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Effect on the bond strengths of glass fiber posts functionalized with poly-dopamine after etching with hydrogen peroxide

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This paper evaluated the push-out bond strengths of glass fiber posts with poly-dopamine (poly-dopa) functionalized after etching with H_2O_2. Forty extracted human, single-rooted teeth were endodontically treated and a 9-mm post space was prepared in each tooth with post drills provided by the manufacturer. Specimens were randomly assigned into four groups (n=10 per group), depending on post surface treatment used: group C (control); group D (poly-dopa); group H (H_2O_2); and group HD (H_2O_2+poly-dopa). The push-out test was performed using a universal testing machine. Results: Bond strengths (MPa) were as follows: 4.678±0.911 (group C); 7.909±1.987 (group D); 6.519±0.893 (group H); and 9.043±1.596 (group HD). The bond strength of the resin cement to posts functionalized with poly-dopa was not affected by H_2O_2 pre-treatment, while conditioning using H_2O_2+poly-dopa resulted in higher bond strengths than H_2O_2 treatment only. Compared to H_2O_2 treatment, the bond strength of poly-dopa conditioning was superior.

Keywords: Poly-dopamine, Hydrogen peroxide, Micro push-out bond strength, Fiber post

INTRODUCTION

Restoration of root canals of severely damaged teeth with relatively complete ferrules often requires placement of a fiber post to ensure adequate retention of the core[1,2]. The similar elastic moduli of fiber posts and dentin are considered to be advantageous for improving the restoration of teeth treated by endodontic means[3]. "Debonding" is the most common type of failure of prefabricated fiber-reinforced composites after restoration[4]. *In vivo* data have shown that bonds at the resin cement-fiber post interface play an important part in the outcome of fiber post-retained restoration[5,6].

To improve the bond strength between the prefabricated fiber post and resin cement, several pretreatment procedures for the surfaces of fiber posts involving mechanical and/or chemical treatment have been investigated[7-10]. With respect to chemical treatment, it has been reported that silane does not bond well with epoxy matrices[10,11]. The organic component of fiber posts is, in general, epoxy resin with a high degree of conversion and is highly crosslinked[12]. These features make formation of a strong chemical union quite difficult[7-10,13]. To improve the bond strength between silane and epoxy resin matrices, chemical and mechanical dual-role procedures for fiber posts have been investigated. Hydrogen peroxide (H_2O_2) may effectively remove the epoxy resin and expose the fibers, which can then be silanated[14,15]. Some studies have shown that etching with H_2O_2 followed by silanization can significantly improve the bond strength between fiber posts and resin composites[16-18].

Dopamine that has been polymerized steadily forms an ultrathin active layer and chemical structure that can support the matrix surface[19]. The adhesive properties of all types of materials, including polytetrafluoroethylene (PTFE), have been improved by dopamine treatment[20]. Polymerized dopamine has been found to improve the hydrophilicity and biocompatibility of polyethylene, PTFE, silicone rubber and glass[21]. Studies from our research team have shown that the bond strength of glass fiber posts (GFPs) treated with poly-dopamine was significantly higher than that of the control group subjected to the mechanical and chemical dual role of inspiration[22].

Here, we wished to evaluate the effect of etching with H_2O_2 followed by modification of the poly-dopamine functionalized surface on the bond strength of prefabricated GFPs. The null hypotheses tested were: (1) the bond strength between the GFP surface and resin cement cannot be increased by etching with H_2O_2 followed by modification of the poly-dopamine functionalized GFP surface, compared with the GFP surface treated with poly-dopamine only; and (2) the bond strength between the GFP surface and resin cement cannot be increased by etching with H_2O_2 followed by modification of the poly-dopamine functionalized GFP surface, compared with the GFP surface treated with H_2O_2 only.

MATERIALS AND METHODS

Forty freshly extracted teeth were selected on the basis of single, straight root canals of length ≥9 mm, no visible

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root cracks, caries, or previous endodontic treatment. They were cleaned of calculus deposits and soft tissues, and stored in 5% chloramine T aqueous solution at 4°C. Crowns were sectioned horizontally 2-mm coronal to the CEJ using a Precision Saw (thickness, 0.4 mm, Isomet 1000, Buehler, Lake Bluff, IL, USA) with distilled water as the coolant. The working length (wl) was set: wl=13 mm. Pulpal tissues were removed with a number-0 Barbed Broach (Mani, Tokyo, Japan). Roots were irrigated with 2 mL sodium hypochlorite (5.25%) and Prep-Rite RC Root Canal Lubricant (Pulpdent, Watertown, MA, USA) prepared using Protaper Rotary Nickel Titanium instruments (SX, S1, S2, F1, F2, F3, Dentsply, York, PA, USA) with a low-speed Rotary Endodontic Handpiece (X-smart, Dentsply), followed by ultrasonic rinsing with distilled water. Specimens were dried with paper points (Gapadent, Beijing, China), then obturated with Gutta-percha Cones (Dayading, Beijing, China) and an Endodontic Sealer (Septodont, Paris, France) using a lateral condensation technique. After endodontic treatment, teeth were stored at 37°C in 0.9% (physiological) saline for 7 days.

