



Improved performance of Bis-GMA/TEGDMA dental composites by net-like structures formed from SiO₂ nanofiber fillers



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ABSTRACT

The major objective of this study was to explore the effects of silicon dioxide (SiO₂) nanofibers on the performance of 2, 2-bis-[4-(methacryloxypropoxy)-phenyl]-propane (Bis-GMA)/tri-(ethyleneglycol) dimethacrylate (TEGDMA) dental composites. At first, the mechanical properties of Bis-GMA/TEGDMA (50/50, w/w) resins containing different contents of SiO₂ nanofibers were evaluated to identify the appropriate composition to achieve the significant reinforcing effect. Secondly, optimized contents (5 or 10 wt.%) of SiO₂ nanofibers were mixed into resins together with SiO₂ microparticles, which was 60 wt.% of the resin. Controls for comparison were Bis-GMA/TEGDMA resins containing only SiO₂ microparticles (60 wt.%) or with additional SiO₂ nanoparticles (5 or 10 wt.%). Properties including abrasion, polymerization shrinkage and mechanical properties were evaluated to determine the contribution of SiO₂ nanofibers. In comparison with SiO₂ nanoparticles, SiO₂ nanofibers improved the overall performance of Bis-GMA/TEGDMA composite resins, especially in improving abrasion resistance and decreasing polymerization shrinkage. The explanations were that one-dimensional SiO₂ nanofibers were able to shield particular fillers from being abraded off, and able to form a kind of overlapped fibrous network to resist polymerization shrinkage. With these approaches, SiO₂ nanofiber-containing Bis-GMA composite resins were envisioned a promising choice to achieve long-term durable restorations in clinical therapies.

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1. Introduction

Composite resins have been used in dental treatment since they were first reported 50 years ago [1,2]. However, some problems still remain, affecting the long-term performance of composite resins in clinical dentistry [3]. The wear resistance of current composite resins is not sufficient to prevent significant mass loss during use, especially for large, stress-bearing restorations [4]. Microleakages are often observed in clinical therapies due to the polymerization shrinkage of composite resins, which is responsible for secondary caries [5]. In certain situations, composite resins with inadequate mechanical properties may lead to restoration failure due to cracking under sufficient external

forces [6]. These issues greatly hinder the longevity of dental composite restorations.

Over the past decade, filler modifications such as the optimization of filler content [7] and packing [8] along with the development of hybrid fillers [9] have been identified as effective approaches to improve the performance of dental composite resins. With the development of nanotechnology, a variety of different nanomaterials [10–12] have shown advantages over traditional fillers in reducing the rate of wear, decreasing polymerization shrinkage and improving mechanical properties. Currently, most commercial dental composite resins contain inorganic nanoparticles to achieve enhanced performance. These improvements are suggested to arise from the high specific surface area and rich surface functional groups of the nanoparticles [13]. Although these nanoparticles have substantially improved composite properties including abrasion resistance, polymerization shrinkage and mechanical strength, more progress is still needed to achieve long-term satisfactory restorations for clinical therapy [14,15].

More, fibrous materials [16–18] have generated interest in dental composite resins research recently. Glass fibers or whiskers were demonstrated to have better load transfer ability compared to particular

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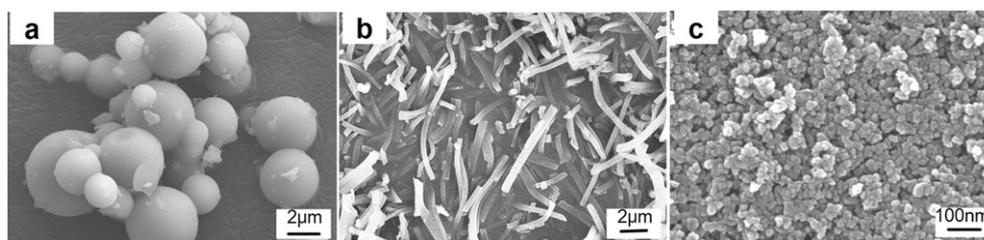


Fig. 1. SEM images of microparticles (a), nanofibers (b) and nanoparticles (c).

