# Electrospun Nano-Scaled Glass Fiber Reinforcement of Bis-GMA/TEGDMA Dental Composites

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**ABSTRACT:** The objective of this study was to investigate the electrospun nano-scaled glass fiber reinforcement of 2,2′-bis[4-(methacryloxypropoxy)-phenyl]-propane/triethylene glycol dimethacrylate (Bis-GMA/TEGDMA) dental composites. The hypothesis was that incorporation of the surface-silanized electrospun nano-scaled glass fibers into Bis-GMA/TEGDMA dental composites would result in substantial improvement on mechanical properties. To test the hypothesis, photo-cured Bis-GMA/TEGDMA dental composites filled with various mass fractions of surface-silanized electrospun nano-scaled glass fibers were systematically fabricated; and their mechanical properties were then evaluated. The results indicated that small mass fraction substitutions (1, 2.5, 5, and 7.5%) of conventional dental filler with the surface-silan- ized electrospun nano-scaled glass fibers, significantly improved the flexural strength, elastic modulus, and work of fracture values of 70% (mass fraction) filled composites, by as much as 44%, 29%, and 66%, respectively. The mechanical properties of the composites could be further improved by optimizing the chemical compositions and the surface treatment methods of the fibers. We envision that the electrospun nano-scaled glass fibers could be utilized to develop the next generation dental composites, which would be particularly useful for large posterior restorations. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2063–2070, 2008

**Key words:** nanocomposites; silicas; fibers; electrospinning; mechanical properties

## INTRODUCTION

Dental composites consisting of resin matrices and inorganic fillers have been available for over four decades. Compared to dental amalgams, the composites possess better esthetic property, have fewer safety concerns, and show reasonably satisfactory clinical results. Consequently, the composites have been widely adopted by the dental profession as the restorative material of choice.

Dental composites are usually cured (hardened) by photo-initiated free radical polymerization (photopolymerization). Camphorquinone (CQ) is a commonly used visible-light initiator, and ethyl-4-($N,N'$-dimethylamino) benzoate (4EDMAB) is a commonly used coinitiator. The monomer 2,2′-bis[4-(methacryloxypropoxy)-phenyl]-propane (Bis-GMA) has been used as an important dental base monomer since it was invented in the early 1960s.[1,2] Bis-GMA is a highly viscous liquid; to improve the handling qualities, a low viscosity diluent monomer, such as triethylene glycol dimethacrylate (TEGDMA), is added to thin the resin. In Bis-GMA/TEGDMA dental resin, Bis-GMA functions to limit the photopolymerization-induced volumetric shrinkage and to enhance resin reactivity, whereas TEGDMA provides for the increased vinyl double bond conversion.[3,4]

Dental composites are typically reinforced with inorganic fillers having a mass fraction of approximately 70%. Although numerous inorganic fillers have been investigated, amorphous $SiO_2$ (glass) is commonly used in the commercially available dental composites. This is because (1) the properties of the glass reinforced composites generally meet the minimum requirements of dental restorations, and (2) the refractive index of glass is similar to that of the dental resins, giving the composites a translucent appearance, which is similar to that of human teeth. Crystalline $SiO_2$ (quartz), on the other hand, is not suitable for making dental composites; one of the reasons is because of the refractive index mismatch. Conventionally, dental composites are reinforced with glass particles ranging in size from tens of nanometers to several microns. However, the strength, toughness, and durability of the glass

particle reinforced composites are inadequate for the expanded uses in large stress-bearing posterior restorations that involve the replacement of cusps. Composites "are not recommended for large posterior restorations."[5] "In situations where occlusal stresses are concentrated, the composites . . . are inappropriate choices."[6] Ironically, the glass particles, which are added to the resins for the purpose of fortifying the materials are actually responsible, at least in part, for their demise.[7,8] During function, the masticatory stress is transmitted through the boluses of foods onto the surfaces of glass particles projecting from the occlusal surface. Because glass particles are considerably harder than resin matrices, in which they are embedded, much of the stress is transmitted through the particles into the resins. Wherever the submerged portions of the particles are angular or irregular in shape, the stress concentration could become excessively high. Such a condition tends to generate small cracks around the particles, thereby weakening the matrices locally. Chopped glass fibers (with diameters of 10–15 microns and aspect ratios larger than 100) have also been studied for the reinforcement of dental resins.[9,10] The resultant composites showed higher mechanical properties, but the improvement was limited probably due to weak interfacial bonding.

