Bio-Medical Materials and Engineering 24 (2014) 2187–2195
DOI 10.3233/BME-141030
IOS Press

Influence of mesoporous silica coating treatment on push-out bond strength of zirconia posts

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Abstract. This study aimed to evaluate the influence of mesoporous silica coating surface treatments on push-out bond strength of zirconia posts. Zirconia posts (Cosmopost) were treated with vehicle (control), sandblasting plus silane application (SB+SI), a combination of sandblasting, mesoporous silica coating and silane application (SB+MSC+SI) (n=10/group). Specimens were cemented with RelyX Unicem (3M ESPE, Germany) then horizontally segmented into three sections and subjected to a push-out test. Surface treatments showed significant higher bond strength than the control group, and SB+MSC+SI group presented higher values than SB+SI group ($P<0.05$). No significant differences were found in bond strength among root regions ($P>0.05$). We conclude that the combination of mesoporous silica coating and silane application greatly enhance the push-out bond strength of zirconia posts.

Key words: Zirconia, posts, mesoporous silica coating, push-out, root region

1. Introduction

Increasing numbers of aesthetic restorations have demanded the development of post materials with better fracture resistance [1,2]. Zirconia post system was introduced in the mid-1990s, and it showed higher fracture resistance than the older posts made of cast gold or titanium [3]. Several short-term clinical studies have reported that zirconia posts yield favorable clinical results although there is a lack of long-term evidence [4]. However, several *in-vitro* studies had suggested that zirconia posts possessed lower retention than other types of posts [5,6].

Therefore, more studies are required to develop coating materials to improve the retention of zirconia posts to dentin. Different surface treatments, such as sandblasting with aluminum oxide particles [7], etching with hydrofluoric acid [8], silane application [9], silica coating [10] or the combination of these treatments [11] to the post surface have been widely used to enhance the adhesion of feldspathic ceramics by increasing the mechanical interlocking or the chemical bond.

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However, the composition and physical properties of high-strength zirconium ceramics have large differences with silica-based ceramics. The absence of glassy phase and silicon dioxide makes them resistant to etching in hydrofluoric acid and not amenable to silanization [12]. Besides, the risk of microcrack generation with the use of air abrasion was also reported [13]. Excessive air abrasion may even induce chipping or loss of ceramics, compromising the mechanical properties and clinical performance of the ceramic restorations. Even though silica coating could enhance the bond strength between zirconium ceramics and composite resin [10], the improvement of bond strength was not satisfying. For these reasons, alternative surface treatments of zirconia prior to bonding are necessary.

There has been a growing interest on nanostructured mesoporous silica materials, which are chemically composed of silica with nanometric pores. These bioceramics exhibit intricate nanoscale porosity, which translates into surface areas above 1000 m^2/g, high selectivity of encapsulating biorelevant molecules and controlled surface chemistry [14]. These unique features make them particularly amenable to physical absorption and chemical modification, whereby organic molecules may be combined to produce new functional materials with great stability [15]. It is reported that mesoporous silica materials has been used in dental composites considering their potentiality in creating micromechanical filler/resin matrix bonding at the interface [16]. However, the roles of mesoporous silica coating on resin luting agents and zirconium ceramics in their bonding strength have not been examined yet.

Based on the above rationale, we aimed to evaluate the influence of mesoporous silica coating treatment and silane application on push-out bond strength of zirconia posts in root canals. We hypothesized that mesoporous silica coating treatment followed by silane application could greatly improve the bonding strength between zircornia posts and the resin composites.

2. Experimental methods and materials

2.1. Specimen preparation

This study was performed with the approval of the local ethical committee. Thirty permanent single-rooted teeth were collected and none of these teeth had carries, cracks or restorations. 2 mm above the mid facial cemento-enamel junction (CEJ) perpendicular to the bonded interface were sectioned using a diamond disc (Songfeng Corporation, China) in order to form a flat surface. Hand files (SybronEndo, CA) were used to instrument root canals, which were then irrigated with 20 ml 5.25% sodium hypochlorite (NaOCl) (Nanguo Corporation, China) and dried using paper points (Edward Corporation, China). Lateral condensation technique with gutta percha (Edward Corporation, China) was carried out for root canal obturation. Afterwards, post spaces were prepared to form a space with 9 mm in length and 1.8 mm in diameter.