fillers due to the effects of fiber bridging and fiber pullout, which provided extra toughening mechanisms [19]. Zhang et al. [20] found that hydroxyapatite (HA) whiskers in composites led to better mechanical properties than HA particle aggregates due to crack deflection, crack bridging, pinning and whisker pullout. Nanofibers have gained popularity as fillers for composite resins because they possess both high surface area and high aspect ratio. Guo et al. [21] reported that zirconia–silica (ZS) or zirconia–yttria–silica (ZYS) ceramic nanofibers significantly improved the mechanical properties and fracture toughness of dental composites. Chen et al. [22] demonstrated that the mechanical properties of dental composites could be improved with the incorporation of only a small mass fraction of HA nanofibers. In addition, the presence of nanofillers and the associated overlapping of the fibers were thought able to reduce polymerization shrinkage [23]. In terms of wear resistance, no systematic study on nanofiber fillers has been reported. However, it was proposed that one-dimensional nanofiber fillers might play an important role in reducing mass loss upon abrasion because of their high surface area and high aspect ratio, which made them bind tightly to resin matrixes.

To understand the effects of nanofibers on the overall performance of dental composite resins, in this study, SiO₂ nanofibers were mixed into Bis-GMA/TEGDMA resins in combination with SiO₂ microparticles. In comparison, specimens containing SiO₂ nanoparticles were used as controls. The contribution of SiO₂ nanofibers to the performance of composites was determined by evaluating the abrasion, polymerization shrinkage and mechanical properties. The null hypothesis of the present study is that the incorporation of SiO₂ nanofibers will not cause significant improvements in the performance of Bis-GMA/TEGDMA dental composites.

2. Materials and methods

2.1. Materials

Bis-GMA and TEGDMA resins, camphorquinone (CQ), 2-(dimethylamino) ethyl methacrylate (DMAEMA) and SiO₂ nanoparticles (mean diameter: 14 nm) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA). SiO₂ nanofibers (diameter: 300–500 nm, length: 5–10 μm) were provided by Beijing University of Chemical Technology

(Beijing, China). SiO₂ microparticles (diameter: 1–8 μm) were supplied by Xi'an Jiaotong University (Xi'an, China). Silane coupling agent, γ-methacryloxypropyltrimethoxysilane (γ-MPS), anhydrous ethanol and acetic acid were purchased from Beijing Chemical Works (Beijing, China).

Fillers including SiO₂ nanofibers, nanoparticles and microparticles were silanized by immersion in a solution containing γ-MPS (12.1 vol.%), acetic acid (12.1 vol.%) and anhydrous ethanol (75.8 vol.%) with magnetic stirring for 24 h at 50 °C. The fillers were filtered and washed with ethanol, followed by drying at 60 °C in air for 12 h. Scanning electron microscopy (SEM) images of different fillers are shown in Fig. 1.

2.2. Preparation of Bis-GMA/TEGDMA composites

Different mass fractions (2, 5, 8, 10 or 15 wt.%) of SiO₂ nanofibers were added into Bis-GMA/TEGDMA (50/50, w/w) resins with photo initiator CQ (0.5 wt.%) and co-initiator DMAEMA (0.5 wt.%). The mixtures were homogenized by ultrasonic dispersion in dark for 30 min. Subsequently, the viscous solutions were transferred into silicone rubber molds, vacuum-degassed under yellow light (to avoid premature curing), photo-cured for 1 min per side under a Coltolux LED (300 mW/cm², Coltene/Whaledent Inc., Cuyahoga Falls, OH, USA) and stored at 37 °C in water for 48 h.

To prepare the composites containing both SiO₂ microparticles and nanofillers, SiO₂ nanofibers or nanoparticles were first ultrasonically dispersed in TEGDMA. Bis-GMA, CQ, DMAEMA and SiO₂ microparticles were then successively mixed in. Referring to previous reports [22,26], the amount of SiO₂ microparticles was set at 60 wt.% in this study. Mixtures were kneaded at room temperature until homogeneous dough was obtained. The dough was fitted into molds and photo-cured as aforementioned.