The electrospun nano-scaled glass fibers are expected to substantially outperform micron-scaled glass particles/fibers in the reinforcement of dental composites. This is because the nano-scaled glass fibers possess desired morphological and mechanical properties including small fiber diameter (and the concomitant large specific surface area), large aspect ratio, and high strength and modulus. The "Bridging" mechanism[11–13] can be adopted to explain the enhancement of the nano-scaled glass fiber reinforcement. If a micro-crack is initiated in the dental matrix under contact wear and/or other stresses, the nano-scaled glass fibers remain intact across the crack planes, supporting the applied load. Therefore, crack opening is resisted by the fibers, and the matrix is reinforced. Compared to the micron-scaled glass fibers, the electrospun nano-scaled glass fibers are over 10-times thinner (i.e., their specific surface areas are more than 10-times larger), and also possess abundant surface silanol (Si—OH) groups that can readily react with silane coupling agents such as 3-methacryloxypropyltrimethoxy (MPTMS). Therefore, the interfacial bonding between the surface-silanized electrospun nano-scaled glass fiber filler and the dental resin matrix can be extremely strong.

Electrospinning is a technique that utilizes electric force to drive the spinning process and to produce fibers with diameters in the nanometer range ($\sim$ 10–1000 nm). Unlike nanotubes, nanowires, and nano-

rods, most of which are made by bottom-up methods, electrospun nanofibers are made through a top-down nano-manufacturing process. This results in low-cost and continuous nanofibers that are relatively easy to process into applications. In the recent decade, the technique of "electrospinning" and its unique product of "nanofibers" have been actively researched worldwide.[14] Electrospun ceramic nanofibers are made by electrospinning spin-dopes containing precursors of ceramics followed by high temperature pyrolysis.[15,16] Among numerous electrospun ceramic nanofibers, silica ($SiO_2$) nanofibers have been investigated with particular interest because of the well-studied precursors and wide applications.[17,18] In the recent years, a variety of spin dopes have been studied. The spin dopes can be generally classified into two types: (1) aqueous spin dopes made from alkoxide precursors such as tetraethyl orthosilicate (TEOS), and (2) organic spin-dopes containing alkoxide precursors and carrying polymers such as polyvinyl pyrrolidone (PVP). The pH value and concentration of the aqueous type of spin dopes have to be judiciously adjusted to precisely control the gelation/hydrolysis extent of the alkoxide precursors and the related spin-dope viscosity. If the spin-dope viscosity is too low, the resultant as-electrospun nanofibers will contain beads and/or beaded nanofibers.[19] If the spin-dope viscosity is too high, electrospinning will not be stable or even cannot be conducted. On the other hand, viscosity and other properties of the organic type of spin dopes are much more convenient to adjust and control; and the as-electrospun nanofibers made from this type of spin dopes are generally more uniform with fewer beads and/or beaded nanofibers. The organic type of spin dopes is therefore more widely adopted. No matter which type of spin dope is used for electrospinning, the as-electrospun nanofibers have to undergo a high temperature pyrolysis process to burn/remove the organic components for the fabrication of the final $SiO_2$ nanofibers. Our previously reported research systematically studied the preparation and characterization of electrospun $SiO_2$ nanofibers.[20] The results indicated that uniform, bead free, and structurally amorphous $SiO_2$ nanofibers (i.e., nano-scaled glass fibers) with diameters of approximately 500 nm could be prepared by using TEOS as the alkoxide precursor, PVP as the carrying polymer, $N,N$-dimethyl formamide (DMF) and acetic acid (HAc) (DMF/HAc volume ratio of 15/1) as the mixture solvent, and pyrolysis temperature between 600 and 1000°C. Additionally, the electrospun nano-scaled glass fibers could well retain their overall fiber morphology when subjected to vigorous ultrasonic vibration, suggesting that the electrospun nano-scaled glass fibers were not only morphological but also structural in nature.

## MATERIALS AND METHODS

### Materials

TEOS, PVP ($M_w$ = 1,300,000), DMF, HAc (glacial), Bis-GMA, TEGDMA, CQ, 4EDMAB, MPTMS, $n$-propylamine, acetone, cyclohexane, and a glass powder (with particle sizes ranging from tens of nanometers to several microns) were purchased from Aldrich Co. (Milwaukee, WI). The commercial dental glass filler used in this study was the finely milled 7% (mass fraction) silanized barium borosilicate glass powder (V-117-2707) provided by Esstech Co. (Essington, PA).