2.2. Fabrication of suspension of mesoporous silica particles

In a typical procedure, tetraethyl orthosilicate (TEOS) (3.2 g), ethanol (2.3 g), Pluronic F-127 (1.0 g) and HNO_3 (0.54 g, 0.3 mol/l) were mixed at room temperature for half an hour to produce suspension of mesoporous silica particles.

2.3. Surface treatment

Zirconia posts (20 mm in length and 1.7 mm in diameter; Ivoclar, Liechtenstein) were divided into three groups (n=10) according to the following surface treatments: Control group: no treatment; sandblasting and silane application group (SB+SI): blasting with 50 -μm Al_2O_3 particles at 0.28 MPa for 15 s at a distance of 10 mm followed by silane application (ESPE Sil, USA); sandblasting then mesoporous silica coating and silane application group (SB+MSC+SI): firstly blasting with 50-μm Al_2O_3 particles at 0.28 MPa for 20 s at a distance of 10 mm, then mesoporous silica coating with a coating machine (SYDC-I, Sanyan Corporation) and drying for 1 h in the oven upon gelation at room temperature, later heat treating at 400°C for 2 h to remove the Pluronic F-127 template followed by silane application (ESPE Sil, USA).

2.4. Post cementation

Posts were cemented with RelyX Unicem, a self-adhesive and dual-polymerized resin cement (3M ESPE, Germany). Root canals were first washed with water and dried. The bonding material was then directly applied into the root canal. The post was placed into the depth of the root canal by finger pressure, which lasted for 8 min after cementation. An explorer was used to remove excess cement. Finally, the bonding material was polymerized using an ultraviolet curing light from different axial angles for 40 s. The specimens were thereafter stored in distilled water at 37°C for 24 hrs.

2.5. Sectioning of tooth segments

Tooth segments were firstly mounted in acrylic resin and then horizontally sectioned under water cooling to produce 4 sections. The top 0.5 -mm section was discarded considering the containing of the extra portion of the post and excess bonding material. Afterwards, the remaining tooth sections (coronal, middle and apical) each with a 1.5 mm in height were prepared and used for the push-out test.

2.6. Push-out test

A universal testing machine (Lloyd Instruments, UK) was used to perform the push-out test. Load application was performed with a special constructed tip (1.2 mm in diameter), which was centered on the post section only. The tip pushed the post at a crosshead speed of 0.5 mm/min. The maximal dislodging force that made extrusion of the specimen was recorded. Bonding strength values were calculated using the following equation:

$$PBS = F/A \tag{1}$$

Where PBS is bond strength values (MPa), F is the peak force (N), A is the adhensive area (mm^2). The bonded area was the lateral surface of the cylinder, which was calculated according to the equation:

$$A = 2\pi rh \tag{2}$$

Where π is constant = 3.14, r is the radius of the post, and h is the thickness of each section.

2.7. Observation of post/cement bonded interface

To observe the micro morphology of cement/post bonded interface, additional 2 coronal, 2 middle and 2 apical sections were selected in each group before the push-out test and coated with gold-palladium alloy using a sputter-coating technique (Anatech Ltd, Alexandria). A scanning electron microscopy (SEM) (FEI, Holland) was utilized to examine the sections at ×3000 magnification at 20 Kv.

2.8. Statistical analysis

Two-way ANOVA was conducted to analyse the data of push-out bond strength values. Tukey's HSD test (α=0.05) was performed to test statistical differences between groups. All analyses were conducted using the SPSS 13.0 software.

3. Results

3.1. Bonding strength of zirconia post to dentin

Descriptive data are presented in Table 1. The two-way ANOVA analysis is presented in Table 2, which indicated significant differences in mean bond strength values among different surface

Table 1

Mean values of push-out bond strength (MPa) of zirconia posts using different surface treatments

Surface treatment	Bond strength (MPa)	Root region	Bond strength (MPa)
Control	7.15 ± 0.87	Coronal	7.22 ± 0.95
		Middle	6.99 ± 0.81
		Apical	6.82 ± 0.76
SB+SI	8.84 ± 0.92	Coronal	9.13 ± 1.20
		Middle	8.83 ± 1.13
		Apical	8.40 ± 1.06
SB+MBC+SI	15.73 ± 1.68	Coronal	16.11 ± 1.84
		Middle	15.82 ± 1.53
		Apical	15.13 ± 1.17

Table 2

Two-way ANOVA on effects of surface treatments and root regions

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Surface treatment	1323.831	2	661.915	987.136	.000
Root region	3.660	2	1.830	2.729	.071
Surface treatment* root region	.519	4	.130	.193	.941
Error	54.314	81	.671		
Total	11424.251	90			

treatments (P<0.05) while no statistical differences among root regions (P>0.05). The mean push-out bond strength in SB+MSC+SC group was the highest (15.23±1.68 MPa), while the values in the control group was the lowest (7.15±0.87 MPa). Multiple comparisons with Tukey's HSD test revealed the bond strength between any two groups had a significant difference ($P<0.05$). n = 10/group.

