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Semi-interpenetrating network composites reinforced with Kevlar fibers for dental post fabrication

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This study evaluates the reinforcement of semi-interpenetrating network composites of 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)-phenyl] propane (Bis-GMA)/ triethyleneglycol dimethacrylate (TEGDMA)/polymethyl methacrylate (PMMA) and 25% titanium dioxide (TiO_2) nanofiller with surface treated Kevlar fibers for potential application as dental posts. The post material was subjected to thermo-cycling and flexural strength determined, characterised by dynamic mechanical analysis, water sorption, radiopacity and cytotoxicity tests. The results were compared with everStick®POST. Kevlar pre-treatment with acetic acid and silane coupling agent demonstrated a clear effect on the flexural strength of the composites with a significant increase compared to composites with fibers without surface treatment. The inclusion of TiO_2 into the final formulation provided the desired radiopacity and improved both aesthetics and flexural strength, which exhibits a higher resistance on thermocycling. The ratios of fatigue limit to static flexural strength were about 0.73 for Kevlar and 0.58 for everStick®POST; MTT assay confirmed the absence of any toxic eluents, indicating its feasibility as new intracanal post material.

Keywords: Dental post, Kevlar fiber, Semi-interpenetrating network, Fatigue resistance

INTRODUCTION

Intracanal posts are generally used to provide retention of the core to improve the structural integrity of the tooth after endodontic treatment. Fiber reinforced composites have been used for fabrication of posts to replace the high modulus metallic posts that make them less desirable due to the tendency to cause root fractures[1].

In FRC's, the fibers act as an effective reinforcement for the polymer matrix and stress is transferred from the matrix to the fibers. The choice of fiber/matrix and the interfacial bonding are important determinants of the integrity of fiber posts[2]. Several fibers such as carbon, glass, quartz, aramid (Kevlar), and ultra-high molecular weight polyethylene (UHMWPE) fibers have been used in dental FRCs with varying degree of success. Among them, the silica and quartz fibers are aesthetically suited that have led to their use in combination with a methacrylate or epoxy resin matrices after surface modification with coupling agents as components of commercial FRC posts. However, the hydrolytic instability of the silicate glass fibers[3], hydrolysis of the silane coupling agent and plasticisation of the polymer matrix in presence of moisture, compromise the interfacial adhesion between fibers and the polymer matrix deemed to cause the mechanical deterioration of these posts[4]. Numerous surface treatments have been attempted to overcome the problems associated with fiber-matrix debonding on hydration, for example glass fibers co-coated with polymethyl methacrylate (PMMA)/polydopamine (PDA)[5] and quartz fibers surface modified with a sol-gel method[6] yielded improvement in mechanical properties, however moisture sensitivity is reported over 4 weeks and no data on fatigue behavior.

In a clinical situation, although the intracanal posts are entombed by other restorative materials, which prevent or reduce their direct contact with fluids, their structure may still be affected on cyclic loading and the induced stresses. Previous studies have shown that mechanical fatigue during cyclic loading that simulates the normal occlusal and masticatory functions contribute to reduction in mechanical properties of FRC posts after ageing[7-9], which renders them flexible and transfer the stress to the post-luting or resin-dentine interface leading to debonding, a frequent failure mode of ETT restored with fiber posts[10]. It is imperative that posts are not moisture sensitive, able to exhibit a predictable bonding to tooth tissue, and possess high flexural and fatigue resistance to prevent flexion of the core during parafunctional movement.

Kevlar fibers exhibit a unique combination of high strength, modulus, toughness and thermal stability[11] and Kevlar composites find extensive use as bullet-proof vests, sporting goods, aviation industry. Kevlar fibers have been used in acrylic dentures to improve fracture and fatigue resistance[12,13], however much less in dental composites due to their inherent yellow color, which interferes with aesthetic requirements.

The ability of Kevlar fibers to reinforce polymeric matrices prompted the present study and were used to reinforce2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)-phenyl] propane (Bis-GMA)/triethyleneglycol

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dimethacrylate (TEGDMA)/PMMA semi-IPN matrix with titanium dioxide (TiO_2) nanofiller composite and characterised to function as a new intracanal fiber post material. The surface of Kevlar fiber is highly crystalline, chemically inert and smooth, which necessitates surface treatment to allow an interfacial adhesion between the fiber and the matrix[11,14]. Thus, the fibers were etched with acetic acid and subsequently subjected to treatment with a silane coupling agent to enhance the matrix-fiber interfacial adhesion. To optimize and study the effect of the surface treatment, the flexural strength of the fiber reinforced composites prepared solely by using the semi-IPN with the untreated, acetic acid etched and etched and silane coupled fibers (the reinforcements) were determined. Based on the results, the fibers that received a combination of acetic acid etching and A174 silanation were used to fabricate the FRC composites with TiO_2 to provide the radiopacity and aesthetics for the intra-canal posts.

MATERIALS AND METHODS

Materials

Kevlar 49® yarn (polyparaphenylene terephthalamide), 12 μm filament diameter, 1.44 g/cm^3 density was purchased from Goodfellow Cambridge, Huntingdon, England. Acetic acid (BDH, VWR, Dorset, UK) and silane coupling agent A-174 (3-Trimethoxysilyl propylmethacrylate, Merck, Frankfurt, Germany) were used for fiber surface treatment. For the semi-IPN system, Bis-GMA and TEGDMA were purchased from Esschem Europe, PMMA (Mw~350,000 g/mol), TiO_2 (nanopowder, <100 nm particle size) and Benzoyl peroxide (BPO) were supplied by Aldrich, Dorset, UK. everStick®POST from Stick Tech, Turku, Finland was used as a commercial reference.