The GFP space of each specimen was enlarged with a standard drill system from the corresponding GFP system (Beijing Oya Biomaterials, Beijing, China) to create a 9-mm GFP space. The GFP space was rinsed with distilled water and dried with paper points.

Group control (group C)
GFPs (Beijing Oya Biomaterials) with a maximum diameter of 1.4 mm and a minimum diameter of 1.0 mm were used. The crown two-thirds portion was parallel to the columnar with 10 mm, and the apical third was 0.08° tapered with 5 mm. The fiber post was composed of 60% volume glass fiber. The glass fibers were SE8400LS (Owens Corning, Toledo, OH, USA). The resin matrix was Epoxy-828 (Shell, the Hague, the Netherlands). The apical potion of the post should be fixed in the root canal. The post surface received no conditioning.

Group poly-dopa (group D)
The post surface was ultrasonically cleaned in ethanol before use (50 Hz, 0.5 h) and conditioned with 2 mg/mL dopamine in 100 mL Tris, pH 8.5 for 14 h at 25°C under continuous stirring[23,24]. The posts were then retrieved and washed with deionized water to remove excess monomer and dried under nitrogen.

Group H_2O_2 (group H)
24% H_2O_2 is diluted from 30% H_2O_2 with distilled water. GFPs were immersed in 24% H_2O_2 for 10 min at room temperature (RT). And then rinsed with distilled water.

Group H_2O_2+poly-dopamine (group HD)
After immersion in 24% H_2O_2 for 10 min at RT, GFPs were treated as described in group D. GFPs (n=10) of the four groups were then cemented to root canals with ParaCore dual-curing resin cement (Coltène-Whaledent; Altstätten, Switzerland), according to the manufacturer's instructions. Finally, all specimens were stored at 37°C in distilled water for 7 days.

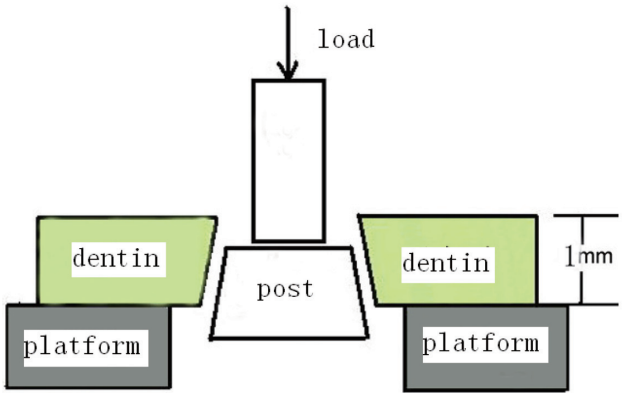

Fig. 1 Schematic illustration of micro-push-out test.

Measurement of water contact angle
Ten additional fiber posts per group were used to repeated contact angle measurement for average value for analyses of surface topography using measurement of water contact angles (Surface Electro Optics, Seoul, South Korea), and then randomly chose one post per group were gold-sputtered and evaluated with scanning electron microscopy (SEM) using an EVO 18 Special Edition Scanning Electron Microscope (Zeiss, Jena, Germany).

Micro push-out test
Samples for micro push-out testing were prepared[25]. Figure 1 shows the schematic illustration of micro-push-out test. Six slices (thickness, 1 mm) were obtained from each root using a Precision Saw (Isomet 1000, Buehler). Push-out tests were undertaken at a crosshead speed of 0.5 mm/min using a universal testing machine (Instron 1121, Norwood, MA, USA). The maximum failure load was recorded in N and converted into MPa[26]. Debonded specimens were examined using a Stereo Microscope (Kestrel, Vision Engineering, Surrey, UK) at ×50 magnification. Failure was classified according to the following criteria: adhesive failure between the cement and GFP; adhesive failure between dentin and cement; cohesive failure within cement; cohesive failure within GFP; cohesive failure within dentin; and mixed failure.

Statistical analyses
Statistical analyses were carried out using SPSS ver13.0 (SPSS, Chicago, IL, USA). $p<0.05$ was considered significant. All four groups were analyzed using one-way ANOVA and repeated-measurement ANOVA which due to heterogeneity of variance in each group

RESULTS

Interfacial strength
Mean values of the micro push-out bond strength,

standard deviation (SD) and the differences between group C[22], group D[22], group H and group HD group results are presented in Table 1 .