2.3. Characterizations

2.3.1. Flexural properties

The flexural strength (*F_s*) and flexural modulus (*E_y*) of different Bis-GMA/TEGDMA composites were measured by three-point bending tests on an Instron 1121 universal test machine (Instron, High Wycombe,

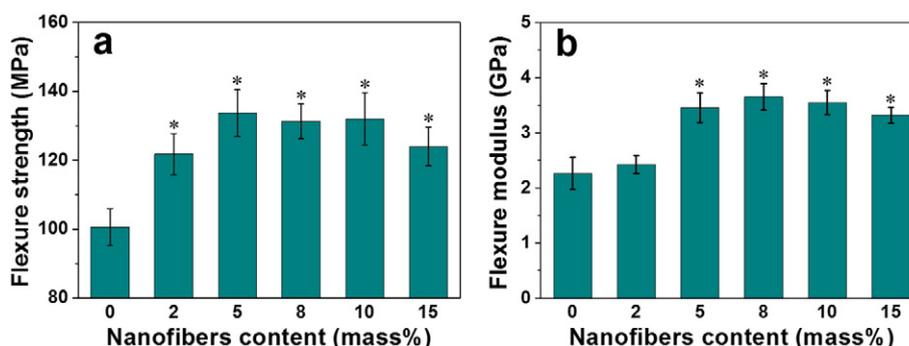


Fig. 2. The mechanical properties of unreinforced and SiO₂ nanofiber-reinforced Bis-GMA/TEGDMA composites: flexure strength (a) and flexure modulus (b).

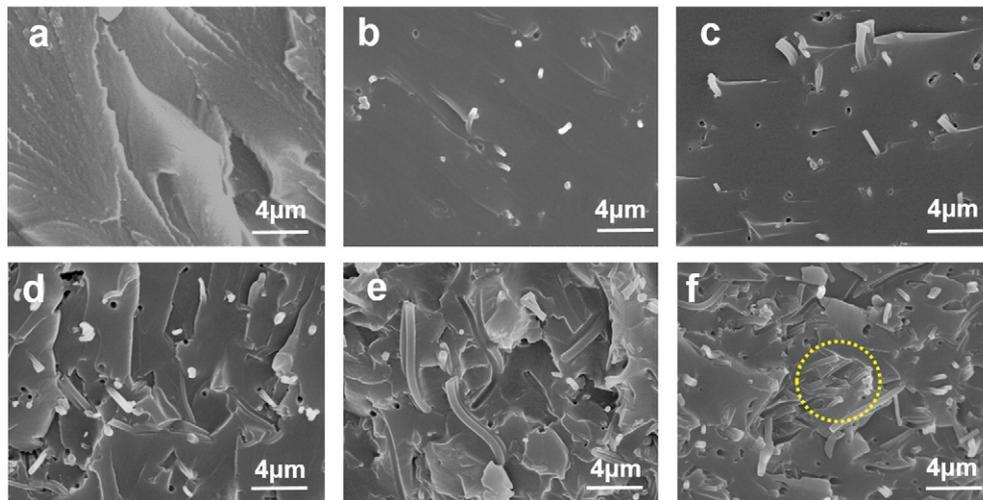


Fig. 3. SEM images of fracture surfaces of the Bis-GMA/TEGDMA resin reinforced with various contents of SiO₂ nanofibers: (a) 0 wt.%, (b) 2 wt.%, (c) 5 wt.%, (d) 8 wt.%, (e) 10 wt.%, and (f) 15 wt.%. The yellow dashed circles denote the nanofiber bundles.

UK) according to the ISO10477:92 standard. Beam-shaped specimens, 25 × 2 × 2 mm (l × w × h) were retrieved from the molds and carefully polished with 2400 grit silicon carbide paper before the test. The span used was 20 mm and crosshead speed 1.0 mm/min. Load-deflection curves were recorded (Composite Material V6.2). F_s and E_y were calculated from the following formulae:

$$F_s = 3Fl/2bh^2, \quad (1)$$

$$E_y = l^3 F_1/4fbh^3, \quad (2)$$

where F is the applied load (N) at the highest point of the load-deflection curve, l is the span length (20 mm), b is the width of the test specimen, and h is its thickness, F_1 is the load (N) at a convenient point in the straight line portion of the trace, f is the deflection (mm) of the test specimen at load F_1 . Each test used eight replicates.

2.3.2. Polymerization shrinkage

Approximately 10 μL of the resin was shaped into a semi-spherical container (diameter: 5 mm) and placed on the pedestal of an AcuVol (Bisco, Inc., Schaumburg, IL, USA). The specimen was allowed to rest for 3 min before being light cured (Coltolux LED, 300 mW/cm², 40 s). The lamp was positioned 2 mm above the top of the specimen. The volume change was measured using single-view volumetric reconstruction modes at the 2 min after curing. Six specimens were tested for each group.