Surface treatment of Kevlar fibers

Kevlar fibers were first treated with 99.9% acetic acid at 55°C for 2 h, washed three times with distilled water and dried under vacuum at 50°C for 8 h (AA treated KF). A part of the AA-treated KF fibers was further subjected to wet silanation using 2% A-174 in a mixture of ethanol-water (90/10 w/w) and then dried under vacuum at 50°C for 8 h before use (AA-silanated KF). The modified fibers were characterised by ATR-FTIR (ATR-Perkin-Elmer-Spectrum One, Waltham, MA, USA) and spectra recorded in the 4,000 to 650 cm^{-1} region with a wavenumber step of 0.5 cm^{-1}. The morphology of the fibers was visualised by scanning electron microscopy (Hitachi High Technologies, S-3500N, Schaumburg, IL, USA) at an accelerating voltage of 10 KeV and a magnification of 1,000×. Untreated Kevlar fiber was used as the reference.

Specimen preparation

1. Preparation of Kevlar fiber/semi-IPN matrix reinforcements

Untreated, AA treated and AA-silanated Kevlar fibers were used to prepare three experimental reinforcements using semi-IPN matrix system prepared by mixing Bis-GMA, TEGDMA and PMMA at a ratio of 54:36:10 (w/w) respectively. BPO was added as a heat curing initiator at 1% by weight of the net resin mix. The fiber feed content and matrix was kept constant for the three formulations and bar-shaped test specimens (2×2×25 mm) were prepared for three-point bending tests using PTFE molds. Two Kevlar fiber bundles (25 mm in length), which consisted of 4 sub-bundles of 1,000 filaments each, were weighed first and impregnated with a constant amount of resin mix for 24 h. The impregnated bundles were then embedded unidirectionally into the mold with an excess of the resin matrix. The mold was clamped with spring clips between two glass slabs and cured in a heat oven for 1 h at 80ºC. After curing, the sides of all specimens were polished with a silica paper (grit 800–1200) to improve the surface finish. The test specimens were stored at room temperature for 24 h before three-point bend testing.

2. Preparation of experimental Kevlar FRC and everStick®POST specimens

The post composites were prepared using the AA-silanated K fibers, which yielded the best flexural strength, in combination with the semi-IPN resin mix (prepared in 1.) and TiO_2 nanofiller (75/25 wt/wt); see Table 1 for details. Rectangular bar-shaped specimens (2×2×25 mm) and cylindrical post samples (2 mm diameter 20 mm long) were fabricated and used for further characterisation (Fig. 1b).

The fiber content in percentage volume was assessed using the formula[15]:

$$V_k(\%) = \frac{D_s - D_r}{D_f - D_r} \times 100 \quad \text{(Eq 1)}$$

where, V_k is the vol% of the KF, D_s is the density of the K FRC sample, D_r is the density of resin matrix and D_f is the density of the KF (1.44 g/cm^3). This method determines the densities (calculated by Archimedes' principle) of FRC sample and resin composite matrix samples by measuring their mass in air and water. An analytical balance (AG 204, Mettler Toledo, Greifensee, Switzerland) equipped with a density kit was used for the measurements.

The everStick® material was used as received and handled according to manufacturer's instructions. To prepare a bar-shaped specimen, two unpolymerized bundles of the material (each containing about 4,000 glass fibers) were rolled together and embedded into a PTFE mold covered with Mylar strips, clamped between two glass slides and then cured by visible light for 40 s each side, using Optilux 501 (Demetron, Danbury, CT, USA) dental curing unit with an irradiance of 650±50 mW cm^{-2}. After manual light-curing, the specimens were further polymerized in a light-curing oven with heat (Licu Lite, Dentsply DeTrey, Dreieich, Germany) for an additional 20 min[16].

Table 1 Composition and flexural properties of experimental Kevlar FRC and commercial everStick®POST materials under static and thermal-cycled conditions [mean (SD), n=6]

FRC group	Description	Flexural Strength in MPa (SD)		Flexural Modulus in GPa (SD)	
		Static	Thermal cycled	Static	Thermal cycled
Experimental Kevlar FRC	Two bundles (4,000 filaments each, 12 μm diameter) of silanized pre-impregnated Kevlar fibers in Bis-GMA/ TEGDMA/ PMMA semi-IPN matrix with 25 wt% TiO_2 nanofillers. Fiber content: 32 vol% Heat-polymerization	450.0 (35.9)	378.4* (33.6)	18.9 (1.6)	18.0 (1.5)
Commercial everStick®POST Patch No.: 2050426-ES-125	Two bundles (4,000 filaments each, 15 μm diameter) of silanized pre-impregnated unidirectional glass fibers in Bis-GMA/PMMA semi-IPN matrix. Fiber content: 48 vol% (Information provided by manufacturers) Light polymerization+Oven (light/heat) polymerization	583.0 (39.5)	381.7* (53.5)	19.2 (2.5)	17.7 (2.1)

*Differences were statistically significant (p<0.05) between static and thermal-cycled conditions within the same group.

