Zhu).

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Table 1 – Synthesis conditions for WMS and other silica particles.

Particle	Diameter (nm)	Reaction mixture (mL)				T (°C)	Time (h)
		Ethanol	Ammonia hydroxide	Deionized water	TEOS		
Si90	90	45	3.3	0	8	RT	16
Si190	190	100	3.9	18	3.2 (dropwise)	60	5
Si507	507	45	30	6	3.5	60	2
WMS	496	See Section 2.2.1			3.5	70	24

causes for failure in clinical applications, which prevents their applications in high-load and large area restorations [5–8].

A strong bond between polymer matrix and inorganic particles is critical to the longevity of resin composites. This bond is usually established with a silane treatment of the filler surface, but silanol and ester bonds can be degraded by water absorbed by the composites [9,10]. A remedy to this problem is to introduce micromechanical interlocking through the penetration of the resin matrix into the porosities of the filler particles [11–19]. Recent efforts in porous fillers in dental composites can be mainly classified into three categories: surface porous fillers [7,12,13], sintered porous fillers [14–16], and interconnected pore fillers [11,17–19]. Zandinejad et al. introduced porous structures to the surface of glass-ceramic fillers by chemical etching using hydrofluoric acid [12]. The results demonstrated that fillers with a higher degree of porosity had a positive effect on flexural strength. However, the etching process exhibited poor control on pore size and uniformity. Sintering process with primary silica nanoparticles also produced porous fillers, with porosity provided by the remaining interstitial voids [14–16]. Apart from the high temperature required (1300 °C for silica), the resulting agglomerates remained the weak point of the fillers due to the lack of resin interpenetration [19]. Recently, mesoporous silica (~4 nm diameter) was prepared through a non-surfactant templated route [17,18]. The particles possess interconnected porous networks [17]. The combination of mesoporous and nonporous silica indeed improved the mechanical properties of the dental composites, compared with either of these fillers alone [11,17]. However, the flexural strength of the final composite with the optimized filler composition was 68 ± 9 MPa, which failed to meet the requirement of ISO 4049-2009 (minimum 80 MPa) [8,20]. Therefore, the variables in mesoporous filler based composites need to be optimized, including the filler morphology and composition.

Recently, wrinkled mesoporous silica (WMS) has drawn much interest due to its unique features such as ordered mesoporous structures, high surface area, and good biocompatibility [21–23], which suggest potential applications in cancer therapies [24], drug carriers [25,26], catalyst supports [27,28], and adsorbents for heavy metal ions [29]. The methods for the synthesis of WMS include the microemulsion method [26,30–32], the microwave-assisted hydrothermal technique [27], and the self-assembly process [23,25]. To the best of our knowledge, its application in dental resin composites is unprecedented.

For dental composites, surface morphology determines the extent of the interfacial interaction between the filler and the matrix. WMS exhibits distinct structure and texture properties. Specifically, this unique structure has a solid spherical core with wrinkles extending radially out from the center. Meanwhile, the radiating wrinkles can interlock with the resin matrix and increase the contact area between filler and matrix, and can thereby improve the strength of the composite. The objective of this study is to investigate the reinforcing effect of WMS and its bimodal fillers with silica particles in dental resin composites.

2. Materials and methods

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%), cyclohexane (anhydrous, 99.5%), *n*-pentanol (99%), cetyltrimethylammonium bromide (CTAB, 99%), ammonium nitrate (98%), *n*-propylamine (99%), and 3-methacryloxypropyl trimethoxysilane (γ-MPS, 99%), bisphenol A glycerolate dimethacrylate (BisGMA), tri(ethylene glycol) dimethacrylate (TEGDMA, 95%), and camphorquinone (CQ, 97%) were purchased from Sigma–Aldrich (Milwaukee, USA). Ethyl 4-dimethylamino benzoate (4-EDMAB, 99%) was purchased by Alfa Aesar (Ward Hill, USA). Urea and ammonium hydroxide (28–30 wt%) were purchased from ACP Chemicals Inc. (Montreal, Canada) and EMD Chemical Inc. (Darmstadt, Germany), respectively. All chemicals were used without further purification.

2.2. Methods

2.2.1. Synthesis of WMS

WMS with an average diameter of 496 nm was synthesized by modifying the reported method [23,31]. Briefly, 3.5 mL of TEOS was added under magnetic stirring to a mixture of 30 mL cyclohexane and 1.5 mL *n*-pentanol. Subsequently, 2.4 g of CTAB, 0.6 g of urea, and 60 mL of deionized water were quickly added into the above solution in sequence. After stirring for 30 min at room temperature (RT, 23 °C), the reaction mixture was heated up to 70 °C, and maintained for 24 h. After cooling to RT, the mixture was centrifuged, and washed with acetone and deionized water. CTAB was removed by extraction in ethanol solution containing ammonium nitrate [33,34].

2.2.2. Synthesis of nonporous silica particles

Monodisperse silica particles (Si90, Si190, and Si507) with the average diameters about 90, 190, and 507 nm were synthesized, respectively, based on the Stöber method [35–37], and the reaction conditions are summarized in Table 1. TEOS was added either in one portion, or dropwise to a mixture of ethanol, ammonium hydroxide, and deionized water. Once the reaction completed, the particles were sedimented by centrifugation, washed with ethanol and deionized water, and vacuum-dried at 50 °C for 16 h.

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