2.3.3. Wear resistance

The wear resistance of composites containing different fillers was evaluated using a CW3-1 wear machine (Peking University, Beijing, China). The operational details have been described by Thomas et al. [24]. Briefly, a rubber plate was used as the antagonist, and a slurry of fluorite mixed with distilled water served as the abrasive. The rotational speed of the antagonist wheel was 130 rpm, and that of the specimen wheel was 60 rpm in the opposite direction. Cylindrical specimens with 10-mm diameters and 6-mm heights were required, and at least three specimens of each type were tested. After 1000 wear cycles, the volume and height losses were calculated according to the method reported by Han et al. [25].

2.3.4. Morphological observation

The fracture and abraded surfaces of the tested specimens were examined by SEM (S-4800, Hitachi, Tokyo, Japan) at an accelerating voltage of 15 kV. Before observation, specimens were sputter-coated (E1010, Hitachi, Tokyo, Japan) with a thin layer of gold under metallization conditions of 20 mA and 10⁻⁴ Pa to improve electrical conduction.

2.4. Statistical analysis

All data are expressed as mean ± standard deviation (SD). Statistical analysis was performed using ANOVA followed by Bonferroni comparison, and significance levels were considered as $p \leq 0.05$.

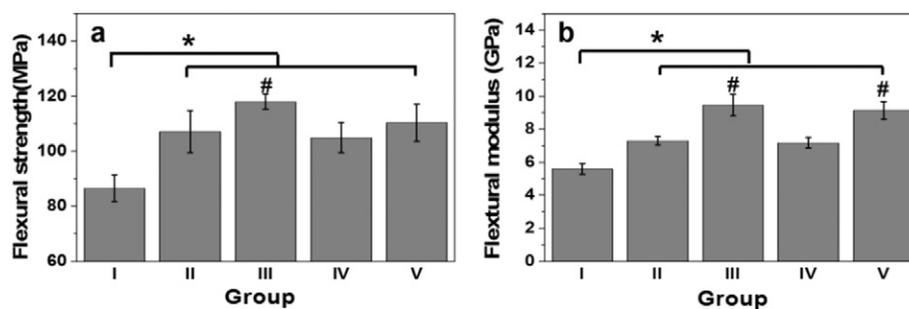


Fig. 4. Flexural properties of different SiO₂ filler-reinforced Bis-GMA/TEGDMA composites: flexural strength (a) and flexural modulus (b). (I. 60 wt.% SiO₂ microparticles; II. 5 wt.% SiO₂ nanoparticles and 60 wt.% microparticles; III. 5 wt.% SiO₂ nanofibers and 60 wt.% microparticles; IV. 10 wt.% SiO₂ nanoparticles and 60 wt.% microparticles; V. 10 wt.% SiO₂ nanofibers and 60 wt.% microparticles.)

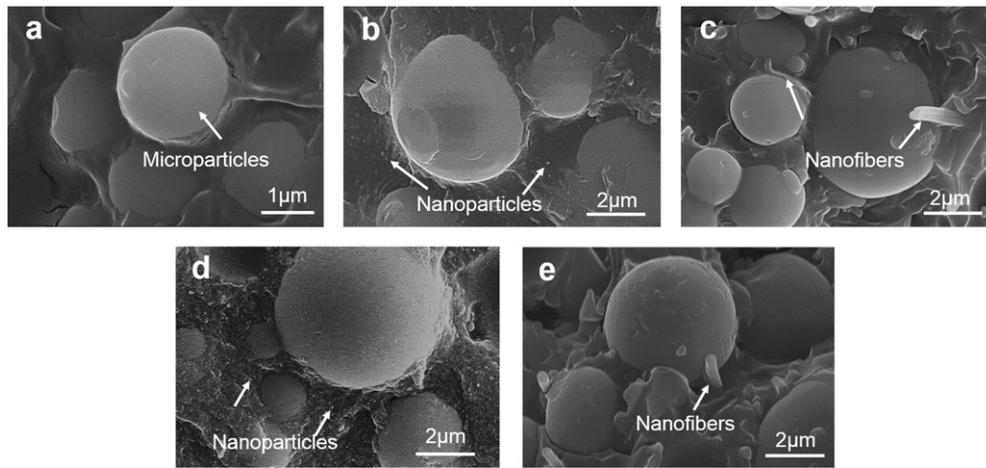


Fig. 5. SEM images of fracture surfaces of the Bis-GMA/TEGDMA composite reinforced with 60 wt.% SiO₂ microparticles (a), 5 wt.% SiO₂ nanoparticles and 60 wt.% microparticles (b), 5 wt.% SiO₂ nanofibers and 60 wt.% microparticles (c), 10 wt.% SiO₂ nanoparticles and 60 wt.% microparticles (d), and 10 wt.% SiO₂ nanofibers and 60 wt.% microparticles (e).