3.2. Illustration

The cementation process of zorconia post to root canal is shown in Figure 1.

3.3. Microscopy

Representative SEM photographs of control group (a), SB+SI group (b), SB+MBC+SI group (c) are shown in Figure 2 at a magnification of ×3000, demonstrating micromorphology of the post/cement bonded interface.

4. Discussion

Tensile and shear tests are most commonly used to assess post retention. However, the two tests are not capable to exert uniform stresses on the tooth surface-due to the large bonding surface area [17]. Microtensile test has overcome these shortcomings with a smaller bonding area. But high premature

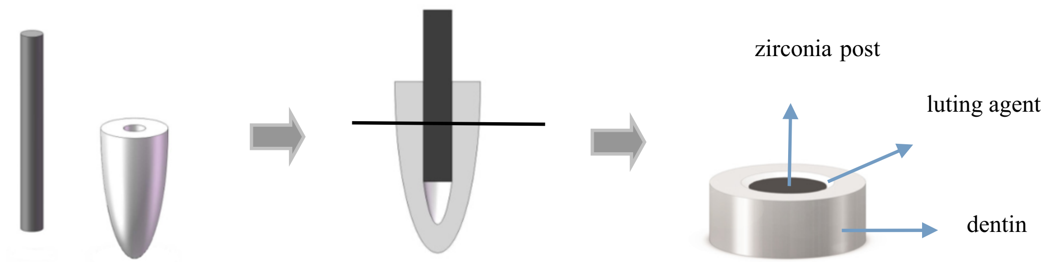
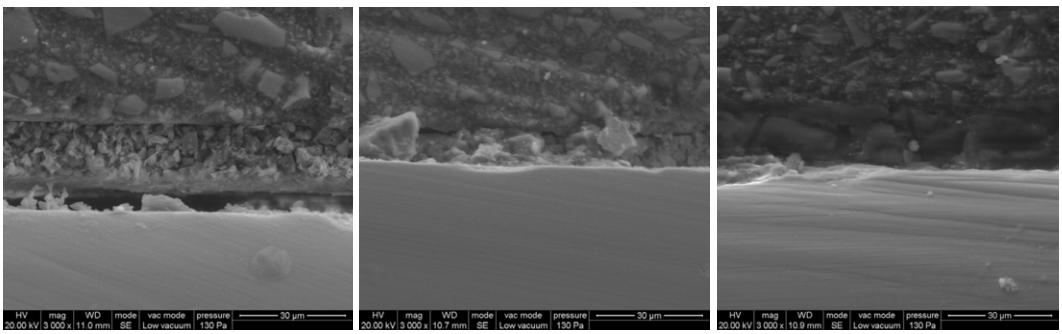


Fig. 1. The schematic illustration of the post cementation.



(a) (b) (c)

Fig. 2. Representative SEM photographs (original magnification ×3000) of post/cement bonded interface: (a) control group, (b) SB+SI group, (c) SB+MBC+SI group.

failure rate during specimen preparation and large data distribution still exist in the microtensile test methodology [18]. Instead, a compromise between the above tests can be offered by push-out tests by using post segments of 1-2 mm in height, which features smaller bonding areas but avoids premature failures. Therefore, a push-out test was adopted in the study.

In the control and SB+SI group, the resin composite did not infiltrate into surface of zirconia post. However, complete fusion of post/cement bonded interface was observed in SB+MSC+SI group (Figure 2). Although it is not recommended to alter post surfaces by the manufacturer of Cosmopost [19], the present study has shown that the application of surface treatments greatly improve bond strength with resin luting agent. The low bond strength values between untreated zirconia posts and composite resin may be attributed to the smooth surface of the posts, which prevent any macromechanical and micro mechanical retention to resin luting agents [20]. Therefore, evaluation of the effect of surface treatments on bond strength of zirconia posts is necessary.

