

Research Article

Performance Enhancement of Dental Composites Using Electrospun Nanofibers

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The objective of the present study is to investigate the effect of electrospun nanofiber reinforcement on the properties of commercially available, hyperbranched polymer modified (Hybrane, 0.3 wt.% DSM) dental formulations. The emergence of functionalized nanoscale reinforcements having large surface area (hundreds of square meters/gram) has enabled the design of novel nanocomposites with new and complex structures leading to enhanced mechanical and physical properties. Electrospun nanofibers from a range of polymer chemistries (PVOH, PLLA, Nylon 6) have been investigated as a reinforcing phase at levels between 0.01 and 0.3 wt.%, with and without a silane coupling agent surface treatment. The experimental results indicate that 0.05 wt.% reinforcement with 250 nm diameter PVOH nanofibers leads to a 30% improvement in compressive strength, coupled with a shrinkage reduction of about 50%. Electrospun fiber reinforcement by other chemistries or at other diameters showed either no property improvement or led to property loss.

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1. INTRODUCTION

A main challenge for centuries has been the development and selection of biocompatible, long-lasting, direct-filling tooth restoratives and prosthetic materials that can withstand the adverse conditions of the oral environment. Polymer matrix composites, comprised of silica-filled UV curable acrylate resins, have emerged as desirable materials for these applications.

Key properties of dental composites include low viscosity prior to cure, biocompatibility, low polymerization shrinkage (both to insure good prosthesis adhesion and to eliminate unfilled space for infection or other contamination), high mechanical properties (especially fracture toughness, compressive strength, and fatigue), surface hardness, abrasion resistance, low moisture uptake, low coefficient of thermal expansion (in the range of body temperature), ease of handling in the oral environment, and the ability to match the esthetics of the patient's teeth [1–4].

The current state-of-the-art dental composites contain modified acrylate resin matrices filled with micro-/nanoscaled ceramic particles. It has been shown that the performance of dental composites can be improved through the use of nanotechnology [5–10], including the use of covalently anchored nanoscaled organic moieties to an inorganic network [6], and the incorporation of nanoscaled monomethacrylate functionalized polyhedral oligomeric silsesquioxanes (POSSs) into an acrylate resin system [11]. Novel polymeric dental restorative composites have been explored, in which polyhedral oligomeric silsesquioxane methacrylate (POSS-MA) monomers were used to partially (or completely) replace the commonly used base monomer, Bis-GMA [10]. Fong explored the use of polyamide nanofibers as a toughening agent in dental acrylate resins. The best performance reported to date for acrylate-based dental composites was achieved by the Dodiuk-Kenig group through the modification of acrylate resin by the incorporation of hyperbranched moieties

into the matrix resin [9]. It has been hypothesized that these hyperbranched moieties assemble to form nanophases that retard motions in the acrylate backbone, leading to improved mechanical performance and reduced polymerization shrinkage [9]. This improved resin system has been commercialized by BJM Ltd. and distributed worldwide by the Premier Dental Company.

Many groups have worked extensively in the area of electrospinning [12–15], focusing on both process understanding and nanofiber applications.

The objective of this study is to investigate the impact of nanofiber reinforcement on the performance of state-of-the-art dental composites.

2. MATERIALS AND METHODS

2.1. Composite fabrication

Nanofiber-reinforced hyperbranch modified acrylate resin composites were prepared in the Israeli laboratories of BJM Ltd. This proprietary process involves the processing of nanofiber mats to produce individual nanofibers (aspect ratio of about 1000), which can then be conveniently dispersed in the acrylate matrix resin at the chosen concentration.

2.2. Materials

The dental formulations utilized in this study were based on the standard used bisphenyl glycidylmethacrylate (Bis-GMA) and triethylglycoldimethacrylate (TEGDMA) acrylate resin system. In all cases, the resin composition was modified by the addition of 0.3 wt.% of hyperbranch polyesteramide into the acrylate matrix polymer. Electrospun nanofibers of a variety of chemistries (PVOH, PLLA, Nylon6) were chosen as a reinforcing phase for the base resin. Criteria for choice were as follows:

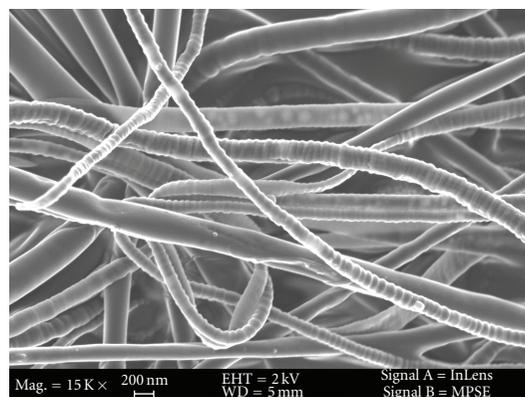
- (i) biocompatibility,
- (ii) functional groups available for reaction with the base resin (e.g., OH groups).