### Preparation of electrospun nano-scaled glass fibers

The detailed studies were reported in our previous publication.[20] The electrospun nano-scaled glass fibers used in this study were prepared using a spin-dope consisting of 13% (mass fraction) TEOS and 13% PVP in a mixture solvent of DMF/HAc (volume ratio of 15/1), and using a pyrolysis temperature of 800°C.

### Surface silanization

The prepared fibers were first dispersed in cyclohexane with a mass fraction of 5%. The suspension was then subjected to vigorous ultrasonic vibration with a 200 W Digital ultrasonic probe, purchased from Branson Ultrasonics Corp. (Danbury, CT), for three 5-min time periods. The ultrasonic vibration converted the continuous nano-scaled glass fibers into short fibers with an average aspect ratio larger than 100.[20] After ultrasonic vibration, the suspension was transferred into a rotary evaporator with MPTMS (mass fraction of 4% to the fibers) and $n$-propylamine (mass fraction of 2% to the fibers). The system was then heated at 90°C until dry. The Aldrich glass powder was also surface-silanized using the same procedure for comparison as one of the two control samples (the other one was the as-received Esstech glass powder that had already been surface-silanized).

### Preparation of dental composites

Two sets of dental pastes were prepared in this study: (1) The first set was prepared by mixing various mass fractions (0, 1, 2.5, 5, and 7.5%) of the surface-silanized electrospun nano-scaled glass fibers into the dental resin system, which consisted of 49.5% Bis-GMA, 49.5% TEGDMA, 0.2% CQ, and 0.8% 4EDMAB. The pastes made of the surface-silanized Aldrich glass powder and the as-received Esstech glass powder were also prepared for comparison. (2) The mass fraction of filler in the second set of dental pastes was maintained at 70%; the filler was the combination of various mass fractions (0, 1, 2.5, 5, and 7.5%) of the surface-silanized nano-scaled glass fibers and the as-received Esstech glass powder. To prepare the three-point flexural testing specimens, the pastes were photo-cured for 1 min on each side in a laboratory-produced mold using three standard visible light curing units (Maxima 480) purchased from L. D. Caulk Co. (Milford, DE). Because the dimensions of the specimens were 2 mm × 2 mm × 25 mm, the tips of three light curing units were placed in a row for effective photo-curing.

### Mechanical properties

A standard three-point flexural test (ASTM D 793) with a span of 20 mm was used to fracture the specimens at a crosshead speed of 0.5 mm/min using a QTEST[TM]/10 mechanical testing machine. Flexural strength (FS), elastic modulus ($E_Y$), and work of fracture (WOF) were acquired. Analysis of variance (ANOVA), a commercial software (Winks, TexaSoft, Cedar Hill, TX), was used for the statistical analysis of the acquired data. Before mechanical testing, the specimens were stored in a humidifier at 37°C for 24 h. Six specimens were prepared for each measurement, and all four sides of each specimen were carefully hand polished with 2400 and 4000 grit silicon carbide paper and water coolant in a longitudinal direction.

### Morphology

A Zeiss Supra 40VP field-emission scanning electron microscope (SEM) was used to examine morphologies of the electrospun nano-scaled glass fibers, the Aldrich glass powder, the Esstech glass powder, and the representative fracture surfaces of the Bis-GMA/TEGDMA dental composites. Before SEM examination, the specimens were sputter-coated with gold to avoid charge accumulation.

