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LETTER

Bis-GMA/TEGDMA dental composites reinforced with nano-scaled single crystals of fibrillar silicate

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Presently, dental composites have been widely adopted by the profession as the restorative material of choice; as compared to dental amalgams, the composites possess better esthetic property, have less safety concern, and have shown reasonably satisfactory clinic results. Dental composites consist of resin matrices and inorganic fillers. The monomer of 2,2′-*bis*-[4-(methacryloxypropoxy)-phenyl]-propane (*Bis*-GMA) has been used as an important dental base monomer since it was invented in the 1960s [1, 2]; for example, *Bis*-GMA is the base monomer in the Z100$^{\mathrm{TM}}$ Restorative Dental Composite produced by the 3M Corporate. *Bis*-GMA is a very viscous, honey-like liquid. To improve handling qualities, a diluent monomer of *tri*(ethylene glycol) dimethacrylate (TEGDMA) is added to thin the resin. In the *Bis*-GMA/TEGDMA dental resin systems, *Bis*-GMA functions to limit the polymerization-induced volumetric shrinkage and to enhance the resin reactivity, whereas TEGDMA provides for the increased vinyl double bond conversion [3, 4].

Albeit dental resins have been reinforced with inorganic fillers of glass/ceramic powders containing surface-silanized particles, relatively low strength and durability of the composites have limited their uses [5–8]: dental composites have flexural strengths typically ranging from 80 to 120 MPa, which can fulfill the requirement of filling tooth cavities but cannot survive large stress-bearing restorations such as crowns and bridges; furthermore, the strength of dental composites decreases substantially after being used for a period of time. The average service lifetime of dental composites is considerably shorter than that of dental amalgams [9, 10]. Investigations of the failures revealed that, among numerous issues, the inorganic filler was a major contributor [11, 12]. Many inorganic filler particles currently used for dental composites are spherical or irregular in shape. Such filler particles at occlusal surfaces are susceptible to dislodgement from the resin matrix during wear with food boluses. This would cause the reinforcement effect to be lost.

Chopped glass fibers and/or high strength whiskers with diameters of 5–50 μm and aspect ratios larger than 10 have also been investigated to reinforce dental resins [13–16], and the resulting composites showed higher mechanical properties. Several reinforcement mechanisms including "Bridging," "Pull-out," and "Load Transfer" were proposed for understanding the fiber/whisker reinforcement [17, 18]; in particular, "Bridging" is a powerful reinforcement mechanism. If a micro-crack is initiated in a resin matrix under contact wear and/or other stresses, the fillers remain intact across the crack planes supporting the applied load. Crack-opening is resisted by the bridging fillers; thus the resin matrix is reinforced. Requirements for fillers to achieve effective "Bridging" reinforcement include high strength and large aspect ratio values; tooth enamel rods are an example of elongated fillers, and crystalline platelets in dental glass/ceramics are another example [19]. Nonetheless, the dental composites reinforced with fibers/whiskers generally possess mechanical properties that still need further improvements; this is

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primarily due to large size (and the related small surface area) of the filler particles and the resulting weak interfacial bonding with the dental resins.

Unlike micron-scaled fibers/whiskers, fibrillar silicate (FS) is composed of nano-scaled single crystals that are 100–3000-nm length and 10–25-nm diameter; the nano-FS single crystals possess an estimated mechanical strength of ~50 GPa, which is over ten times higher than that of micron-scaled fibers/whiskers [20, 21]. The FS used in this study was attapulgite with chemical formula being $Mg_5[Al]Si_8O_{20}(HO)_2(OH_2)_4 \cdot 4H_2O$. Although the single crystals in FS usually agglomerate into micron-sized particles, the agglomerates/particles can be readily separated into single crystals by simply dispersing the FS in polar solvents such as ethanol followed by vigorous stirring. This is due to the reason that the interaction among the single crystals in FS is much weaker than that among the silicate layers in montmorillonite [20, 21]. It is also noteworthy that the nano-FS single crystals possess abundant surface silanol groups that can react with silane coupling agents such as 3-methacryloxypropyltrimethoxy (MPTMS); therefore, the interfacial bonding between the surface-silanized nano-FS single crystals and the dental resins can be strong.