In each case, the same hyperbranched polymer-modified acrylate matrix resin was reinforced with electrospun nanofibers of a given chemistry and given concentration. All samples were analysed for composite compressive strength (ISO 9917), flexural strength (ISO 4049), diametral tensile strength, and linear shrinkage. Nanofibers were incorporated into the resin over a broad weight fraction range (0.05–1% wt.) to establish the relationship between amount of reinforcement and composite performance.

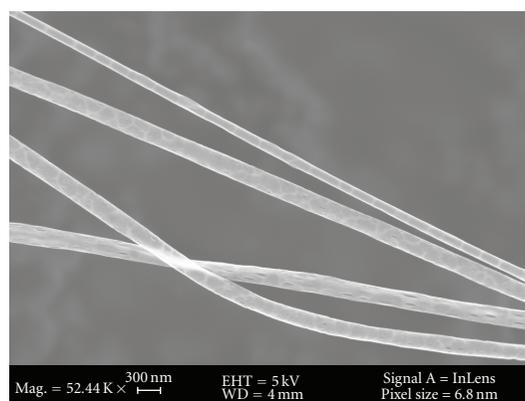
The materials used in this study are shown in Tables 1(a) and 1(b).

2.3. Electrospinning

Electrospun nanofibers were produced in the Medical Device Concept Laboratory (Department of Biomedical Engineering, New Jersey Institute of Technology, USA). Electrospinning was performed within a closed chamber,



(a)



(b)

FIGURE 1: (a) SEM image of PVOH nanofibers (250 nm diameter), 200 nm magnification. (b) SEM image of PLLA nanofibers (250 nm diameter), 300 nm magnification.

fitted to a mild vacuum to minimize atmospheric changes during spinning. Solution was supplied to a standard syringe with a Harvard infusion pump and charging of the fluid was effected through use of a Gamma high-voltage source model RR60-0.3R. The solvent for PVOH spinning was deionized water; PLLA was spun from methylene chloride. Takeup was accomplished on a flat aluminum plate. More than 50 repeats of each spinning condition were performed to generate sufficient fiber for composite fabrication and testing. Fiber diameters were determined by averaging of multiple SEM micrographs from multiple runs. Typical SEM micrographs are shown in Figures 1(a) and 1(b).

The nanofibers were either used as produced or were silane surface treated with a 1 wt.% γ -Methacryloxypropyltri-methoxy-silane in 80 : 20 wt by wt ethanol: water solution and dried at 120°C for 30 minutes prior to their incorporation into the resin matrix.

2.4. Testing methods

The compressive strength was determined using a Lloyd Testing Machine (Model LR 10K, Lloyd Instruments, serial no. 9211) in accordance with ISO 9917. The crosshead

TABLE 1

(a) Description of the matrix resin

Component	Chemical composition
Organic resin matrix	Acrylic mono- or multifunctional monomers and oligomers
Photosensitizers for the light curing process	Camphorquinone (CQ) and Ethyl-4-dimethylaminobenzoate (EDB)
Initiators for polymerization	Tertiary amine and Benzoyl peroxide
Dendritic modifier component	Hyperbranched polyesteramide

(b) Description of electrospun nanofibers

Nanocomponent Type	Nanocomponent	Brand name, manufacturer	Description
Electrospun Nanofibers	PVOH	Medical Device Concept Laboratory, Department of Engineering, NJIT, USA	Electrospun Polyvinyl Alcohol Nanofibers
	PLLA	Medical Device Concept Laboratory, Department of Engineering, NJIT, USA	Electrospun Poly-L-Lactic Acid Nanofibers
	PA6	Elmarco s.r.o., Czech Republic	Nylon 6 (Polyamide 6) Nanofibers

speed was 1.0 mm/min and ten specimens were prepared for each composite formulation. The two resin parts (nanofiber-reinforced matrix and crosslinking agent) were stored separately at 4°C prior to preparation. The specimens were prepared by polymerization in a cylindrical Teflon mold of 4.0 ± 0.1 mm diameter and 8.0 ± 0.1 mm length. After polymerization, the specimens were taken out of the mold and held at room temperature for 1 hour and then immersed in water at $(37 \pm 1)^\circ\text{C}$ for 24 hours prior to measurement.