## RESULTS AND DISCUSSION

The SEM images in Figure 1 showed the representative morphologies of the Aldrich glass powder (A), the Esstech glass powder (B), and the electrospun nano-scaled glass fibers after ultrasonic vibration (C). To prepare the SEM specimens, the silanized Aldrich glass powder, the as-received Esstech glass powder, and the silanized nano-scaled glass fibers were first dispersed in acetone with a mass fraction of ~ 1%, and the suspensions were then mechanically stirred for 30 min at 400 rpm using the Heidolph RZR 50 heavy duty stirrer. Subsequently, small pieces of aluminum foil were dipped into the suspensions and quickly removed. After the acetone
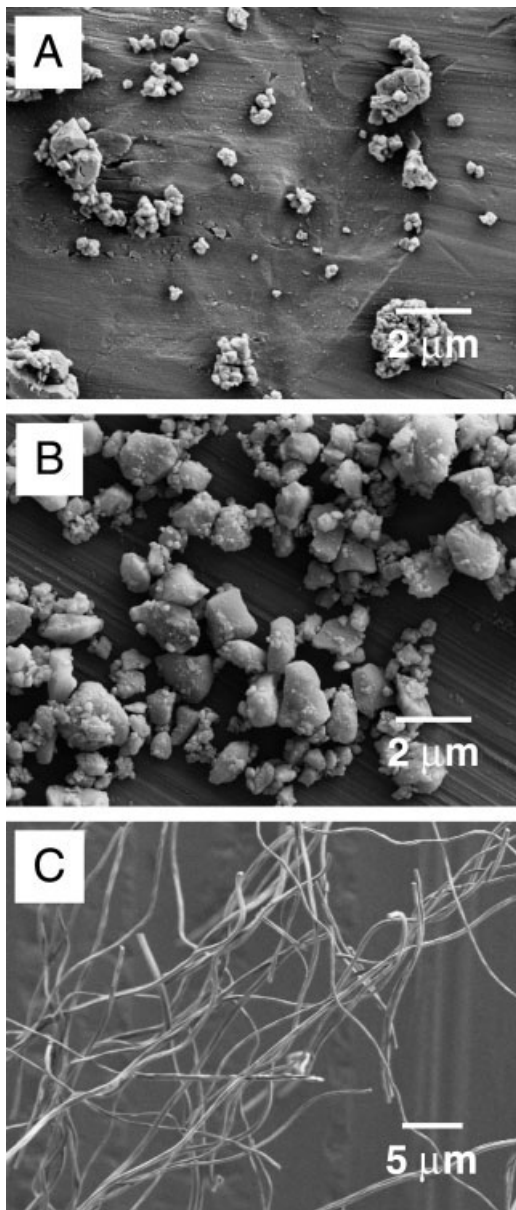
**Figure 1** SEM images showing the representative morphologies of the Aldrich glass powder (A), the Esstech glass powder (B), and the electrospun nano-scaled glass fibers after ultrasonic vibration (C).

in the suspensions left on the aluminum foil pieces evaporated, the specimens were used for SEM examinations. It was evident that both the Aldrich and Esstech glass powders had the particle sizes ranging from tens of nanometers to several microns, though the average particle size of the Esstech glass powder appeared to be smaller than that of the Aldrich glass powder. The electrospun nano-scaled glass fibers, on the other hand, were very uniform with the diameter of $\sim$ 500 nm and the aspect ratios larger than 100.