3. Results

3.1. SiO₂ nanofiber-reinforced Bis-GMA/TEGDMA resin

3.1.1. Mechanical properties

With the addition of SiO₂ nanofibers, all the composites demonstrated better flexural properties than the neat resin (Fig. 2). When the content of SiO₂ nanofibers was in the range of 5–10 wt.%, the flexural property of the composites was better than the others. Compared to the neat resin, the average *F_s* and *E_y* increased over 30.0% and 50.0%, respectively. When the content of SiO₂ nanofibers was further increased to 15 wt.%, the *F_s* and *E_y* values of the corresponding composites decreased slightly.

3.1.2. Morphological observation

The fracture surfaces were examined by SEM (Fig. 3). When SiO₂ contents were below 10 wt.%, the nanofibers were observed to be well-dispersed within the resin matrix and to have good interfacial adhesion to the matrix. As shown in Fig. 3f, nanofiber bundles were clearly observed when the SiO₂ nanofiber content was 15 wt.%.

3.2. Nano/micro-scaled filler co-reinforced Bis-GMA/TEGDMA resins

Bis-GMA/TEGDMA resins filled with 60 wt.% of SiO₂ microparticles served as the control in the study of the effect of nanosized fillers. As mentioned in Section 3.1.1, the optimized SiO₂ nanofiber content was in the range of 5–10 wt.%. Accordingly, Bis-GMA/TEGDMA composites containing 5 or 10 wt.% of SiO₂ nanofibers or SiO₂ nanoparticles plus 60 wt.% of SiO₂ microparticles were produced and evaluated.

3.2.1. Mechanical properties

The composite reinforced with only SiO₂ microparticles exhibited the lowest *F_s* (86.52 ± 4.88 MPa) and *E_y* (3.6 ± 0.32 GPa) values (Fig. 4). Incorporation of 5 wt.% SiO₂ nanoparticles increased the values of *F_s* and *E_y* to 107.1 ± 7.7 MPa and 7.3 ± 0.3 GPa, respectively, while the incorporation of 5 wt.% SiO₂ nanofibers increased the values to 118.0 ± 2.8 MPa and 9.5 ± 0.7 GPa, respectively. Compared to these 5 wt.% SiO₂ nanofiller composites, however, no significant improvement in mechanical properties was detected when the content of SiO₂ nanofibers or nanoparticles was increased to 10 wt.%.

3.2.2. Morphological observation

The fracture surfaces of the five co-reinforced specimens were observed by SEM (Fig. 5). SiO₂ microparticles demonstrated good dispersion and adhered well to the surrounding resin matrix without

visible gaps. Both nanoparticles and nanofibers were well-dispersed in the spaces among microparticles. Due to their one-dimensionality, SiO₂ nanofibers adjacent to microparticles formed a kind of shielding structure over the microparticles.

3.2.3. Polymerization shrinkage

The polymerization shrinkages of the Bis-GMA/TEGDMA composites containing different fillers are shown in Fig. 6. The composite filled with only SiO₂ microparticles displayed a shrinkage volume as high as 3.9 ± 0.1%. With the incorporation of SiO₂ nanoparticles or nanofibers, the volume shrinkage decreased dramatically, showing a clear decreasing trend with the increasing nanoscale filler content. In cases containing the same filler contents, the nanofibrous fillers were clearly more effective in reducing polymerization shrinkage than the nanoparticulate fillers.