The flexural strength was measured using rectangle specimens $25 \times 2 \times 2$ mm produced in split Teflon molds in accordance with ISO 4049, 9917. The specimens were stored for an hour at ambient temperature and then stored in distilled water at 37°C for 24 hours. Testing was performed using a Lloyd Testing Machine (Model LR 10K, Lloyd Instruments, serial no. 9211) equipped with a load cell of 10 N and Bencor multi-T testing device as a flexural test apparatus (described in ISO/TS 11405:2003). Each specimen was placed under continuous loading at 1.0 mm per minute.

Linear shrinkage measurements were performed using glass capillary tubes (4.15 mm diameter) which were filled with composite material and self polymerized by a free-radical mechanism. The length (height of the specimens) was measured by using an optical microscope “WILD Herrbrugg,” magnification $\times 10$, with the intrinsic scale accurate to 0.1 mm. The measurements were carried out during the polymerization process as a function of time (5 minutes, 30 minutes, 60 minutes) then immersed in water at $(37 \pm 1)^\circ\text{C}$ for 24 hours. The value of linear shrinkage (%) was calculated $(1 - l_0/l_0)$.

Atomic force microscope (AFM) was used to characterize the three-dimensional topography of the various dental composite systems evaluated.

A high-resolution scanning electron microscope (HRSEM) was employed to characterize the internal structure and topography of the various dental composite systems (JEOL Ltd., 2004, 2005).

All data was statistically analyzed by the analysis of variance (ANOVA) method to ensure the statistical significance of differences noted experimentally.

3. RESULTS

The compressive strength (CS), diametral tensile strength (DTS), flexural strength (FS), and linear shrinkage (LS) of the base resin reinforce with different concentrations of PVOH, PLLA, and PA6 nanofibers (with different diameters) are shown in Table 2.

Atomic force microscope (AFM) and scanning electron microscope (SEM) imaging were used to study the resultant nanostructure and morphology of the nanofiber-containing dental composites. Figure 2(a) illustrates the surface nanotopography of a 1.0 wt.% 250 nm PVOH nanofiber-reinforced dental composites as observed by AFM.

SEM studies of composite fracture surfaces are instructive in understanding the mechanism of property enhancement exhibited by some of the PVOH nanofiber-reinforced dental composites. An SEM micrograph of a PVOH nanofiber-reinforced composite, silanised and unsilanised, is shown in Figures 2(b) and 2(c).

In cases where improvements are noted, good adhesion between fiber and matrix, as evidenced by resin coating on the fiber (Figure 2(b)), is observed. Conversely, poorer properties are associated with fiber pull-out on the fracture surfaces (Figure 2(c)). It is evident from Figure 2(c) that the treated fibers system shows better fibers–matrix interaction than the untreated ones.

TABLE 2: Mechanical properties of QC STD H UF as a function of electrospun nanofibers.