The results of one-way ANOVA analyses revealed that different treatments had significant influences on the micro push-out bond strength of adhesive resin cements to GFPs ($p<0.05$). Results of multiple comparisons with different groups shows in Table 1. Group HD had the highest value in the four study groups. However, compared with group D, there was no significant difference ($p=0.084$). Group HD showed higher mean values of micro push-out bond strength

Table 1 Mean (MPa) and standard deviation (SD) values of micro-push-out bond strengths using ParaCore resin cement, and the statistical analysis results with different groups

Surface condition of GFP	Bond strength (mean±SD)	Comparing Group	Mean difference	*p*
No conditioning (group C)	4.678±0.911	D	−3.2309	0.000
		H	−1.8407	0.007
		HD	−4.3642	0.000
Poly-dopamine (group D)	7.909±1.987	C	3.2309	0.000
		H	1.3902	0.036
		HD	−1.1333	0.084
H_2O_2 (group H)	6.519±0.893	C	1.8407	0.007
		D	−1.3902	0.036
		HD	−2.5235	0.000
H_2O_2+poly-dopamine (group HD)	9.043±1.596	C	4.3642	0.000
		D	1.1333	0.084
		H	2.5235	0.000

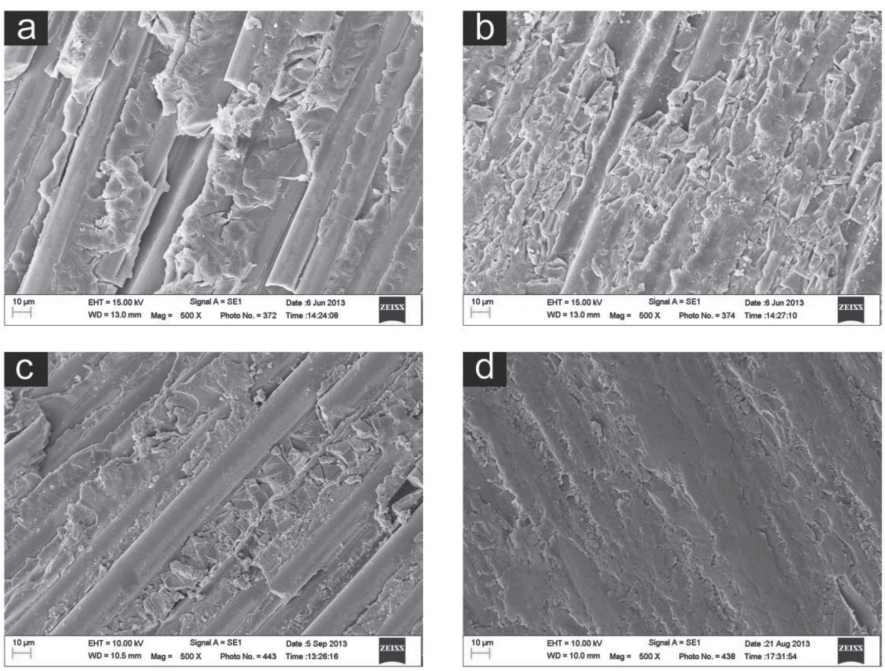

Fig. 2 Representative SEM micrographs of treated GFP surfaces.
(a) Control group (group C): untreated GFP surface. (b) Poly-dopamine-treated group (group D): the surface of the GFP has new attachment compare with (a). (c) H_2O_2-etched group (group H): more fractured fibers and significantly more exposed fibers are evident. (d) H_2O_2+poly-dopamine-treated group (group HD): due to the effect of H_2O_2, the surface of GFPs are coated more attachment compare with (b), but the etching has been lost.

than group H ($p<0.05$). The numbers of each type of adhesive failure were presented in Table 2. In groups D and C, adhesive failure was the most common type of failure[22]. Mixed failure was the most common type of failure in group H and group HD.

Measurement of water contact angle

Untreated GFPs had rough surfaces, and demonstrated a water contact angle of 63.8°. After H_2O_2 treatment, the surfaces became rougher, and the water contact angle decreased to 54.5°. The hydrophilicity of GFP surfaces have been shown to be improved by treatment with poly-dopamine, which forms an ultrathin active layer and chemical structure[19]. The water contact angle was 48.4° after treatment with poly-dopamine alone. After combination with H_2O_2, the water contact angle decreased to 41.1°.

SEM observations

SEM evaluation revealed that the morphology of GFP surfaces was modified. Compared with untreated GFP surfaces (Fig. 2a)[22], the surface of the GFP has new attachment (Fig. 2b)[22]. H_2O_2 treatment dissolved the epoxy resin matrix of GFPs and exposed more glass fibers of GFPs (Fig. 2c). Due to the effect of H_2O_2, the surface of GFPs are coated more attachment compare with Fig. 2b, but the etching has been lost (Fig. 2d).

