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Non-thermal plasma enhanced bonding of resin cement to zirconia ceramic

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1. Introduction

Zirconia materials differ from other high strength dental ceramics because of their distinct mechanism of stress-induced transformation toughening, which means that the material undergoes microstructural changes when submitted to stress[1,2]. Conventional methods of adhesive cementation, which include prior acid etching of the ceramic surface with hydrofluoric acid and further silanation, are usually considered not efficient for zirconia ceramics because of their lack of a silica and glass phase [3–5].

Investigations have been concentrated on enhancing zirconia bonding to dental substrates for long-term stability. To achieve micromechanical attachment, physical abrasion (particle air-abrasion or diamond bur) is used [6, 7]. This treatment raises the concern that such an aggressive modification can impart critical flaws at the surface which in turn could facilitate premature catastrophic failure [8–10]. The application of tribochemical silica has been shown to exhibit high bonding strengths and is clinically acceptable; however, it involves physical abrasion, embedding small silica particles into the roughened yttria-stabilized zirconia (YSZ) surface. Long-term stability of this interface is uncertain and may vary

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widely depending upon application technique. Coupling such treatments with silanation has been shown to create chemical bonding through siloxane bonds resulting in increased relative bonding strengths [11]. However, these interfaces are susceptible to hydrolytic degradation. Furthermore, long-term stability of these bonds primarily relies on a physical (ZrO)A(SiO) bonding and can thus degrade over time [12].

Non-thermal plasma technique provides a well-controlled and reproducible way to clean, activate, etch, or modify substrate materials to improve their characteristics or achieve totally new surface properties [13]. This has led to an enormous success in surface engineering and processing of solid state materials, including plastic, metal, or ceramic materials. Non-thermal atmospheric plasma can produce a flux of various active uncharged species of atoms and molecules. These active uncharged species typically include ozone (O_3), NO, OH radicals, etc. More importantly, the most distinguishing characteristic of plasma treatment is a significant flux of charged species including both electrons and ions. Depending on the plasma gas chemistry, these highly reactive plasma species, including electronically excited atoms, molecules, ionic and free radical species, react with, clean, and disinfect living tissue/organ surface materials, or form a nano-scale thin layer of plasma coating. There is a great flexibility in optimizing the plasma for specific purposes, for example, the amount of NO, ozone, O_2^- , and H^- .

In this study, we used an atmospheric cold plasma brush (ACPB) to modify the surface chemical composition and hydrophilicity of zirconium ceramic surfaces and thus improve ceramic adhesion. To our best knowledge, it is the first time that a non-thermal plasma brush has been used as a novel approach to modify zirconium surfaces for better bonding strength.

2. Materials and methods

2.1 Specimen preparation

Recently extracted non-carious bovine incisors were used to obtain cylindrical enamel specimens. The labial surfaces of incisors were flattened using an Isomet 5000 diamond saw (Buehler, Lake Bluff, IL, USA) and 3.5-mm thick slices with enamel surface were obtained. The slices were sectioned in the “x” and “y” axis, which resulted in cubes with a $2 \times 2 \times 3.5$ -mm dimension. Forty cubes with enamel surface were prepared and stored in distilled water at 37°C. Thirty zirconia plates with a dimension of $5 \times 3 \times 0.75$ mm were obtained from a 94% ZrO_2 stabilized by 5% Y_2O_3 ceramic (Cercon Smart Ceramics, Degudent, Hanau, Germany) and ten plates with the same dimension obtained from lithium silicate (IPS ceramic, Ivoclar, Lichtenstein). Atmospheric cold plasma brush was set as following: argon flow 3 slm (standard liter per minute), oxygen flow 30 sccm (standard cubic centimeter per minute), output current 10 mA, output voltage 0.8kV. The distance between the surfaces of the ceramic specimens and the tip of the plasma torch nozzle was fixed at 5 mm.

2.2 Group assignment and treatment procedure

Thirty yttrium-stabilized tetragonal zirconia plates (Y-TZP) were randomly allocated into three groups (n=10) according to the surface treatment and ten lithium silicate plates were assigned as the positive control group. Three groups each with 10 Y-TZP plates were

submitted to one of the following surface treatments: none (negative control), 2-min plasma treatment and 5-min plasma treatment. Ten specimens of lithium silicate as positive control received hydrofluoric acid (HF) etching and silane coupling-agent treatment.

After receiving assigned plasma treatment, the zirconia specimens were coated with silane agent immediately and completely dried with compressed air. The adhesive resin cement (Calibra Dentsply USA) was applied and light cured for 20 seconds using a halogen light source. The enamel surface was etched with 35% phosphoric acid for 15 seconds, rinsed with water for 15 seconds and dried with compressed air. The resin cement was applied to both enamel surface and ceramic surface. The enamel cube was then cemented to the ceramic surface and was light cured for 20 seconds using a Spectrum 800 (Dentsply, Milford, DE, USA) following the product manual. In the positive control group, the cleaned lithium silicate plates were etched with 4% hydrofluoric acid (Porcelain Etchant, Bisco) for 4 min, rinsed with copious amount of water, dried with compressed air, and then treated as the same as the other groups.

2.3 Shear bonding strength test and Fracture analysis

Plastic boxes made by 3D printer with the size of $8 \times 10 \times 5$ mm were used as molds to mount the enamel cube-ceramic plate specimens. The epoxy resin was used as mounting material. The mounted specimens were stored in a humid chamber at 37°C for 24 h prior to testing. Each ceramic plate with its enamel cubes was fixed to a microshear device adapted to a miniature load testing machine (Instron 3367, Norwood, MA, USA). The shear force was applied at a crosshead speed of 1 mm/min until debonding.