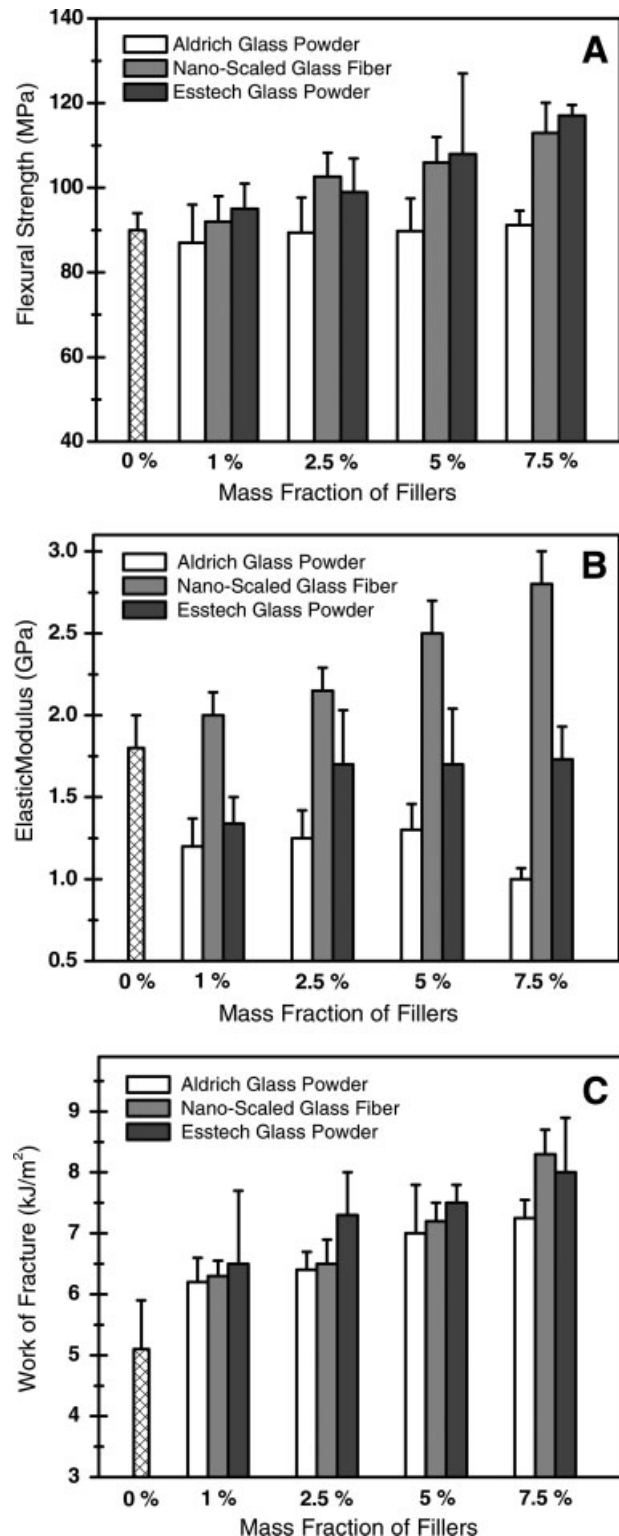Figure 2 showed the FS, $E_Y$, and WOF of Bis-GMA/TEGDMA (1/1 mass ratio) dental composites



**Figure 2** Mechanical properties including (A) flexural strength, (B) elastic modulus, and (C) work of fracture of Bis-GMA/TEGDMA (1/1 mass ratio) dental composites containing various mass fractions (0, 1, 2.5, 5, and 7.5%) of the silanized Aldrich glass powder (white bars), the silanized electrospun nano-scaled glass fibers (gray bars), and the as-received Esstech glass powder (black bars). Each datum is the mean value of six measurements with the error bar representing one standard deviation.

containing various mass fractions (0, 1, 2.5, 5, and 7.5%) of the silanized Aldrich glass powder (white bars), the silanized electrospun nano-scaled glass fibers (gray bars), and the as-received Esstech glass powder (black bars). Each datum in the plots provided the mean value of six measurements with the error bar representing one standard deviation. Figure 2 indicated that FS, $E_Y$, and WOF values of the composites reinforced with the silanized electrospun nano-scaled glass fibers were all higher than those of the composites reinforced with the silanized Aldrich glass powder. This suggested that the fiber morphology outperformed the particle morphology on the composite reinforcement due to the Bridging effect as described in the "Introduction" section. However, the FS and WOF values of the composites made from the silanized fibers were statistically the same as those of the composites made from the as-received Esstech glass powder (one-way ANOVA, $P > 0.05$), whereas the $E_Y$ value of the fiber reinforced composites was significantly higher than that of the Esstech glass powder reinforced composites (one-way ANOVA, $P < 0.05$). The following are our proposed explanations. The mechanical properties (particularly the strength) of composites are strongly influenced by the amount and distribution of structural defects. The incorporation of surface-silanized electrospun nano-scaled glass fibers (particularly the ones that are weakly bonded to the resin matrix) could result in the formation of structural defects that would weaken the composites. In other words, the incorporation of nano-scaled glass fibers into dental composites could lead to two opposite effects, including a reinforcing effect due to the "Bridge" mechanism and a weakening effect due to the formation of structural defects. Additionally, it is noteworthy that both the chemical compositions and the surface silanization conditions/procedures of the electrospun nano-scaled glass fibers were the same as those of the Aldrich glass powder while different as those of the Esstech glass powder. The Esstech glass powder was the 7% (mass fraction) silanized barium borosilicate glass powder, whereas both the electrospun nano-scaled glass fibers and the Aldrich glass powder were 4% silanized silica. We believe that the mechanical properties of the electrospun nano-scaled glass fiber reinforced composites could be further improved by optimizing the chemical composition and the surface treatment method of the fibers.