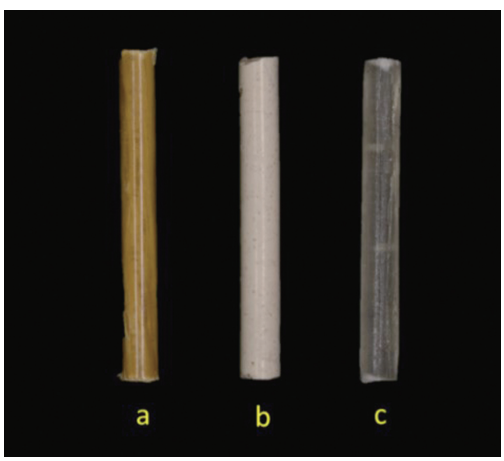


Fig. 1 Experimental K FRC posts (a) without TiO_2 nanofiller and (b) with TiO_2 nanofiller, the inclusion of TiO_2 offsets the yellow colour of Kevlar; (c) everStick® commercial post.

Flexural properties of KF reinforcements and FRC post materials

Three-point bending tests were carried out according to ISO 10477 standards at a cross-head speed of 1 mm/min and span length fixed at 20 mm on a universal testing machine (M5569A, Instron, High Wycombe, UK) to determine the flexural properties of K fiber reinforcements, experimental K FRC post and everStick®POST materials. To evaluate the effect of thermal stress, test specimens from experimental K FRC post and everStick®POST materials were thermo-cycled for 10,000 cycles in water from 5 to 55°C, with a dwell time of 30 s in each bath and a transfer time of 5 s.

Flexural strength (σ) in MPa and flexural modulus (E) in GPa were calculated using Eqs. (2) and (3), respectively.

$$\sigma=\frac{3FL}{2bh^2} \quad \text{(Eq 2)}$$

$$E=\frac{L^3}{4bh^3}\times\frac{F}{Y} \quad \text{(Eq 3)}$$

where F=maximum strength, L=distance between the rests, b=width of the specimen, h=height of the specimen, and F/Y=slope of the linear part of the stress-strain curve.

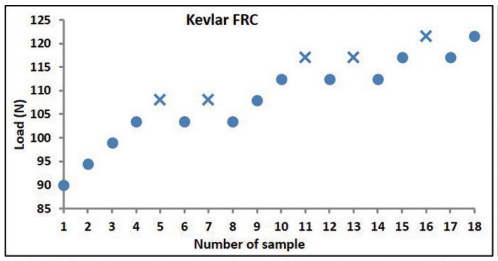
Characterisation of FRC post materials

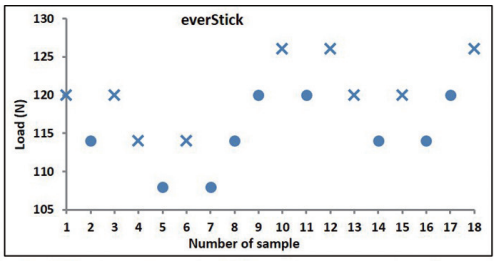
1. Dynamic mechanical analysis (DMA)

Tan delta measurements were carried out using a DMA7 analyser (Perkin-Elmer) in a three-bending mode at a frequency of 1 Hz and a heating rate of 5°C/min within 25 and 200°C temperature range.

2. Fatigue test

A fatigue testing machine (ElectroForce® System, Bose, Eden Prairie, MN, USA) was used to evaluate the flexural strength fatigue limits of the post materials in the three-point bending mode at a frequency of 2 Hz for 5×10^5 cycles or until failure. The test was started by loading the first specimen in each group at approximately 60% of its static flexural load obtained earlier. The staircase method was employed with a stress increment of 4.5 N for Kevlar FRC and 6 N for eveStick® (5% of the initial load). Since this specimen did not fail in 5×10^5 cycles, the second specimen was stressed with a load one increment higher. If it failed in less than 5×10^5 cycles, the next specimen was applied to the test at a stress level one increment lower. This procedure was continued until eighteen specimens of each group were tested. Tests





Load (N)	i	ni (failures)	in_i	i^2n_i
121.5	2	2	4	8
117	1	2	2	2
108	0	2	0	0
		N=Σ ni = 6	A=Σ in_i =6	B=Σ i^2n_i =10

Load (N)	i	ni (failures)	in_i	i^2n_i
126	2	3	6	12
120	1	4	4	4
114	0	2	0	0
		N=Σ ni = 9	A=Σ in_i =10	B=Σ i^2n_i =16

Fig. 2 Staircase method with data analysis required to determine the mean fatigue limits and standard deviation at 5×105 cycles for K FRC and everStick®.
×: Failed specimen, ●: Non-failed specimen.

were carried out at a room temperature and kept moist during cycling via continuous irrigation. The data of the staircase method employed for both groups and their analysis are shown in Fig. 2.

The mean fatigue limit and standard deviation for each group were calculated using the formulae reported by Draughn[17].

$$\bar{X}=X_0+d\ [A/N\pm½] \quad \text{(Eq 4)}$$

$$SD=(1.62d[\frac{NB-A2}{N2}]+0.029) \quad \text{(Eq 5)}$$

Where, $\bar{X}$ is mean fatigue strength limit; X_0 is the load at the lowest stress level at which the fracture or non-fracture of specimens occurred; d is the stress increment; SD is the standard deviation. In formula 1, the positive sign is used when the analysis is based on non-failed specimens, and the negative sign used when failed specimens were considered.

3. Water sorption and solubility

Cylindrical specimens (2 mm diameter×20 mm length) were initially weighed (Mi) to an accuracy of ±0.0001 g (AG64, Mettler-Toledo), and then kept in individual containers in 10 mL deionized distilled water at 37°C. Water uptake was recorded at regular interval during 28 days until there was no significant change in the mass (M_s). A desorption cycle was carried out at 37°C to a constant dry mass (M_d). The water sorption (W_{SP}) and solubility (W_{SL}) in μg/mm³ were calculated using the following equations:

$$W_{SP}=M_s-M_d/V \quad \text{(Eq 6)}$$

$$W_{SL}=M_i-M_d/V \quad \text{(Eq 7)}$$

where, V is the volume of the sample.