mechanical property	concentration [%wt.]	PVOH nanofibers			PLLA nanofibers		PA6 nanofibers
		Φ250 nm	Φ125 nm	Φ250 nm	Φ250 nm	Φ125 nm	Φ250 nm
CS [Mpa]	0	184.0	184.0	184.0	184.0	184.0	184.0
	0.01	121.4	140.7	137.2	136.2	144.2	132.1
	0.05	213.9	126.4	206.3	165	182.1	77.8
	0.1	138.2	100.5	145.3	143.9	133.3	63.1
	0.3	89.9	94.1	115.6	94.0	125.0	67.6
	P [ANOVA]		0.003 (<i>n</i> = 6)	0.002 (<i>n</i> = 10)	0.0003 (<i>n</i> = 10)	0.004 (<i>n</i> = 10)	0.05 (<i>n</i> = 10)
DTS [Mpa]	0	30	30	30	30	30	30
	0.01	22.3	27.5	28.9	30.0	28.6	31.9
	0.05	27.8	27.6	29.5	24.9	27.6	20.8
	0.1	21.3	21.5	28.8	22.4	22.0	18.9
	0.3	23.5	18.1	21.9	18.8	22.7	21.6
	P [ANOVA]		0.73 (<i>n</i> = 6)	5.04E-6 (<i>n</i> = 10)	0.0001 (<i>n</i> = 10)	1.12E-4 (<i>n</i> = 10)	1.22E-7 (<i>n</i> = 10)
FS [Mpa]	0	314	314	314	314	314	314
	0.01	260.3	214.7	354.4	290.2	363.7	257.5
	0.05	171.8	226	357.3	293.4	267.9	236.6
	0.1	225.6	145.5	317.6	317.6	307.5	249.5
	0.3	244.9	230.5	189.6	342.9	280.5	234.3
	P [ANOVA]		0.001 (<i>n</i> = 6)	0.02 (<i>n</i> = 9)	1.17E-8 (<i>n</i> = 9)	0.1 (<i>n</i> = 10)	0.02 (<i>n</i> = 10)
LS [%]	0	4	4	4	4	4	4
	0.01	1.2	3.1	2.0	2.8	2.6	3.9
	0.05	2.0	2.8	2.8	2.4	2.2	2.1
	0.1	3.0	2.3	3.0	2.5	2.3	3.2
	0.3	2.2	2.4	2.0	2.7	1.8	2.7
	P [ANOVA]		0.71 (<i>n</i> = 6)	0.09 (<i>n</i> = 10)	0.95 (<i>n</i> = 10)	0.05 (<i>n</i> = 10)	0.47 (<i>n</i> = 10)

4. DISCUSSION

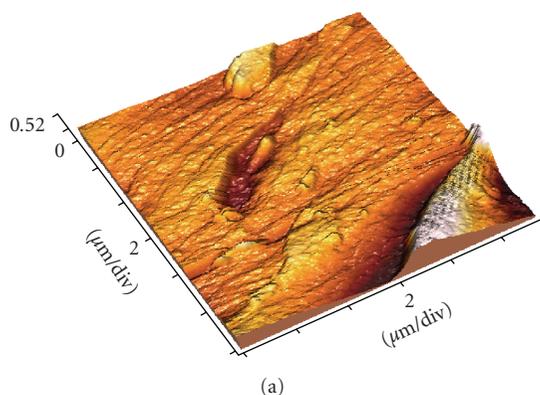
The compressive strength results for all nanoreinforcements studied are shown in Figure 3 as a function of reinforcing fiber concentration.

Figure 3 illustrates that a significant improvement in compressive strength is exhibited by the dispersion of t of 0.05 wt.% PVOH nanofibers to the standard dental composite matrix. This is probably in part due to the increase in reactive hydroxyl group concentration of the PVOH, but the fiber morphology within the composite also plays an important role—note lack of improvement of the 150 nm diameter PVOH fiber-reinforced samples. The improvement noted for the 0.05 wt.%, 250 nm PVOH nanofiber-reinforced composite was s manifest in both compressive strength increases and linear shrinkage decreases. No other nanocomposites tested, including the PLLA nanofiber (125 nm diameter, 250 nm diameter), the PA6-based nanocomposites, or the 125 nm PVOH nanofiber-reinforced composites, showed consistent property improvements. These results suggest that the mechanical properties of these nanofiber-reinforced

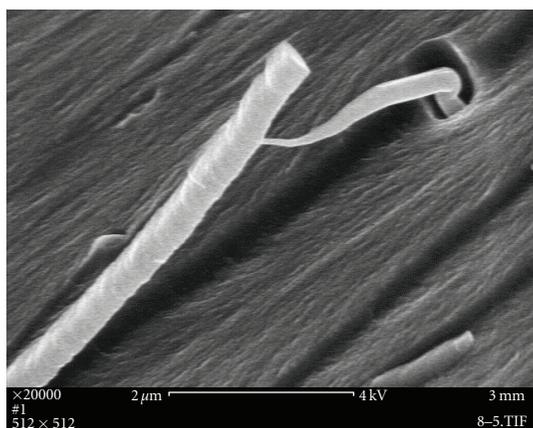
acrylate composites are very sensitive to fiber dispersion within the matrix and fiber matrix bonding.