Figure 3 showed the FS, $E_Y$, and WOF of Bis-GMA/TEGDMA (1/1 mass ratio) dental composites containing various mass fractions (0, 1, 2.5, 5, and 7.5%) of the silanized electrospun nano-scaled glass fibers. The total mass fraction of filler in the composites was maintained at 70%; yet the filler was the combination of the silanized electrospun nano-
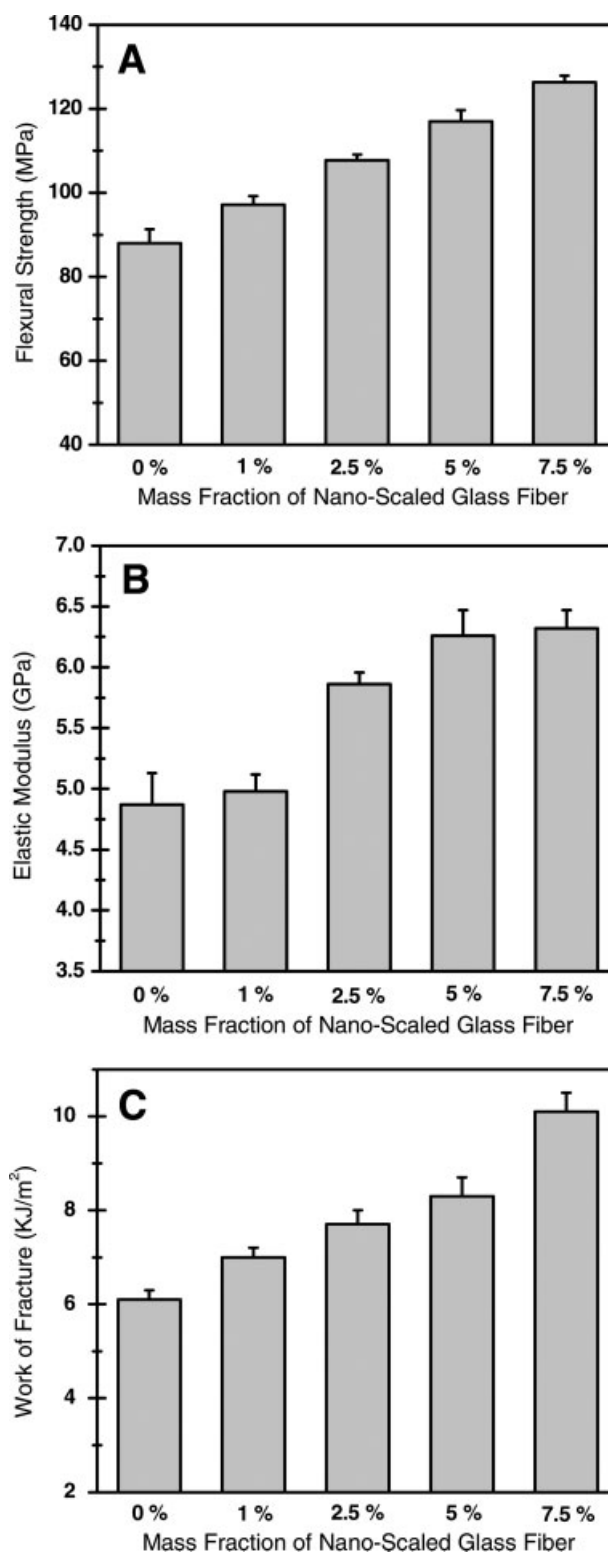