4. Radiopacity

Five posts (2 mm diameter×20 mm length) from both groups were digitally photographed alongside a high purity aluminium step-wedge (1,100 alloy) with thickness varying from 1 to 10 mm with increments of 1 mm as a reference according to ISO 4049. The images were taken using a dental X-ray unit (Heliodent, Sirona, Bensheim, Germany) operating at 70 kV, 8 mA, and 0.2 s) with a phosphor plate system (Digora® Optime, Soredex, Tuusula, Finland). ImageJ processing and analysis in java, version 1.47v was used to measure the grey value of the sample and aluminium in the resulting images.

5. Cytocompatibility

The cytocompatibility of the post materials was evaluated using human gingival fibroblast (HGF) cells (obtained at passage number P8) taken from ScienCell™ Research laboratories, Buckingham, UK. The cells were cultured at 37°C humidified atmosphere with 5% CO_2 in fibroblast medium (FM-2301, ScienCell™) consisting of 500 mL basal medium, 10 mL of fetal bovine serum (FBS, Cat.no. 0010, 5 mL of fibroblast growth supplement (FGS, Cat.no. 2352) and 5 mL of penicillin/streptomycin solution (P/C Cat.no. 0503).

MTT assay was used to evaluate cell viability at 24 and 48 h according to the International Standard ISO 10993-5. The specimens were first sterilised with 70% ethanol in water and then with ultraviolet irradiation. Composites eluents were obtained by immersing the samples in 3 mL of sterile fibroblast medium within bijou vials, which were then placed onto a roller at room temperature. The supernatants were collected at 24 and 72 h time points and refrigerated at 20°C to be used for cytotoxicity measurements.

HGF cells were cultured at 37°C humidified atmosphere with 5% CO_2 to reach about 80% confluent, trypsinized and then seeded on a 96-well plate (100 μL/well) at a density of 1×10^4 cells/well. The cells were incubated at 37°C, 5% CO_2 for 24 h to allow for the cell to attach and acclimatisation prior to addition of the test eluents. After 24 h, the fibroblast media were removed from both plates and replaced with 100 μL of the leached eluents from composites. Untreated cells served as a

negative control while positive control cells were treated with 10% v/v ethanol solution. Each group consisted of five replicate wells. Then the plates were incubated for 24 or 48 h (exposure times), after which the test eluents were removed and replaced with 100 µL of MTT (5 mg/mL PBS) for 4 h. MTT solution was then removed and 100 µL dimethyl sulfoxide (DMSO) was added to each well. The plate was shaken for 5 min and the absorbance of the purple colored solution was measured using a UV–visible spectrophotometer plate Reader at wavelength 570 nm (Opsys MR, Dynex Technologies, Chantilly, VA, USA). Relative cell viability is expressed as a percentage of untreated negative control reading. Each experiment was done in duplicates.

Statistical analysis

After analysing the normality of data distribution, a one-way (ANOVA) and Tukey's *post hoc* test were employed to determine the effects of different surface modifications on flexural properties of KF reinforcements and cytotoxicity testing. A Mann-Whitney (non-parametric) test or Independent *t*-test (for normally distributed values) was used to detect the other variances between the experimental and commercial composites tested. In all tests, the level of significance was set at $p<0.05$.

RESULTS

Kevlar fiber surface modification

The FTIR spectra of the untreated Kevlar fiber showed three main peaks at 3,313, 1,640 and 1,538 cm^{-1}, arising due to the –NH– stretching, conjugated –C=O stretching and –NH– bending, respectively. The absorption bands at 1,511, 1,017 and 820 cm^{-1} are due to the (C–H) of the aromatic ring. The acetic acid treatment of the fibers led to the appearance of low intensity peak at 1,718 cm^{-1} corresponding to the C=O stretching band and the broad bands between 2,800 and 3,000 cm^{-1} of the OH– and CH– stretching, which clearly indicated that the surface was modified. The spectra of the AA & A-174 silanated fibers showed the appearance of a new absorption band at 1,718 cm^{-1}, corresponding to the carbonyl stretch, whilst the peaks at 3,313 $cm^{-1}$and at 1,538 cm^{-1} due to the –NH groups disappeared by virtue of the silanation (Fig. 3). This confirmed that the silane coupling agent reacted through the N–H group of the KF.

The surface morphology examined by scanning electron microscopy showed that the untreated fibers

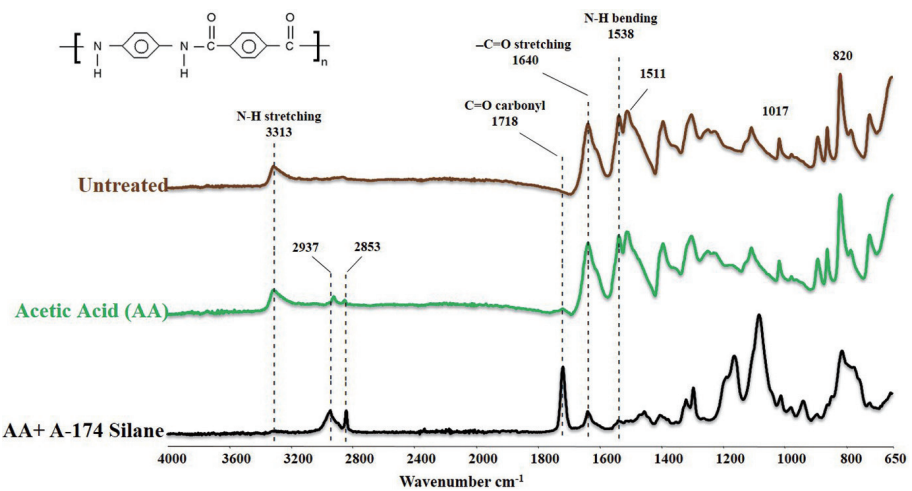


Fig. 3 FTIR spectra of virgin and modified Kevlar fibers.