3.2.4. Wear resistance characterization

Wear resistances of different designed composites were evaluated with a rubber plate as the antagonist for 1000 wear cycles. The composites filled with only SiO₂ microparticles showed the poorest wear resistance with the highest height and volume losses among all specimens (Fig. 7). The incorporation of SiO₂ nanoparticles increased the wear resistance, and the addition of SiO₂ nanofibers further improved the anti-wear capacity. Among all specimens, the composites containing

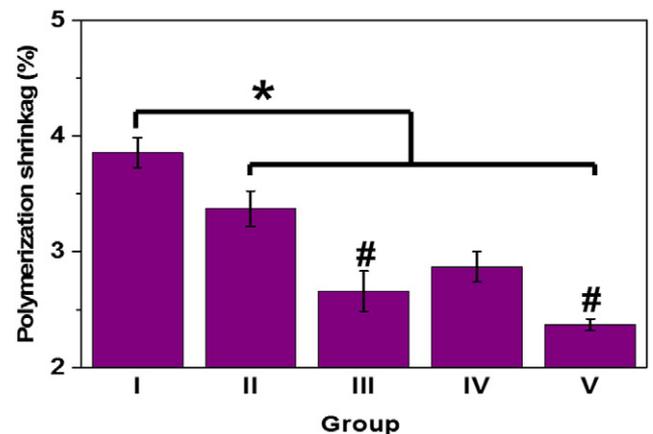


Fig. 6. The polymerization shrinkage of composites containing different fillers. (I. 60 wt.% SiO₂ microparticles; II. 5 wt.% SiO₂ nanoparticles and 60 wt.% microparticles; III. 5 wt.% SiO₂ nanofibers and 60 wt.% microparticles; IV. 10 wt.% SiO₂ nanoparticles and 60 wt.% microparticles; V. 10 wt.% SiO₂ nanofibers and 60 wt.% microparticles.)

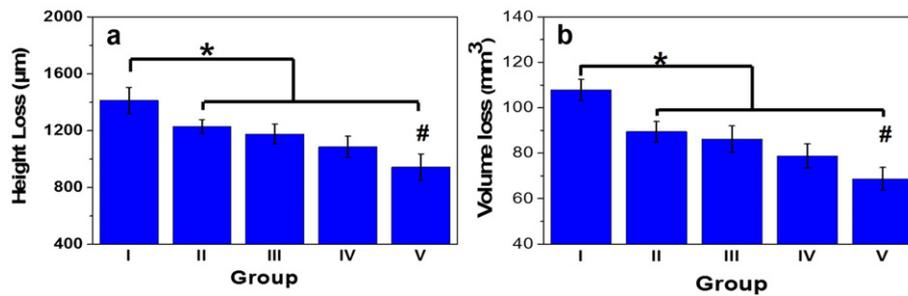


Fig. 7. The abrasive losses of composites containing different fillers: height loss (a) and volume loss (b). (I. 60 wt.% SiO₂ microparticles; II. 5 wt.% SiO₂ nanoparticles and 60 wt.% microparticles; III. 5 wt.% SiO₂ nanofibers and 60 wt.% microparticles; IV. 10 wt.% SiO₂ nanoparticles and 60 wt.% microparticles; V. 10 wt.% SiO₂ nanofibers and 60 wt.% microparticles.)

60 wt.% of SiO₂ microparticles and 10 wt.% of SiO₂ nanofibers showed the best performance, with the lowest height loss (0.94 ± 0.09 mm) and volume loss (68.7 ± 5.1 mm³) upon abrasion.

The abraded surfaces were observed by SEM (Fig. 8). Microsized particles were easily stripped away during abrasion. When the spaces among microparticles were filled with nanosized fillers, the microparticle loss during abrasion was significantly reduced. When one-dimensional nanofibers were employed as co-fillers, the loss of microparticles was mostly prevented, indicating the shielding effect of the fibrous fillers.

4. Discussion

Excellent mechanical characteristics, high wear resistance, and low polymerization shrinkage are important requirements of dental composites for the long-term success of restorations in clinical dentistry. Although Bis-GMA/TEGDMA composite restorations have been substantially improved by formulation changes, abrasion, breakdown and secondary caries are still prevalent failure modes [14,15]. In an attempt to mitigate these issues, SiO₂ nanofiber-containing composites were produced in this study, and their overall performances were greatly improved in comparison to SiO₂ nanoparticle-containing ones. The improvement was suggested mainly from the high surface area and high aspect ratio of one-dimensional nanofibers.