Our previously reported study revealed that the impregnation of nano-FS single crystals into *Bis*-GMA/TEGDMA dental composites significantly improved the mechanical properties at a low filler level of 7.5 wt% or less [22]; nonetheless, that study was targeted on the application of filling tooth cavities, thus the composites were cured by light. For other dental applications such as making crowns and/or bridges, the composites are usually cured by heat instead of light. It is well known that different curing methods may lead to substantial discrepancies on mechanical properties [23]. The aim of this study was to prepare and evaluate the heat-cured *Bis*-GMA/TEGDMA dental composites containing varied amounts of nano-FS single crystals; some composites also contained conventional dental glass fillers as described below. The mechanical properties including flexural strength, elastic modulus, and work of fracture of the heat-cured composites were measured and compared to those of the photo-cured composites.

During the study, the as-received FS powder was first dispersed into ethanol to make a mixture containing 5 wt% of FS; the mixture was then vigorously stirred for 4 h at 400 rpm using a Heidolph RZR50 Heavy Duty Stirrer. Previous research indicated that this process could effectively separate the FS agglomerates/particles into nano-scaled single crystals [21]. Thereafter, the mixture was transferred into a rotary evaporator together with MPTMS (10 wt% of FS) and *n*-propylamine (5 wt% of FS). After gradual removal of ethanol through evaporation at 80 °C, the surface-silanized nano-FS single crystals were obtained. Subsequently, the surface-silanized nano-FS single crystals (0, 2.5, 5.0, 7.5, and 10 wt%) were uniformly mixed into a dental resin system consisting of 49 wt% *Bis*-GMA, 49 wt% TEGDMA, and 2 wt% BPO; the mixtures were further blended with the same weights of a conventional glass filler (V-117-2707, provided by the Esstech Co., Essington, PA, USA) to prepare the dental pastes. Finally, both the mixtures and the pastes were placed into 2 mm × 2 mm × 25 mm Teflon molds and heat-cured at 140 °C for 30 min to prepare the dental composites without and with the conventional glass filler, respectively. A standard three-point flexural test (ASTM D 793) with a span of 20 mm was used to fracture the specimens under the room temperature of ~25 °C at a crosshead speed of 0.5 mm/min using a QTEST^{TM}/10 universal mechanical testing machine, and the values of flexural strength, elastic modulus, and work-of-fracture (WOF) were recorded. A Hitachi H-7000 FA TEM and a Zeiss Supra 40VP SEM were employed to examine fracture surfaces of the specimens and distributions of nano-FS single crystals in the composites, respectively. Prior to TEM examination, the specimens were microtomed at room temperature using a Reichert-Jung Ultracut Microtome and mounted on 200-mesh copper grids. For SEM examination, the specimens were sputter-coated with gold to avoid charge accumulation.

The TEM images in Fig. 1 indicated that the nano-FS single crystals were uniformly distributed in the composites when the content of FS was low (2.5 wt%), while they tended to re-agglomerate when the content was high (10 wt%). It is noteworthy that the agglomerates with loosely stacked nano-FS single crystals would act as mechanical weak points (structural defects); and the presence of such agglomerates could considerably reduce mechanical properties (especially strength) of the composites. The SEM images in Fig. 2 showed representative fracture surfaces of different three-point flexural specimens. The fracture surface of the neat *Bis*-GMA/TEGDMA resin was smooth with oriented fracture lines that were resulted from the extension of crazings initiated by stress concentration points (Fig. 2a), whereas the fracture surface of the nano-FS-reinforced resin (Fig. 2b) was rough without clearly identifiable fracture lines. These results suggested that the presence of nano-FS single crystals could deflect micro-cracks and effectively increase the resistance to applied force. When the cracks finally broke away from the single crystals, a rough fracture surface was created, suggesting energy consumption during breaking. Compared to the composite filled with conventional glass filler only (Fig. 2c), the composite filled with both glass filler and nano-FS appeared to have some voids/holes (Fig. 2d). These voids/holes were probably formed by the separation/detachment of FS agglomerates. We believed that the distribution of nano-FS single crystals and the mechanical