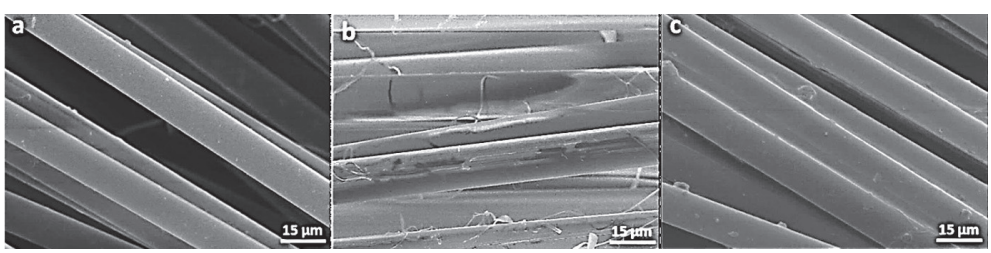


Fig. 4 SEM images of Kevlar fibers at 1,000×.
(a) Untreated KF: showed typical Kevlar features, which has a relatively smooth surface with some small impurities; (b) AA treated KF: the surface of the fiber became rougher and more blisters and pimples produced in etching; (c) AA-silanated KF: a coat of silane agent covered the surface of the fiber and some blisters are clearly visible.

Table 2 Flexural strength (FS) and flexural modulus (FM) of the semi IPN of BisGMA/TEGDMA/PMMA reinforced with Kevlar fibers subjected to different surface modifications [mean (SD), n=6]

KF surface modification	Flexural properties of KF reinforcement	
	FS in MPa (SD)	FM in GPa (SD)
Untreated KF	283.2 (47.7)*	15.4 (1.3)
Acetic acid treated KF	340.0 (36.6)	15.3 (1.7)
Acetic acid+A-174 silanated KF	394.0 (43.4)*	16.5 (2.9)

*Differences were statistically significant (p<0.05).

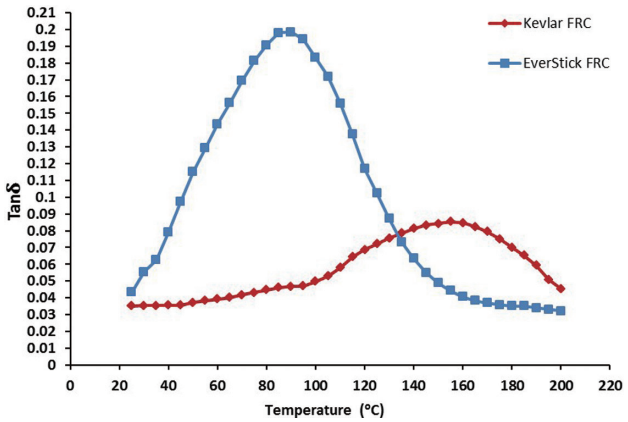


Fig. 5 DMA curves showing the temperature dependence of tan δ of the experimental composite and commercial material.
The tan δ for everStick® increased sharply with temperature comparing to Kevlar FRC; both materials show one relaxation peak (Tg). The low value tan δ of Kevlar FRC at the Tg indicates better interfacial adhesion between the fibers and the matrix.

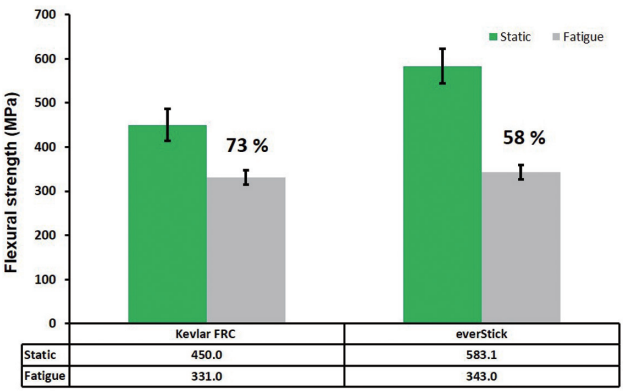


Fig. 6 Flexural strength fatigue limit at 5×105 cycles for K FRC and everStick® material.

(Fig. 4a) had a smooth texture whilst the AA-treated fibers appeared to be etched with a rough surface (Fig. 4b). However, on silanation of the AA fibers, a smooth surface reformed with some blisters (Fig. 4c) probably associated with the underlying etched surface.

The influence of fiber surface modifications on flexural properties of KF/matrix reinforcements is shown in Table 2. A statistically significant increase in the flexural strength was observed in the AA-silanated Kevlar containing fiber composites in comparison to the untreated fibers, however, there were no differences in their flexural moduli.

