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Investigation on the physical–mechanical properties of dental resin composites reinforced with novel bimodal silica nanostructures

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ABSTRACT

The aim of this study was to investigate the influence of bimodal silica nanostructures comprising of SiO_2 nanoparticles (SiO_2 NPs, ~70 nm) and SiO_2 nanoclusters (SiO_2 NCs, 0.07–2.70 μm) on physical–mechanical properties of resin-based composites (RBCs). SiO_2 NPs and SiO_2 NCs were prepared with the Stöber method and the coupling reaction, respectively, then silanized and employed as fillers to construct RBCs using a mixture of bisphenol A glycerolate dimethacrylate (Bis-GMA) and tri(ethylene glycol) dimethacrylate (TEGDMA) as the organic matrix. Results showed that the properties of RBCs were influenced by the filler ratios of bimodal silica nanostructures, and the appropriate amount of SiO_2 NPs could effectively increase the activating light efficiency and filler packing density of RBCs. Among all experimental RBCs, RBC 50–20 (SiO_2 NPs:SiO_2 NCs = 50:20, wt/wt) presented the highest degree of conversion (71.6 ± 1.1%), the lowest polymerization shrinkage (2.6 ± 0.1%), and the enhanced flexural strength (104.8 ± 4.4 MPa), flexural modulus (6.2 ± 0.3 GPa), and compressive strength (205.8 ± 14.3 MPa), which were improved by 44%, 19%, 28%, 48%, and 42% in comparison with those of RBC 0–60 (SiO_2 NPs:SiO_2 NCs = 0:60, wt/wt), respectively. Besides, in vitro cytotoxicity evaluation of RBC 50–20 indicated its acceptable cytotoxicity. Although the best performance was achieved by commercial Z350 XT, the introduction of bimodal silica nanostructures might provide the enhanced physical–mechanical properties of RBCs, compared with those of RBC 0–60 reinforced with unimodal SiO_2 NCs.

1. Introduction

Clinical use of light-cured dental restorative composites has increased rapidly due to their distinguished esthetics and biocompatibility, compared with metallic dental amalgams [1]. However, the main reason for failure is still secondary caries followed by fracture of restoration [2,3].

Resin-based composites (RBCs) generally consisted of a polymeric matrix admixed with silanized inorganic fillers and photo-initiators, and could be cured to form the polymer network structure under the light irradiation. The development of RBCs has resulted in the optimization of filler types, compositions and loading, leading to an enhancement in their physical–mechanical properties [4–7]. Satterthwaitea et al. [6,7] found out that shrinkage values were lower for RBCs containing different sizes of spherical fillers with appropriate weight ratios compared to those with irregular fillers. Wang et al. [8] introduced the novel porous diatomite and nano-sized silica particles as co-fillers to increase the mechanical performance of RBCs by regulating their filler compositions. These works are related to the development of hybrid RBCs, which have been launched into the dental market and widely used in clinical application, owing to their intermediate esthetics and excellent mechanical performance compared with macro-filler and micro-filler based composites [9].

A recent response to the challenge of combining excellent esthetics and mechanical performance is the application of nanotechnology, and thus "nanoclusters (NCs)" described as a combination of individually dispersed nano-sized particles and their agglomerations have been introduced as inorganic fillers to meet all requirements of both posterior and anterior restorations to the most degree [10]. The latest commercial product is Z350 XT (3M ESPE, St. Paul, MN, USA) containing silica and zirconia nanoparticles (NPs), which are partially calcined to prepare micron-sized cluster fillers using the "bottom to top" method and then silanized prior to mixing with polymer matrix. These NCs provide a distinct reinforcing mechanism and the improved resistance to crack propagation and water corrosion, compared with micro-filler or hybrid based composites, resulting in the significant improvement in the

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Table 1
Compositions of the commercial resin composites (RBCs).

Resin composite	Matrix type	Particle type	Manufacturer
Esthet-X (Shade A3)	• Bis-GMA • Bis-EMA • TEGDMA	• Silicate glass particles (<1 μm) • Nanosilica (0.04 μm) • Filler loading: 77 wt.%	Dentsply, York, PA, USA
Z350 XT (Shade A3)	• Bis-GMA • UDMA • TEGDMA • Bis-EMA (6) • PEGDMA	• Non-agglomerated/non-aggregated silica filler (20 nm) • Non-agglomerated/non-aggregated zirconia filler (4–11 nm) • Aggregated zirconia/silica cluster filler (0.6–10 μm) • Filler loading: 78.5 wt.%	3M ESPE, St. Paul, MN, USA

Bis-GMA is bisphenol A glycerolate dimethacrylate.
Bis-EMA is ethoxylated bisphenol A glycol dimethacrylate.
TEGDMA is tri(ethylene glycol) dimethacrylate.
UDMA is urethane dimethacrylate.
Bis-EMA (6) is hexaethoxylated bisphenol A glycol dimethacrylate.
PEGDMA is polyethylene glycol dimethacrylate.

strength and the longevity of the restoration [11,12]. However, the new preparative ways of cluster fillers suitable for resin restorative applications and the relevant reinforcing mechanism still need to be explored clearly.