**Figure 3** Mechanical properties including (A) flexural strength, (B) elastic modulus, and (C) work of fracture of the Bis-GMA/TEGDMA (1/1 mass ratio) dental composites (with the total filler mass fraction at 70%) containing various amounts (0, 1, 2.5, 5 and 7.5%) of the silanized electrospun nano-scaled glass fibers. Each datum is the mean value of six measurements with the error bar representing one standard deviation.
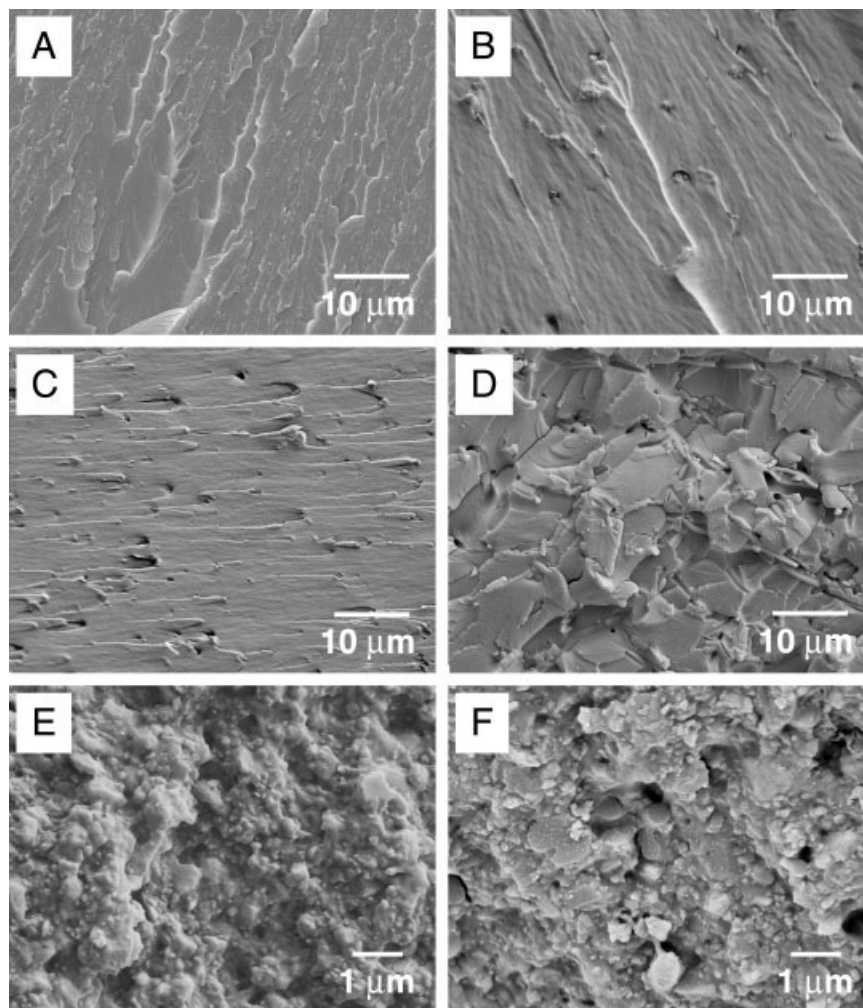
**Figure 4** SEM images showing the representative fracture surfaces of the unfilled Bis-GMA/TEGDMA resin (A), the composites filled with 5% silanized Aldrich glass powder (B), as-received Esstech glass powder (C), and silanized electrospun nano-scaled glass fibers (D) as well as the composite containing 70% as-received Esstech glass powder (E), and the composite containing 65% as-received Esstech glass powder and 5% silanized electrospun nano-scaled glass fibers (F).

scaled glass fibers and the as-received Esstech glass powder. For example, the sample containing 2.5% fibers was made from 2.5% silanized electrospun nano-scaled glass fibers, 67.5% as-received Esstech glass powder, and 30% Bis-GMA/TEGDMA. It was found that the substitution of Esstech glass powder with electrospun nano-scaled glass fibers in dental pastes substantially increased the viscosity. If the mass fraction of the fibers was higher than 7.5%, while the total mass fraction of filler remained at 70%, the paste would become too viscous to process/handle. Figure 3 indicated that the FS, $E_Y$, and WOF values of the composites (with a total filler level at 70%) were all substantially increased by replacing small mass fractions of the as-received Esstech glass powder with the silanized electrospun nano-scaled glass fibers. For the 7.5% fiber reinforced composite, the FS, $E_Y$, and WOF values

(mean $\pm$ standard deviation, $n = 6$) were (127 $\pm$ 2) MPa, (6.3 $\pm$ 0.2) GPa, and (10.1 $\pm$ 0.4) kJ/m$^2$, respectively. The FS, $E_Y$, and WOF values of the control sample (containing 70% Esstech glass powder alone) were (88 $\pm$ 3) MPa, (4.9 $\pm$ 0.3) GPa, and (6.1 $\pm$ 0.2) kJ/m$^2$, respectively. This indicated that the FS value was improved by 44%, the $E_Y$ value was improved by 29%, and the WOF value was improved by 66%. It is noteworthy that the FS, $E_Y$, and WOF were improved simultaneously. Suggested reasons are: (1) the fibers, which were strongly bonded to the resin, strengthened the composites and resulted in improved FS; (2) the modulus of the fibers was higher than that of the resin, causing improved $E_Y$; and (3) the fibers, which were weakly bonded to the resin, could be separated (pulled out) when the load was applied; this created frictional force that allowed stress to