At first, the mechanical properties of Bis-GMA/TEGDMA (50/50, w/w) resins containing different contents of SiO₂ nanofibers were evaluated to identify the appropriate composition to achieve the significant reinforcing effect. The optimal SiO₂ nanofiber content was determined to be 5 or 10 wt.%, in which, the mechanical properties of resulting composites achieved high *F_s* and *E_y* owing to the crack bridging and energy adsorption during fiber pullout (Figs. 2 and 3). Higher content of SiO₂ nanofibers

(e.g. 15 wt.%) was liable to form bundles, which acted as mechanical weak points, to decrease the mechanical properties of composite resins adversely [16,17].

To achieve good performance, especially high wear resistance and low polymerization shrinkage, most commercial dental composite resins contain a high content of inorganic fillers in the range of 60–80 wt.%. Also, this is a normal addition amount of inorganic fillers in publications relating to composite resins for dental restoration [22,26]. In considering the large specific surface area of nano-scaled filler and the processibility of resulting resin mixture, in our present study, 60 wt.% of SiO₂ microparticles were used because of 5–10 wt.% of nanofillers being further introduced into the composite resins. The Bis-GMA/TEGDMA composite filled with only SiO₂ microparticles performed the poorest among all the samples in terms of its mechanical properties, polymerization shrinkage and wear resistance. Its *F_s* and *E_y* values were even lower than those of the neat resin (Fig. 4), and also lower than those of nanofiber reinforced composite (Fig. 2). Similar phenomenon was reported in published data [22,27]. One explanation for this phenomenon was the inevitable defects resulting from high addition of inorganic SiO₂ microparticles, which led difficulty in filler dispersion and wettability. The other reason could be the extension of cracks, which were initiated by points of concentrated stress at the sites around rigid SiO₂ microparticles [28]. Thus, it inspired us that the combination of nanofillers and microfillers might be an efficient way to ameliorate this shortcoming, because the presence of nanofillers might be able to cover those defects between microfillers.

When SiO₂ nanoparticles were added, the nanoparticles were able to enter into the spaces among microparticles (Fig. 5), providing extra reinforcement and resistance to polymerization shrinkage and abrasion. When SiO₂ nanofibers were added instead of SiO₂ nanoparticles, similar

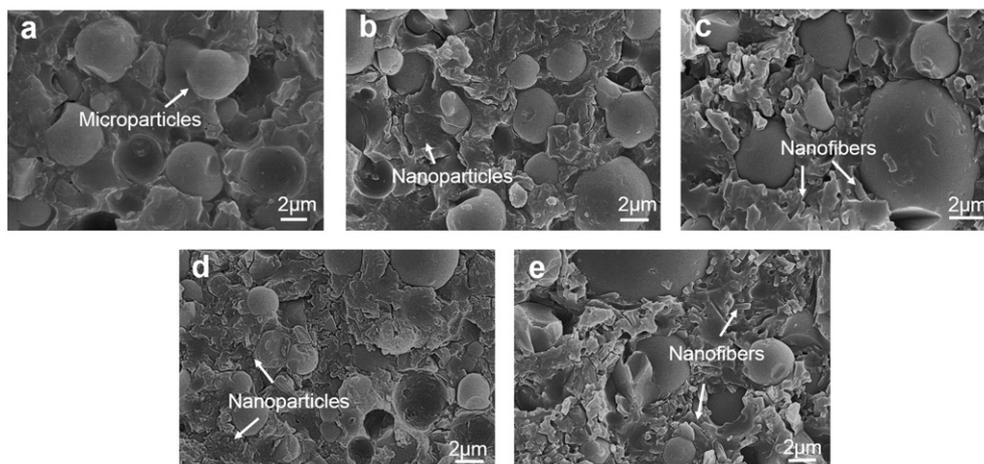


Fig. 8. SEM images of composites containing different fillers after wear tests: 60 wt.% SiO₂ microparticles (a), 5 wt.% SiO₂ nanoparticles and 60 wt.% microparticles (b), 5 wt.% SiO₂ nanofibers and 60 wt.% microparticles (c), 10 wt.% SiO₂ nanoparticles and 60 wt.% microparticles (d), and 10 wt.% SiO₂ nanofibers and 60 wt.% microparticles (e).