Characterisation of FRC post materials

1. Flexural properties

The flexural modulus (E) of the experimental K FRC was comparable to that of the commercial material, whilst its flexural strength was significantly lower (p<0.05), detailed in Table 1. Thermocycling in water significantly decreased the flexural strength of both FRC materials whilst it had no significant effect on their flexural modulus (E) (p>0.05). However, the reduction in FS of K FRC (16%) after thermal cycling was much lower than that of everStick® (35%).

2. DMA

Figure 5 illustrates the evolution of tan δ with temperature for the experimental Kevlar FRC and the commercial everStick® materials. The peaks in the tan δ curves correspond to the drop in the storage modulus (E') curves and represent the Tg values for the composites. As the temperature was increased, the K FRC showed a steady reduction in E' value and a relatively constant tan δ value, with a broad peak at ~155.2°C, whilst everStick® exhibited a sharp decrease in E' value at a higher temperature and the tan δ curve appeared to peak at 87°C.

3. Fatigue test

The static flexural strengths versus its fatigue limits at 5×10^5 cycles of FRCs results are shown in Fig. 6. The flexural fatigue limit of the experimental K FRC was about 73% of the static FS, whilst that of everStick® material was about 58% of the static value.

4. Water sorption and solubility

No statistically significant difference (p>0.05) in water uptake measured up to 28 days was observed between K

Table 3 Water sorption (Wsp) and solubility (Wsl) after 28 days immersion period in distilled water [mean (SD), n=5]

FRC group	Wsp in μg/mm^3 (SD)	Wsl in μg/mm^3 (SD)
Kevlar FRC	53.3 (3.0)	5.4 (0.67)
everStick®	47.24 (5.0)	27.2 (8.3)*

*Differences were statistically significant (p<0.05).

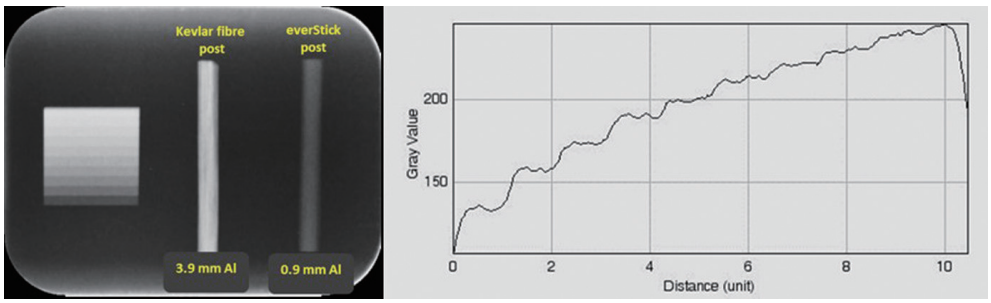


Fig. 7 Representative radiographs of experimental K FRC and everStick®POST in relation to the density of the aluminium step wedge.

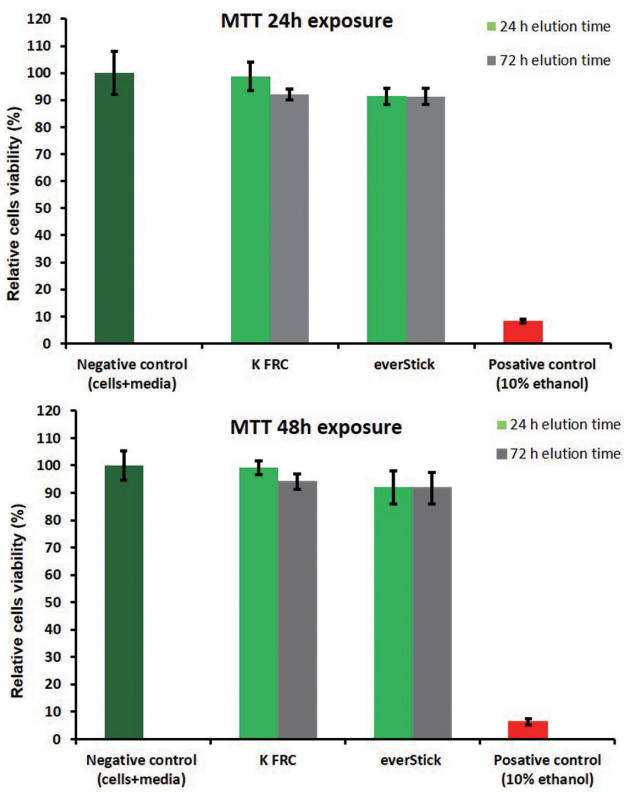


Fig. 8 The relative cell viability measured by MTT absorbance and presented as percentage of the negative control group which was set to represent 100%.
Values are the average of five replicate wells and expressed as mean and SD.

RFC and everStick®, however, the solubility of everStick® was significantly higher than that of the experimental K FRC (Table 3).

5. Radiopacity
The radiopacity of the experimental and commercial posts with the grey-scale value of aluminium step wedge measurements in (mm AL) shown in Fig. 7 indicate that K FRC posts exhibited significantly higher radiopacity (3.9±0.3 mm Al) than everStick®POST (p<0.05) at about 0.9±0.1 mm Al.

6. Cytotoxicity
The MTT assay results demonstrated that extracts from K FRC exposed for 24 and 72 h exhibited no significant reduction (about 10%) in cell viability in comparison to the negative control. No statistically significant differences were observed with everStick® (86% cell viability), however as expected the positive control had a 90% reduction in cell viability (Fig. 8).

