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Evaluation of the filler packing structures in dental resin composites: From theory to practice

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ABSTRACT

Objectives. The aim of this study is to evaluate the packing properties of uniform silica particles and their mixture with secondary particles yielding maximally loaded dental composites. We intend to verify the difference between the idealized models (the close-packed structures and the random-packed structures) and the actual experimental results, in order to provide guidance for the preparation of dental composites. The influence of secondary particle size and the resin composition on the physical–mechanical properties and the rheological properties of the experimental dental composites was also investigated.

Methods. Silica particles (S-920, S-360, and S-195) with average diameters of 920, 360, and 195 nm were synthesized via the Stöber process. Their morphology and size distribution were determined by field-emission scanning electron microscopy and laser particle sizer. A series of silica fillers, S-920, S-920+195, S-920+360, and S-920+360+195, were then formulated with two Bis-GMA/TEGDMA resins (weight ratios of 70:30 and 50:50). For these experimental dental composites, their maximum filler loadings were assessed and compared to the theory. The mechanical properties, degree of conversion, depth of cure, and polymerization shrinkage of these composites were then evaluated. Their rheological behaviors were measured with a rheometer.

Results. Unimodal S-920 had the maximally filler loading of 70.80 wt% with the 5B5T resin, close to the theoretical estimation of the random loose packing (71.92 wt%). The maximum loading of the S-920+360+195 filled composite was 72.92 wt% for the same resin, compared to the theoretical estimation of 89.29 wt% obtained for the close-packed structures. These findings indicate that random loose packing matches more closely to the real packing state for the filler formulations used. When maximally loaded, the composite with S-920+360+195 produced the best mechanical properties and the lowest polymerization shrinkage. The degree of conversion and depth of cure were higher with secondary particles added, and the viscosity of all unpolymerized pastes exhibited shear thinning behavior.

Significance. Theoretical estimations of filler packing structures provide a useful guidance in the design of multimodal filler formulations and the preparation of dental composites with higher filler loading, improved physical–mechanical properties.

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1. Introduction

Light-curable dental resin composites are now widely used as filling materials for repairing damaged or decayed tooth structure, mainly due to their superior esthetic appearance [1]. These composites primarily consist of a polymerizable resin matrix and the silanized inorganic fillers [2]. The most commonly seen morphologies of inorganic fillers are spherical or irregular [3]. Apart from the work on different commercial composites, some studies also examined the influence of filler morphology on properties of dental composites. Satterthwaite et al. found that the composites with spherical fillers had lower values of shrinkage stress and strain in comparison to irregular fillers [4,5]. For the composites with multimodal spherical fillers, the incorporation of smaller particles also improved the shrinkage-strain as well as the wear performance [6]. Although the use of hybrid fillers has been reported, the choice of the multimodal filler formulations is often based on empirical estimates. A more rational formulation with theoretical guidance is needed to minimize the amount of work needed and also to improve the performance of the final composites. For practical reasons, spherical particles are used in this work, as they often showed lower shrinkage-stress and shrinkage-strain, reducing the occurrence of secondary caries in clinical applications [4,5]. Additionally, they are also much easier to model.

We examined the theory of close-packed structures of identical spherical particles, including face centered cubic (FCC) and hexagonal close packed (HCP), in dental composites [7]. The highest packing factor (74.05 vol%) of this theoretical model indicates that identical spheres cannot completely fill the entire space [8,9]; thus for dental composites, the remaining voids can be occupied with the resin matrix and secondary particles. The maximum size of secondary spherical particles which can fit into a tetrahedral void ($d_4 = 0.225\ D$) and an octahedral void ($d_8 = 0.414\ D$) of primary particles is also studied, where D is the diameter of the close-packed primary spheres, and d_4 and d_8 are the diameters of the particles that may fit xactly into the tetrahedral and octahedral voids, respectively. For a representative primary spherical particle (D = 1000 nm), the best packing factor is increased to 81.19 vol% after embedding two secondary particles with the respective sizes of 225 nm (d_4) and 414 nm (d_8) into the tetrahedral voids and octahedral voids of primary particles. This packing factor is higher than the structure embedded by either one of these secondary particles. Such theoretical calculations may not be the exact situation for the dental composites due to the viscosity of the materials upon the addition of monomers, but it would be interesting to test it and use as a guideline in the optimization of the multimodal filler formulations for dental resin composites.

After being loaded with fillers, the viscosity of uncured composite pastes determines the way materials flow and thus their handling properties for dentists. Much effort was made to study the effects of the composition and ratio of resin monomers and the filler composition, including filler loading, morphology, and size distribution [10–13]. However, no previous work has explored the rheological properties of dental composites with spherical particles at the highest loading levels.

The objective of this study is to evaluate the use of all the theoretical estimations in the formulation of dental composites of two different compositions of dental monomers (7B3T and 5B5T) designed to affect the viscosity of the pastes. The effects of the secondary particle size and the viscosity of two resins on the maximum filler loading, the physical–mechanical properties, and the rheological behavior of dental composites have also studied to point out the accordance and deviation of the theoretical model in the practical formulation of dental composites.

2. Materials and methods

2.1. Materials

Tetraethoxysilane (TEOS) was purchased from Alfa Aesar (Haverhill, MA, USA). Ammonium hydroxide (35 wt%) and anhydrous ethanol were purchased from Fisher Scientific (Waltham, MA, USA). 3-methacryloyltrimethoxypropylsilane (γ-MPS), bisphenol A glycerolate dimethacrylate (Bis-GMA), and triethylene glycol dimethacrylate (TEGDMA) were purchased from VWR (Radnor, PA, USA). Camphorquinone (CQ) and ethyl 4-dimethylamino benzoate (4-EDMAB) were purchased from Sigma-Aldrich (Oakville, ON, Canada). All chemicals were used without further purification.

2.2. Methods

2.2.1. Synthesis of monodisperse silica particles and characterization

Monodisperse silica particles (S-920, S-360, and S-195) with the respective average diameters of 920, 360, and 195 nm were synthesized using the Stöber method [14], as described in our previous work [3,15]. All these particles obtained were silanized with γ-MPS following a previously used method before mixing with the resin matrix [3]. Here, S-920 is used as primary particles while S-360 and S-195 serve as secondary particles, which will theoretically fit into the voids of FCC and HCP structures of the close-packed S-920.

The size of silica particles was determined with laser diffraction (Horiba Laser Particle Sizer LA-950, Japan) in water. Field-emission scanning electron microscopy (JEOL JSM-7400F FE-SEM, Japan) was further used to confirm their size, dispersity, and morphology with an accelerating voltage of 1.5 kV.

2.2.2. Preparation of dental composites

The resin matrix was first prepared by dissolving CQ and 4-EDMAB (0.5/0.5, wt/wt; total concentration: 1 wt% of the final resin) into the resin monomers (Bis-GMA/TEGDMA) under magnetic stirring at room temperature (RT, 23 °C) for 6 h. In consideration of the common compositions of resin monomers reported previously [16–18] and to vary the viscosity of the resins, the weight ratios of Bis-GMA/TEGDMA were fixed at 50:50 and 70:30 in this study, respectively, abbreviated as 5B5T and 7B3T, with the respective viscosities of 0.201 and 2.29 Pa s reported in the literature [13].

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