transfer across matrix cracks, increasing the material resistance to fracture (WOF). Unlike the composites filled with small mass fractions of fillers (Fig. 2), the composites filled with a total mass fraction of 70% filler (which is the combination of the as-received Esstech glass powder and the surface-silanized electrospun nano-scaled glass fibers) probably had similar amount and distribution of structural defects. Therefore, the Bridging mechanism (reinforcement effect) alone played an important role, and resulted that the composites with nano-scaled glass fibers possessed significantly higher FS, $E_Y$, and WOF values (one-way ANOVA, $P < 0.05$). We believe that the electrospun nano-scaled glass fiber reinforced Bis-GMA/TEGDMA dental composites could be tailored to possess high strength and/or high toughness by judicious adjustment of the interfacial bonding strength between the fiber filler and the resin matrix.

The SEM images in Figure 4 showed the representative fracture surfaces of the unfilled Bis-GMA/TEGDMA resin (A), the composite filled with 5% silanized Aldrich glass powder (B), the composite filled with 5% as-received Esstech glass powder (C), and the composite filled with 5% silanized electrospun nano-scaled glass fibers (D) as well as the composite containing 70% as-received Esstech glass powder (E), and the composite containing 65% as-received Esstech glass powder and 5% silanized electrospun nano-scaled glass fibers (F). The unfilled Bis-GMA/TEGDMA [Fig. 4(A)] fractured as a typical ductile resin. The fracture surface was smooth with oriented fracture lines that had resulted from the extension of crazings initiated by the stress concentration points. Conversely, the fracture surface of the nano-scaled glass fiber reinforced composite [Fig. 4(D)] was rough with no clearly identifiable fracture lines. These results suggested that the presence of nano-scaled glass fibers could deflect the microcracks and effectively increase resistance to the applied force. When the cracks finally broke away from the fibers, a rough fracture surface was created, suggesting energy consumption during breaking. Some voids/holes were observed on the fracture surfaces of the nano-scaled glass fiber reinforced resin [Fig. 4(D)] and composite [Fig. 4(F)]. These voids/holes were probably formed by the separation (pull out) of the fibers, suggesting the interfacial bonding strength still needed to improve to achieve higher mechanical strength. We believe that the mechanical properties (particularly strength) of the electrospun nano-scaled glass fiber reinforced composites could be further improved by fusion of $SiO_2$ nanoparticles (with sizes of 10–20 nm) on the surface of the fibers to achieve the desired physical interlocking between the fiber filler and the dental resin matrix.[21]

## CONCLUSIONS

The aim of this study was to investigate the electrospun nano-scaled glass fiber reinforcement of Bis-GMA/TEGDMA dental composites. The hypothesis was that incorporation of the surface-silanized electrospun nano-scaled glass fibers into Bis-GMA/TEGDMA dental composites would result in significant improvements of the mechanical properties. To test this hypothesis, photo-cured Bis-GMA/TEGDMA dental composites filled with various mass fractions of surface-silanized electrospun nano-scaled glass fibers were systematically fabricated; the mechanical properties were then measured using the standard three-point flexural testing method. Analysis of variance (ANOVA) was used for the statistical analysis of the acquired data. The results indicated that small mass fraction substitutions (1, 2.5, 5, and 7.5%) of conventional dental filler with the surface-silanized electrospun nano-scaled glass fibers significantly improved the FS, $E_Y$, and WOF values of 70% (mass fraction) filled composites, by as much as 44%, 29%, and 66%, respectively. We believe that the mechanical properties (particularly the strength) of the electrospun nano-scaled glass fiber reinforced composites could be further improved by optimization of the chemical composition and the surface treatment method of the fibers, and by fusion of $SiO_2$ nanoparticles (with sizes of 10–20 nm) on the surface of the fibers to achieve the desired physical interlocking between the fiber filler and the dental resin matrix. We envision that the electrospun nano-scaled glass fibers could be utilized to develop the next generation dental composites, which would be particularly useful for large posterior restorations.

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