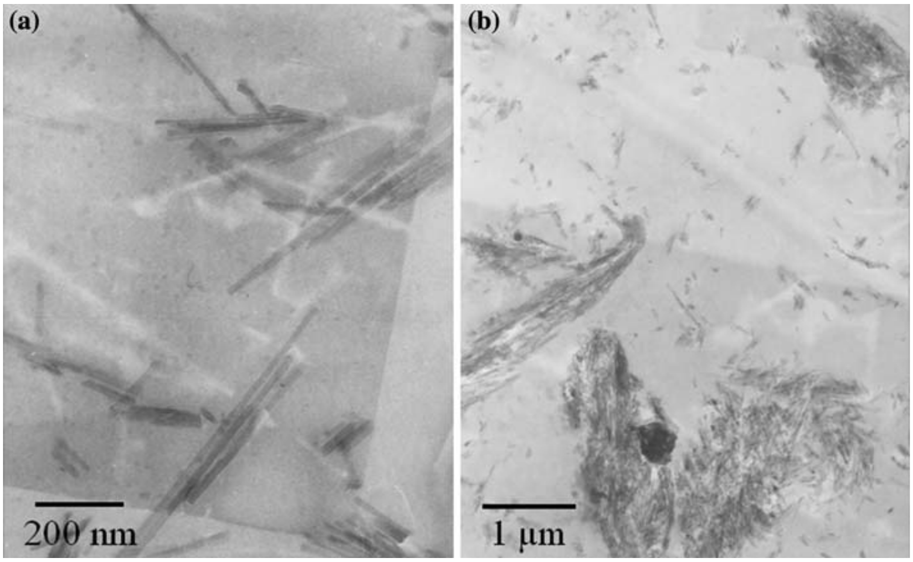

Fig. 1 TEM images showing *Bis*-GMA/TEGDMA dental composites (without glass filler) containing 2.5 wt% (**a**) and 10 wt% (**b**) surface-silanized nano-FS single crystals

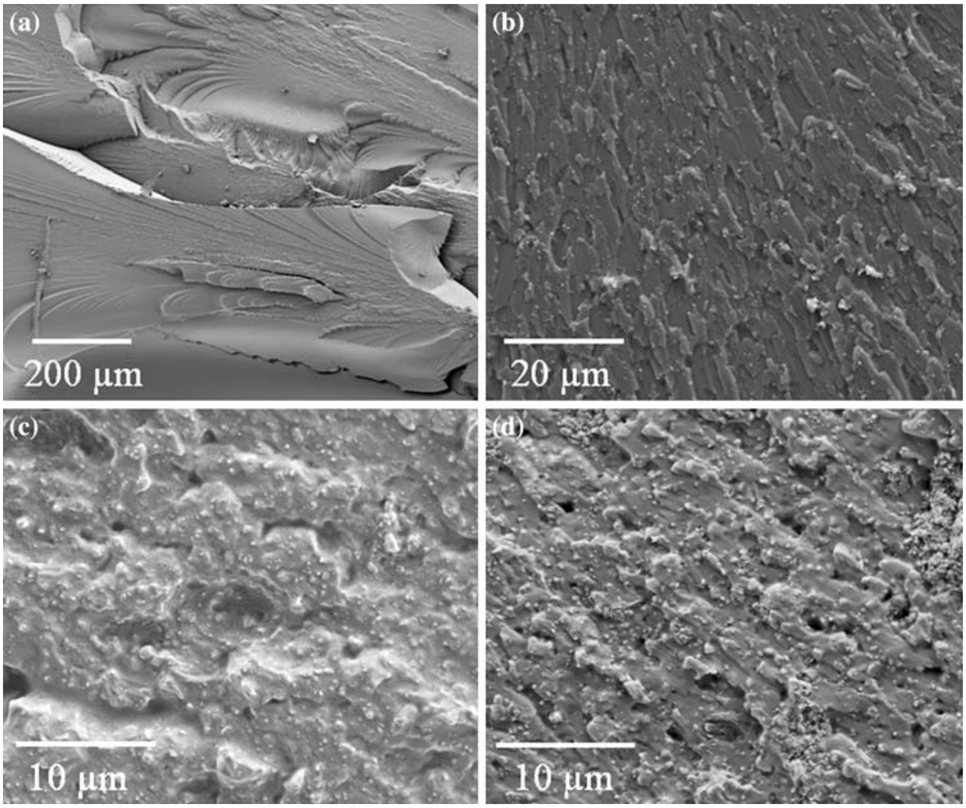

Fig. 2 Representative fracture surfaces of three-point flexural specimens: **a** neat *Bis*-GMA/TEGDMA, **b** *Bis*-GMA/TEGDMA filled with 2.5 wt% nano-FS single crystals, **c** *Bis*-GMA/TEGDMA filled with 50 wt% glass filler, **d** *Bis*-GMA/TEGDMA filled with 2.5 wt% nano-FS single crystals and 50 wt% glass filler

properties (particularly strength) of dental composites could be further improved by optimization of the surface treatment for nano-FS. The combined surface treatment of nano-FS through both plasma nano-coating technology and surface silanization is in progress.