In our previous work, RBCs with bimodal silica nanostructures including SiO_2 NPs and SiO_2 NCs as fillers at the optimum weight ratio have been developed and confirmed to possess excellent wear resistance, due to the reduced interparticle spacing and the increased filler packing, leading to the lower wear volume and the smoother worn surface with respect to that of the microhybrid Esthet-X (Dentsply, York, PA, USA), which was also comparable with that of Z350 XT [13]. Therefore, as a continuation of this work, the relevant physical–mechanical properties will be further estimated so as to investigate the effect of the bimodal silica nanostructures on degree of conversion, polymerization shrinkage, mechanical performance, as well as the cytotoxicity of RBCs, compared with those of Esthet-X and Z350 XT.

2. Materials and methods

2.1. Materials

Anhydrous ethanol, tetraethoxysilane (TEOS), ammonia solution (25–28 wt.%), cyclohexane, n-propylamine, and 3-methacryloxypropyl trimethoxysilane (γ-MPS) were received from Sinopharm Chemical Reagent Co., Ltd (SCRC, Shanghai, China). 3-Aminopropyl triethoxysilane (APTES), 3-glycidoxypropyl trimethoxysilane (GPS), bisphenol A glycerolate dimethacrylate (Bis-GMA), tri(ethylene glycol) dimethacrylate (TEGDMA), camphorquinone (CQ) and ethyl 4-dimethylamino benzoate (4-EDMAB) were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, USA). Human dental pulp cells (HDPCs) were obtained from Shanghai Ninth People's Hospital Affiliated Shanghai Jiaotong University School of Medicine (Shanghai, China). Dulbecco's modified eagle's medium (DMEM; Gibco, Grand Island, NY, USA), fetal bovine serum (FBS; Hyclone, Logan, UT, USA), penicillin and streptomycin (Shanghai Sanda Jinyi Tech Info Co., Ltd., Shanghai, China), 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT; Sigma-Aldrich, Milwaukee, USA), dimethyl sulfoxide and glutaraldehyde (Simopharm Chemical Reagent Co., Shanghai, China) were acquired and used as received. Furthermore, commercial microhybrid Esthet-X (Dentsply, York, PA, USA) and nanocomposite Z350 XT (3M ESPE, St. Paul, MN, USA) were introduced as controls in this work, which were specified in Table 1, based on their technical profile.

2.2. Methods

2.2.1. Silanization of inorganic fillers

Inorganic fillers consisted of SiO_2 NPs (~70 nm) and SiO_2 NCs (0.07–2.70 μm), which were prepared using the Stöber method and the coupling reaction between epoxy and amino functionalized SiO_2 NPs, respectively, according to our previous work [13]. Subsequently, these

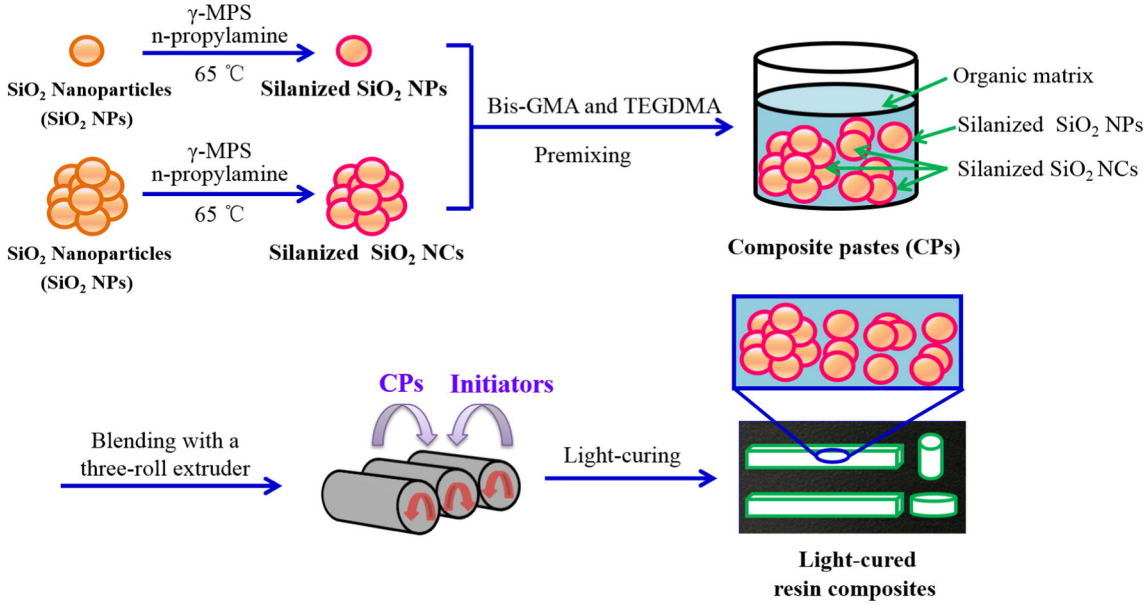

Fig. 1. Representative scheme of the fabrication of light-cured resin composites with silanized SiO_2 NPs and SiO_2 NCs.