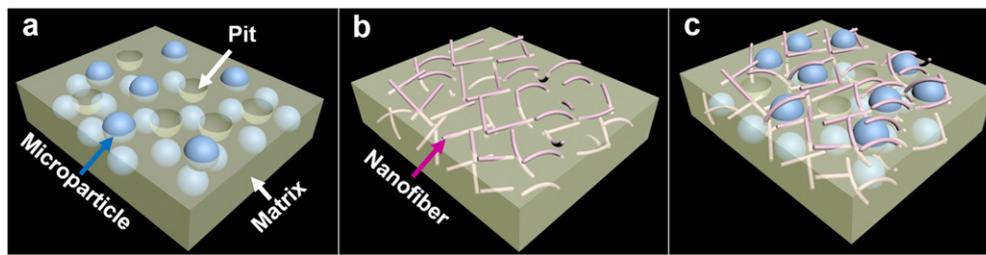


Fig. 9. Schematic representation of composites containing microparticles (a), SiO₂ nanofibers (b), and SiO₂ nanofibers and microparticles (c).

trends of reduced polymerization shrinkage, improved mechanical properties and wear resistance were observed (Fig. 6). It was obvious that the total content of inorganic fillers in the composite resins contributed to these improvements. Noticeably, however, the nanofiber fillers were more effectively improving these composite characteristics because their one-dimensional structure facilitated the formation of network structures by overlapping nanofibers.

As shown in Fig. 5, the SiO₂ nanofibers dispersed well among microparticles and were very close to the microparticles. Their high aspect ratios created overlaps in the nanofibers, allowing them to form a network around the microparticles. This kind of network structure was envisioned to provide higher load transfer ability along with resistance to shrinkage and abrasion compared with particular fillers. The network might act as the “skeleton” of the composite, further improving the mechanical properties via fiber bridging and fiber pullout [19]. And the hard ceramic nanofibers could help retain a stable structure when the polymeric resin shrank [23], resulting in lower volumetric shrinkage. Among the benefits to the composites, the increase in wear resistance was thought to be the characteristic contribution of the fibrous network structure.

Leinfelder et al. [29] pointed out that the wear process normally contains two steps: the softer resin matrix is first ground off, exposing the harder fillers, and the fillers are then separated from the resin by external force. Many efforts have been made to improve composite wear resistance by altering the shape, size, and surface features of fillers [30,31]. Silanization of the SiO₂ has been commonly recognized as a good way to improve the fillers/resins interfacial adhesion [32–34]. Strong interactions between fillers and the resin matrix would be very helpful in preventing filler detachment from the resin matrix, and resulting in low material loss [35–37]. Due to their high surface areas and rich surface functional groups, nano-scaled fillers demonstrated stronger adhesion to the resin matrix than traditional micro-scaled fillers. Thus, the shielding and pullout effects of fibrous fillers made them excellent fillers for dental composite resins [38]. As shown in Fig. 8, the SiO₂ microparticles were retained in the resin matrix with the help of SiO₂ nanofibers; this retention was not observed in the other composites.

A schematic diagram is shown in Fig. 9 to clarify the effect of SiO₂ nanofibers on composite wear. The SiO₂ microparticles in the composite were liable to be stripped away with the loss of surface resin layer (Fig. 9a); however, when SiO₂ nanofibers were incorporated, the well-dispersed nanofibers overlapped to form a network structure due to their high aspect ratios. Thus, the microparticles were shielded by the SiO₂ nanofibrous networks, efficiently inhibiting the loss of microparticles during the wear process. The SiO₂ nanoparticles did not function in such a manner. In addition to improving wear resistance, the nanofibrous network structure was thought to have the positive effects of reducing polymerization shrinkage and improving mechanical properties.

5. Conclusions

Due to the difference in sizes, nanoscale fillers were able to fill the spaces among microscale fillers. Thus, they demonstrated synergistic

effects in reducing polymerization shrinkage, improving mechanical properties and increasing wear resistance of dental composite resins. Due to the formation of fibrous network structures, the application of one-dimensional nanofibers with high aspect ratios as fillers could further improve overall composite performance. Resulting from the overlapping of nanofibers, the proposed network structure was envisioned as the “skeleton” of the composite resins. In addition to structurally reinforcing the composite and decreasing polymerization shrinkage, this skeleton efficiently improves wear resistance by shielding the particular fillers from being peeled away upon abrasion. The nanofiber-containing composite resins produced in this study possess great potential for improving the efficiency and durability of dental restorations.

Acknowledgments

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