The present study evaluated several surface treatments including mechanical and chemical bonding procedures. In SB+SI group, mechanical bonding was achieved by roughening post surfaces using 50-μm grain sized Al_2O_3 particles. The roughening procedure increases the total bonding area and the wettability of the zirconia post with resin luting agent [21]. Madani et al. [22] and Awliya et al. [23] found that airborne-particle abrasion was more effective in producing high bond strength between resin luting agent and a zirconium ceramic substrate compared to hydrofluoric acid, a diamond rotary cutting instrument grinding, or polishing treatments. In addition, the application of silane coupling agent also contributes to the bonding values by promoting a chemical bond to resinous materials via cross-linkages with methacrylate groups as well as improving the substrate surface energy and surface wettability to resin [24].

Nevertheless, the bond strength value in SB+SI group (8.84 ± 0.92 MPa) was significant lower compared to that in SB+MSC+SI group, which supports the hypothesis that the bond strength between zirconia posts and the resin composites could be greatly improved by using mesoporous silica coating treatment. This finding may be explained with the combination of nanostructured mesoporous silica materials, whose chemical composition is silica present in nanometric pores, and silane coupling agent. Although surface roughening creates mechanical retentive areas where silane molecules lodge and link inorganic molecules of the ceramic crystalline phase to organic molecules in the resinous material, improvement of the bond strength between high-strength ceramics and resin may be limited because of low silica content of these materials [25]. Therefore, the silica-coating technique in SB+MSC+SI group is supposed to increase the surface silica content and to establish chemical silica-silane (siloxane) bonding. Furthermore, nanostructured mesoporous silica materials, including mesoscopic order, tunable pore dimensions in the molecular size range, a high pore volume and surface area [26], allows for much higher bonding area and surface energy, as well as a great improvement of surface wettability to resin. Difference in surface texture among SEM photographs further confirms that silane infiltrating roughened structures is facilitated by mesoporous silicone coating.

The mesoporous silica material used in this study was prepared by using a surfactant template solution-gelatin (sol-gel) method. This method involves inserting a surfactant template to HNO_3-catalyzed sol-gel reaction of tetraethyl orthosilicate. The templates are removed by heating when the monolith is generated, leaving the silica particles like interconnected porous structure [27]. This system has an advantage that silica-coating units are available without the requirements of special equipments or high expenses. It has been reported that a tribochemical silica coating could increase the bond strength between high-strength ceramics and resin luting agent [10,11]. However, this silica-coating method is technically complicated and cannot produce nanometric coating matercials.

A number of studies have been conducted to investigate the effect of bonding materials on the renention of zirconia posts to denin. It is known that conventional bonding materials such as glass ionomer and resin-modified glass ionomer provide lower retention compared to adhesive resin luting agents [28–30]. In addition, conventional resin cements are reported to be less capable than chemically adhesive resin cements [31]. RelyX Unicem is a representative self-adhesive resin cement, which posesses high chemical bonding capacity to dentin because of its contents-phosphoric acid monomer and methacrylate monomers [32]. Bitter et al. [33] indicated that the bond strength of zirconia posts cemented with RelyX Unicem resin cement was similar to other types of chemically adhesive resin cements. Considering this reason, RelyX Unicem was selected as the bonding material in the present study.

Considering the influence of different root regions on bond strength values in this investigation, the coronal sections were found to have the highest values and apical sections demonstrated the lowest values regardless of the surface treatment used (Table 1). However, there were no significant differences among different root regions. This finding can be explained with the simplified cementation process of RelyX Unicem which does not require pretreatment and is applied directly into the root canals. This result is consistent with other studies [34,35].

It was also reported that the high initial bond strength of zirconia posts obtained by surface treatments might decrease due to artificial aging such as water storage at a constant temperature [36]. However, the current study was limited to test instant bond strength. Consequently, more investigations on the evaluation of the influence of surface treatments on retentive values after artificial aging are necessary. Moreover, other mechanical properties, such as flexural strength of zirconia posts with the use of mesoporous silica coating should also be analysed.

In summary, the combination of mesoporous silica coating and silane application can significantly increase the bond strength between zirconia posts and resin luting agents. In contrast, the root regions have no significant influence on the bonding strength between zirconia posts to dentin when cemented with RelyX Unicem.

Acknowledgment

This work was supported by National Natural Science Foundation (31070857 and 50973045), Project on the Integration of Industry, Education and Research of Guangdong Province (2012B091000147) and Open Project Program of Shanghai Institute of Ceramics, Chinese Academy of Sciences (SKL201207SIC).

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