DISCUSSION

The fibers play an important role in improving the mechanical properties of FRC's and enable the transfer of stresses from the weaker matrix under applied loads[18]. FRC posts with clear glass fiber reinforcements have gained popularity among clinicians; however longitudinal studies report various degrees of failure rates ranging between 12.8% at 2 years and 32.5% at 6.5 years[19,20]. The harsh oral environment adversely affects the mechanical properties of fiber posts, which in turn shortens the clinical durability of the restorations supported by fiber posts leading to decementation. Considering the biomechanical behavior and need of

hydrolytic stability we reported the use polyethylene-hydroxyapatite (PE-HA) thermoplastic based composite fibers as potential new post material[21], however, the structural flexibility of the composite fibers limit their use in small diameters due to the significantly lower strength compared with metal and some fiber posts. Kevlar, on the hand, has extremely good mechanical properties, however, its use in endodontic fiber posts is very limited with one study by Kim *et al.*[22], where Kevlar, glass and UHMWP fibers were used to reinforce thermosetting resin matrices fabricating three kinds of experimental FRC posts. The flexural properties of Kevlar posts obtained were between glass and polyethylene, however, the high performance of the Kevlar fibers with respect to high tensile strength and modulus was not fully utilized because of the surface inertness[23]. Hu *et al.* recently reported the feasibility of applying a high-performance fiber, poly p-phenylene-2,6-benzobisoxazole (PBO), in FRCs as a new option to develop posts with improved flexural strength using a combination of coupling agent and argon plasma methods to treat the fibers[24].

Hence employing Kevlar fibers for FRC posts required that the interfacial adhesion between the matrix and fibers be enhanced and the yellow coloration was offset to provide adequate aesthetics for a post. Kevlar fibers were thus pre-treated with acetic acid alone and also followed by silanation, especially as acid etching has been shown previously to improve the interfacial adhesion of Kevlar fibers[25]. The treatment of K fibers with AA showed changes in the surface texture (roughness) caused by etching evidenced by SEM. FTIR spectra of the etched and untreated fiber were not identical; however, detection of a few carbonyl groups present was difficult due to masking by the high intensity peaks arising from Kevlar itself (Fig. 3). However, the subsequent coupling on pre-treated Kevlar fibers clearly showed the peaks due to carbonyl absorption at 1,715 cm^{-1} confirming the successful chemical attachment of the silane coupling agent on the fibers surface[26,27]. Kevlar silanation using 2% of 3-Trimethoxysilyl propylmethacrylate silanation solution was efficient as confirmed by FTIR data, suggesting the formation of a monolayer from this coupling agent. The use of a higher concentration may lead to the lack of effectiveness resulting from over treatment with silane compounds and subsequent cohesive failure within the thicker silane coatings.

The flexural strength of the composites increased with the AA-treated fiber composites, which was attributed to mechanical interlocking resulting from surface micro-roughness of the fibers post etching. The subsequent silane coupling agent resulted in considerable chemical changes on the surface of the fibers, efficiently bound the modified fibers to the polymer matrix upon polymerization. Therefore, Kevlar/semi-IPN matrix reinforcements with superior interfacial and flexural properties were developed by using the combined benefits of chemical and physical changes obtained with these surface treatment procedures that are compatible with the resin matrix.

The rationale behind the use of semi-IPN structures, which are formed by the polymerization of the cross-linking monomers (Bis-GMA/ TEGDMA) in the presence of solvated linear polymers PMMA, is to improve both mechanical[16] and chemical adhesion[28] between polymer-based materials. The absence of a chemical union between the methacrylate-based resin composite and epoxy resin matrix of the fiber posts is the primary cause of weakness in post-to-composite bonds[29]. Epoxy polymers exhibit a high degree of conversion and highly cross-linked structures. The use of semi-IPN technology has been proved to be an effective method to enhance the adhesion of glass fibers to Bis-GMA matrix[30]. Consequently, an individually formed and *in situ* polymerized glass FRC post (everStick®) has been introduced by Stick Tech, which is used as a control in the present study.

The TiO_2 nanofillers incorporated in the final post formulation distinctly contributed to off-setting the yellow coloration due to Kevlar fibers (Fig. 1) and additionally enhanced the radiopacity, an important requirement for endodontic posts. The weight fraction of the filler was selected on the basis of optimal mechanical properties and radiographic appearance. The experimental K FRC exhibited excellent radiopacity (3.9 mm Al equivalent) to function as an endodontic post. Ideally, the radiodensity of a post material must be higher than that of dentine (1 mm Al) and similar to or slightly greater than that of enamel (2 mm Al) to facilitate their radiographic detection[31]. In contrast, everStick®POST failed to meet this requirement with significantly lower value at 0.9 mm Al, which was similar to that reported by Dündar *et al.*[32]. The titanium oxide also increased the flexural strength and modulus by about 14% (Table 1) due to the dispersion of these particles between fiber filaments, which increases the bending resistance.

Nevertheless, KF posts are less translucent than everStick® and other commercial glass fiber posts. It has been suggested that the ability of light to be transmitted along translucent posts could increase the conversion degree of light-cured resin cements with a consequent improvement of their mechanical properties, however, the efficiency of this propagation, especially in the deeper regions has still to be investigated[33]. A previous report showed no significant difference in root dentine bond strength values between translucent and opaque fiber posts[34]. On the other hand, the use of newly developed dual-cured or self-curing composites in fiber posts cementation is highly recommended to secure polymerization in deep parts of the canal[35].