As shown in Fig. 3, the values of WOF, elastic modulus (E_Y), and flexural strength (S_F) were all substantially increased by impregnating small amounts of nano-FS single crystals into the *Bis*-GMA/TEGDMA dental composites. Compared to those of the neat resin without conventional glass filler, the WOF, E_Y, and S_F values of the composites filled with 2.5 wt% nano-FS were improved by 108, 27, and 38%, respectively. Compared to those of the composites with conventional glass filler, the WOF, E_Y, and S_F values of the composites filled with both the glass filler and nano-FS were also distinguishably higher. It is noteworthy that the S_F, E_Y, and WOF were improved simultaneously. Suggested reasons are (1) some nano-FS

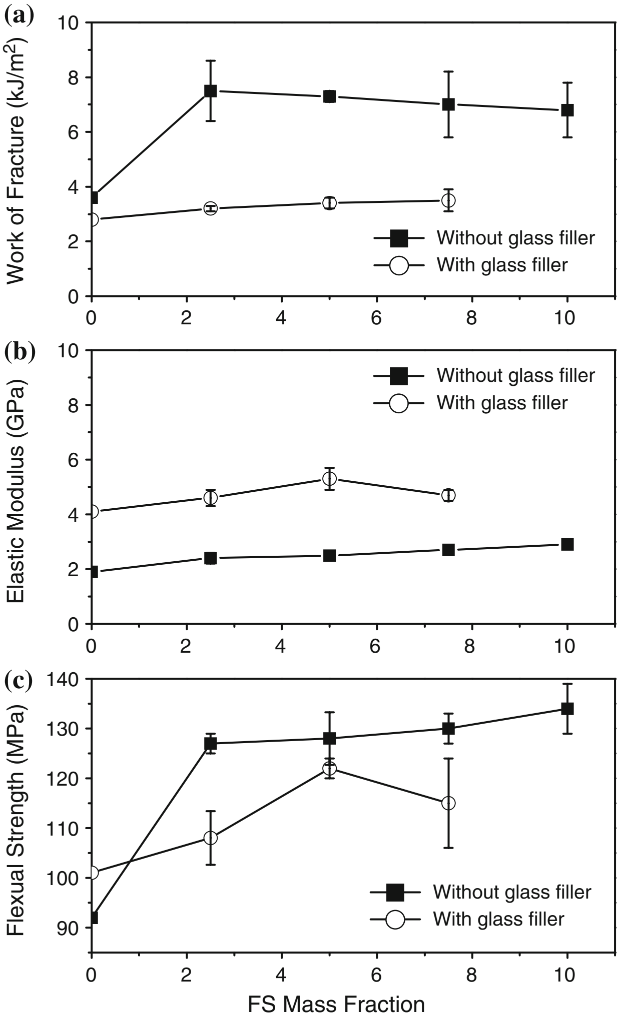

Fig. 3 WOF (**a**), elastic modulus (**b**), and flexural strength (**c**) of *Bis*-GMA/TEGDMA dental composites filled with varied mass fractions of nano-FS single crystals. Each datum is the mean value of six measurements with error bar representing one standard deviation

single crystals, which were strongly bonded to the resin, strengthened the composites, and resulted in the improvement of S_F; (2) the modulus of the nano-FS single crystals was substantially higher than that of the resin, leading to the improved E_Y; and (3) some nano-FS single crystals, which were weakly bonded to the resin, could be detached (pulled out) when the load was applied; this created frictional force that allowed stress to transfer across matrix cracks, resulting in the increase in resistance to fracture (WOF).

In comparison with the photo-cured *Bis*-GMA/TEGDMA dental composites (without the conventional glass filler) containing nano-FS single crystals, the heat-cured composites had similar values of WOF, E_Y, and S_F [22]. With 50 wt% conventional glass filler, the heat-cured composite had slightly lower flexural strength than the photo-cured composite (108 ± 5 vs. 121 ± 6 MPa) at 2.5 wt% nano-FS filler level but slightly higher flexural strength (115 ± 9 vs. 101 ± 6 MPa) and elastic modulus (4.7 ± 0.2 vs. 3.7 ± 0.4 GPa)] at 7.5 wt% nano-FS filler level. These results confirmed that the incorporation of surface-silanized nano-FS single crystals into the *Bis*-GMA/TEGDMA dental composites (either with or without the conventional glass filler) would result in substantial improvement on mechanical properties. Additionally, the values of vinyl double bond conversion and volumetric shrinkage from both photo-cured and heat-cured dental composites were also similar (results not shown). These suggested that the heat-cured *Bis*-GMA/TEGDMA dental composites reinforced with small amounts of nano-FS single crystals could probably fulfill the requirements for the crown/bridge applications.

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