DISCUSSION

The first null hypothesis of the present study was confirmed: the strength of the bond of the resin cement to a prefabricated GFP functionalized with poly-dopamine was not affected by H_2O_2 pretreatment. The second null hypothesis was not confirmed: the bond strength between the GFP and resin cement was significantly greater after surface conditioning with poly-dopamine after H_2O_2 treatment rather than with surface conditioning with H_2O_2 alone.

Previously, we showed that surface conditioning of GFPs with poly-dopamine significantly increased bond strength between the GFP and resin cement regardless of the cement type employed[22]. The bond strength of ParaCore to GFPs was not significantly different to that of RelyX Unicem[22]. Upon consideration of the convenience of clinical application, ParaCore was chosen for the present study. Modification of the surfaces of GFPs using poly-dopamine introduces carboxyl, hydroxyl and amino groups, which react further with organic functional monomers, thereby improving hydrophilicity and enhancing chemical combination[27].

Some authors have found that etching with H_2O_2 increases the bond strength of the adhesive core of resin composite materials to fiber posts[10,15-18]. However, few studies have shown that H_2O_2 treatment has a significant influence on the micro push-out bond strength of the adhesive resin cement to GFPs. In the present study, group H showed greater mean values of micro push-out bond strengths than group C. These results were in accordance with those of other works[28]. This effect was due to the ability of H_2O_2 to remove epoxy resin bonds through substrate oxidation[29-32] and expose the fibers, which can then be silanated[14,15]. Unlike etching methods using more corrosive forms of industrial epoxy resins (*e.g.*, sodium ethoxide, permanganate), H_2O_2 etching is a considerably milder method, whereby the mechanical properties of GFPs have been shown to be unaltered by etching with H_2O_2[33]. SEM images of the cross-sections of GFPs after treatment with 24% H_2O_2 for 10 min have shown that dissolution of the epoxy resin from GFP surfaces expose the quartz fibers to a depth of 50 μm, and allow creation of additional spaces for micro-mechanical retention of flowable composites[18]. SEM in our study showed that dissolution of the matrix of the epoxy resin created retentive areas among the fibers. Through etching, such as with potassium permanganate[10], besides exposing the quartz fibers, may activate GFPs by improving their hydrophilicity. In the present study, after H_2O_2 treatment, GPF surfaces became rougher, and the water contact angle of GFP surfaces decreased to 54.5° from 63.8°.

Previously, we were the first research team to investigate the effect on the micro push-out bond strengths of GFPs functionalized with poly-dopamine[22]. Both micromechanical retention and chemical action have effect on the bond between adhesive resin cement and fiber posts. However, chemical bonding may reduce long-term effects of micro-leakage[34], so promoting chemical bonding has been expected. Compared with the H_2O_2 treatment shown in the present study, poly-

Table 2 Failure mode of four groups

Surface condition	Failure mode (number of slices)					
	Adhesive failure		Cohesive failure			Mixed failure
	post/cement	cement/dentin	cement	post	dentin	
Group C	45	4	4	0	1	6
Group D	50	5	2	0	0	3
Group H	15	1	16	1	3	24
Group HD	7	2	10	3	3	35

dopamine showed its superiority with regard to a lower value of water contact angle: 48.4°. Moreover, group HD had significantly higher bond strength than group H. Treatment with poly-dopamine provided hydrophilic groups and chemical-bonding groups which induced chemical bonding with the resin cement[22].

The strength of the bond of the resin cement to prefabricated GFPs treated with poly-dopamine was not affected by H_2O_2 pretreatment. In this regard, group HD had higher values than group D, but the difference was not significant. The water contact angle was 48.4° after treatment with poly-dopamine alone. Upon combination with H_2O_2, the value decreased to 41.1°. The hydrophilicity of GFP surfaces was improved by treatment with poly-dopamine in combination with H_2O_2. SEM showed that the depth of etching with H_2O_2 was reduced because of the poly-dopamine coating. In groups D and C, Table 3 showed that adhesive failure between resin cement and fiber post was the most common type of failure[22]. In group HD, cohesive and mixed failure were the main modes of failure (Table 3). These results were similar to those from another study[35]. These results demonstrated that the relatively greater strength of the post-composite bond appeared to be stronger than the resin cement or GFP itself due to stress transfer. A study[33] shows that GFP treated with H_2O_2 might not impair the mechanical strength that need to be tested in future research.

In the present study, changes in the surface properties of GFPs resulted in better interfaces for chemical unions. Conditioning of GFP surfaces with poly-dopamine is a relatively novel method and merits further research in contrast to H_2O_2 treatment. More studies are required to evaluate novel fiber post surface treatment techniques compared to other classical methods.

CONCLUSION

Surface functionalization with poly-dopamine was shown to be a reliable method for improving the bond strength of resin-luting agents to GFPs. Compared with H_2O_2 treatment, the bond strength of conditioning with poly-dopamine was superior.

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