Studies of composite surfaces and fracture indicate that mechanical performance correlates with fiber adhesion to matrix. The AFM result, shown in Figure 2(a), suggests that the nanostructure of 1% wt. PVOH nanofiber composite (diameter 250 nm) system correlates with lowering of mechanical properties from those exhibited by the matrix alone. As the concentration of the nanofibers increases, increased fiber pullout is evident from the increase of surface roughness (302.4 nm at 1 wt.% PVOH nanofibers).

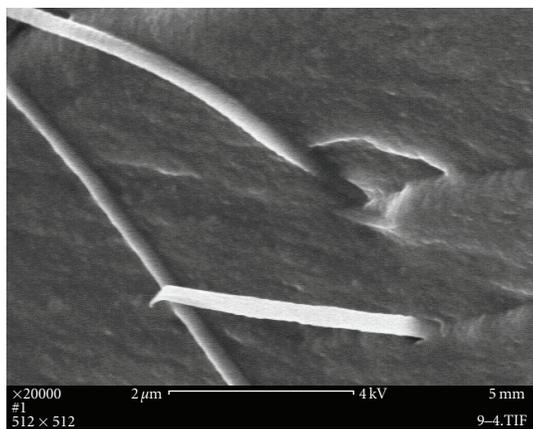
The SEM results (Figure 2(c)) imply that the finest structure and strongest matrices-fiber interaction were obtained in the case of the 0.05 wt.% PVOH nanofibers (diameter 250 nm) composite system. This critical nanostructure correlates with the highest compressive strength of the dental composites as well as with the lowest linear shrinkage exhibited. The results show conclusively that the nanofibers survive composite processing and that property improvement correlates with fiber adhesion to the matrix.



(a)



(b)



(c)

FIGURE 2: (a) AFM nanotopography of QC STD H UF (standard) + 1.0 wt% PVOH (250 nm). (b) SEM of QC STD H UF 1.0 wt% PVOH (250 nm) unsilansed, 2 micron magnification. (c) SEM of QC STD H UF 1.0 wt% PVOH (250 nm) silansed, 2 micron magnification.

These preliminary results indicate that the introduction of hydroxyl-rich nanophases with specific composite architecture (need to differentiate from 150 nm PVOH) into acrylate matrix dental composites can lead to significant and unexpected improvement in clinically important dental material performance. In the case of acrylate resin modi-

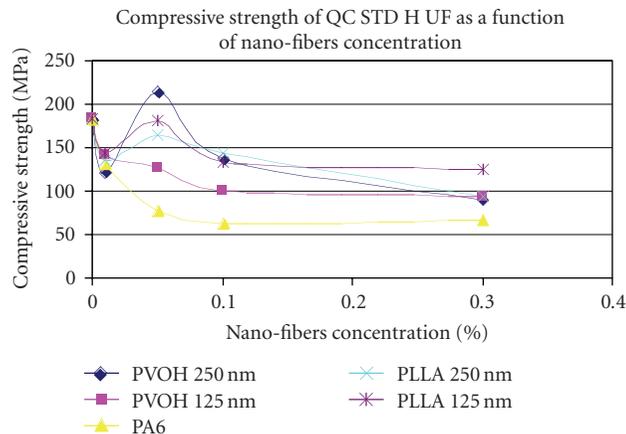


FIGURE 3: Compressive strength of QC STD H UF as a function of nanofibers concentration and type.

fied by hyperbranched polyesteramide, the improvement is attributed to crack blunting by the nanophase inclusion, coupled with increased system cross linking through the hydroxy-rich chemistry [9]. The addition of the hydroxyl-rich PVOH nanofiber phase further increases crosslinking density, while improving overall system toughness by allowing cracks to run and dissipate energy along the fiber-matrix interface. These results are consistent with the complex mechanisms suggested for the toughening of polymers, polymer blends, and fiber-reinforced composites [16]. While a detailed mechanism is beyond the scope of the present work, it is clear that composite performance is a function of matrix chemistry, fiber diameter, fiber dispersion, and fiber matrix interaction. In a more general sense, this work shows that significant improvement to the performance of simple polymer systems, in this case acrylates, can be effected by the introduction of small weight percentage (<1 wt.%) of nanoscale reinforcements. The introduction of more than one such phase can, as illustrated here by the inclusion of both hyperbranch (0.3 wt.%) resin modification and PVOH nanofiber (250 nm diameter, 0.05% wt.), can be synergistic and lead to even greater improvement of key performance properties. Future work will concentrate on the definition of detailed mechanisms of property enhancement and the extension of these concepts to new chemistries.

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