A comparison of the experimental posts under static conditions indicated the flexural modulus was similar to that of human dentine (17.5±3.8 GPa)[1]. However, the flexural strength of K FRC with 32 vol% fiber content (experimental measurement) was significantly lower when directly compared with everStick® with 48 vol% (manufactured information) fiber content. The differences in material compositions and their fabrication processes with a lower concentration of fiber content may explain this observation[15]. The controlled

manufacturing process also enables incorporation of higher fiber content with fewer voids and defects in contrast to manual adaptation[2].

Thermocycling is considered as a clinically relevant testing method, representative of the hot-wet conditions in the oral cavity. The thermo-cycled posts exhibited a significant reduction in FS, consistent with literature findings[7,36]; however, K FRC exhibited a decrease of only 16% compared to 35% of everStick® (Table 1), indicating greater thermal stability (good hot–wet properties), which is expected to enhance clinical longevity. Since KF fibers have superior thermal stability in comparison to glass[14] and KF composites have better resistance to water[37], the lower extent of damage of the K FRC post thermocycling is indicative of the significant contribution of the Kevlar fibers. Hydrolytic degradation induced by leaching of glass forming oxides can weaken the silane-promoted adhesion between the glass fiber and polymer matrix[38], hence are less resistant to moisture, especially at higher temperatures. These results are also in agreement with the water sorption data that also showed a high level of solubility in everStick® indicating the elution of leachable components even on 28 days storage in water.

Under cyclic loading, restorative materials can fail considerably below their ultimate flexural strength measured in static conditions. A staircase method was used to determine the fatigue limit of each composite and the stress was defined as the stress below which failure would not occur in 5×10^5 load cycles. The experimental K FRC exhibited a fatigue limit of about 73% of its static FS value. This limit was within the range of other dental FRC materials reported earlier[39] but was significantly higher than that of everStick® (58%). The repeated loading, which weakens the fiber-matrix interfacial bonding and/or propagates a potential area of weakness (voids or cracks), affects fatigue life. The choice of fiber type and wetting resin is known to significantly influence fatigue life. Since both the experimental and commercial composites were based on IPN's the essential differences were the type of fiber reinforcements, additional use of a nanofiller and manual versus mechanical fabrication. The everStick® system has been reported to form an *in situ* semi-IPN nano-interface between the matrix and the fiber improving the mechanical properties in FRC materials. This allows the assumption that the superior performance of K FRC might be a result of the improved interfacial adhesion between fiber and matrix due to the efficient surface treatment process and the presence of the titanium oxide nano particles, which may have decreased voids and defects. Despite the manual fabrication, which is usually detrimental to fatigue due to defects present, K FRC system exhibited superior fatigue properties. The high fatigue resistance is considered as a significant factor in determining the long-term success of endodontically treated teeth as it is one of the main causes of failure of dental restorations [40].

The DMA was performed to evaluate the viscoelastic properties of post composites. As shown in Fig. 5, the variations of tan δ with temperature, which reflects the changes in modulus of the resin phase, are markedly different between the materials. For the experimental K FRC, a broader tan δ peak (Tg) at ~155.2°C was observed and the value of tan δ at this peak was significantly lower than that of everStick® material which appeared to peak at 87°C. The lower tan δ values of K FRC at temperature range experienced in the oral cavity and the higher Tg value indicate the ability of post material to retain its dimension when stresses are applied. The presence of nanofiller particles in the composites may introduce a broadening of the tan δ curve[41], whilst the extended transition region results from the high degree of structural heterogeneity and crosslinking of the polymeric network[42,43]. Here, the molecular chain interlock effect between linear PMMA and cross-linked resin of the experimental semi-IPN presented considerable advantage over the network of everStick® commercial material. The synergistic effect induced by the forced compatibility of individual components in IPN-based composites plays a critical role in determining their thermal stability and mechanical properties[44].

It is important to note that, the *in situ* light-polymerisation of everStick®POST could also result in inferior mechanical properties[16], which adversely affect clinical durability[45]. However, in this study everStick® test specimens were additionally polymerized in a light-curing oven with heat to allow further conversion of unreacted methacrylate within the polymer matrix. A lower Tg value ~55°C of everStick® material has been reported when polymerized by light only[46], with the risk of loss in dimensional stability inside the oral environment if exposed to a higher temperature exceeding its Tg.

The biocompatibility of KF and KF reinforcements has been previously reported in the literature[47], the cytotoxicity of the K FRC as a new combination from treated KF and semi-IPN matrix was evaluated by *in vitro* MTT assay. K FRCs showed no release of leachable toxic components. The cell viability was higher than 90% both at 24 and 48 h suggesting the non-toxic nature of the material. Furthermore, the use of a methacrylate based resin rather than epoxy resin as a matrix is advantageous as it overcomes any potential toxicity arising from bisphenol A[48], the most commonly used polymer matrix of commercially available FRC posts. The extracts from everStick® showed slightly higher toxicity than that of K FRC especially after 48 h of treatment, which may be attributed to the higher amount of unreacted residuals also shown *via* the water solubility study.

This study provides a new option for intracanal posts with the experimental K FRC materials exhibiting advantages over everStick® material in terms of mechanical stability and fatigue resistance. Further studies employing stress analysis, bond strength, and *in vivo* cytotoxicity tests are necessary for the clinical application of these materials.

CONCLUSION

The successful surface treatments of Kevlar fiber with AA and silane coupling agent enhanced its reinforcing

effect and its feasibility in fiber post fabrication. The compatible combination of treated KF and semi-IPN based composite results in development of new FRC with enhanced interfacial adhesion exhibit appropriate properties as intracanal post material with respect to mechanical strength and fatigue resistance as well as favourable radio-opacity and cytocompatibility.

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