After debonding, the fractured surfaces were evaluated with an optical microscope (AMscope, California, CA, USA) to classify the failure modes into one of the following categories: (A) adhesive failure at the interface between the ceramic and resin cement or between the resin cement and the enamel interface; (C) cohesive failure within the ceramic, within the resin cement or within the enamel only; and (M) mixed failure for adhesive and cohesive failure at the same site. The fractured surfaces and cross sections of selected debonded specimens were evaluated using a field-emission scanning electron microscope (SEM).

2.4 Scanning electron microscope (SEM) and energy-dispersive spectroscopy (EDS)

Six additional Y-TZP plates were used and examined with scanning electron microscopy (Quanta 600, FEI, OR, USA) to evaluate the changes in the ceramic topography after the plasma treatments and after being coated by silane agent. The Y-TZP plates ($n=2$ for each group) were plasma treated and then coated by silane agent as described previously. They were then assessed with SEM. Moreover, energy-dispersive spectroscopy (EDS) was used for identifying and quantifying elemental composition of the treated areas of specimens. Quantitative analysis of the percent weight concentration of the probed elements was performed by nonstandard analysis.

2.5 Contact angle measurement

At room temperature the Sessile drop method was performed to evaluate the wettability of a planar untreated, 2-min-surface treated, and 5-min-surface treated Y-TZP specimens by gently dropping a droplet of deionized water onto the specimen surface. The static contact angle values were obtained by a goniometric method ($n = 5$).

2.6 Statistical analysis

Bonding strength data was statistically analyzed by one-way ANOVA, with surface treatment as the main factor. Multiple pair-wise comparisons were accomplished using the Tukey test. Statistical analysis was carried out in SAS 9.1 with a significance level of 5%.

3. Results

Shear bond strength results are presented in Table 1. The experimental groups with plasma treatment had significantly greater shear bond strength than the untreated group ($p < 0.05$). Although conventional lithium silicate group using HF etching and silane coupling agent exhibited the highest shear bond strength, two-minute plasma treatment of Y-TZP plates resulted in 64.6% increase in shear bond strength and five-minute plasmas treatment produced 88.6% increase in shear bond strength, compared to no-treatment Y-TZP group. Although the five-minute plasma treatment group had higher shear bond strength than the two-minute group, the difference was not statistically significant. More importantly, the five-minute plasma treatment of Y-TZP resulted in a shear bond strength statistically equivalent to that of the conventional lithium silicate plate using HF etching and silane coupling agent (Table 1).

Adhesive failures were most prevalent in the negative control group, accounting for about 80% of fracture failure mode. Other treatment groups had only about 30–40% fracture failure being adhesive fracture. As the plasma treatment time increased, the percentage of adhesive fractures decreased while other types of fractures increased (Table 1). A typical cohesive failure was observed in experimental group and illustrated in Fig 1a and 1b.

Scanning electron microscopy (SEM) was used to evaluate the morphological changes of ceramic surfaces in different treatment groups. SEM images showed no significant morphologic changes on the Y-TZP plates after plasma treatment. Plasma treatment did not modify the surface mechanical property of Y-TZP plates (Fig 1c and 1d). No perceivable cracks were observed in the Y-TZP plate surface after plasma treatment. Plasma treatment group had lower contact angles. The mean angle was 76.5 degree for the untreated Y-TZP group and 7.4 degree for the 2-minute plasma treatment Y-TZP group (Figure 1e and 1f). A lower contact angle after plasma treatment indicates that the zirconium surface becomes more hydrophilic, thus increasing its wettability and potential surface reactivity.

SEM evaluation (Figure 2a–2f) showed the difference of silane-agent distribution on the surface of the Y-TZP plates between no treatment and plasma treatment groups. Untreated Y-TZP surfaces coated with silane-agent showed gathering of silane-agent, while silane-agent spread widely and equally on plasma treated Y-TZP surfaces. Plasma treatment changed the surface reactivity of Y-TZP plates and increased the affinity of silane agent to

the surface. With increasing plasma treatment time, the silane-agent spread more widely and homogeneously. Figure 3 showed the EDS analysis of Y-TZP surfaces coated with silane agent. Fig. 3a is the EDS spectrum of a specific spot of the surface without plasma treatment prior to silane agent application, which showed no Si content detectable, indicative of patchy surface salinization. Meanwhile, the surface with plasma treatment followed by silane agent application (Fig. 3b) exhibited considerable amount of Si. As a matter of fact, the mean silicon content on untreated Y-TZP surfaces was 5.3%, while it was 8.1% on plasma-treated Y-TZP surfaces. Plasma treatment greatly increased the silicon content by 52.8% as compared to the untreated.

4. Discussion

Zirconia material is widely used in clinical applications not only because of its outstanding mechanical property but also its high opacity, especially for the cases where dark abutments are involved. Unfortunately, the poor bonding strength of zirconia is a clinical challenge and limits its usage in veneer restoration, which requires less reduction of the prepared tooth than the crown.

Previous studies showed that air abrasion increases surface area which favors wettability [14–16]. Some Y-TZP manufacturers suggest the use of air abrasion or tribochemical coating prior to adhesive cementation. Other studies have suggested the use of Er: YAG (erbium-doped yttrium aluminum garnet) laser to enhance the bond strength of adhesive materials to resin composites used for indirect restorations and lithia-based ceramics [17,18]. However, some studies showed that the microporosities created by surface treatments, such as air abrasion or laser, may act as crack initiators, weakening ceramic materials [8–10]. The long-term effect of these alterations on the durability of Y-TZP restorations is unknown and needs further research. In this study, ACPB is mild non-thermal plasma treatment and thus less physically aggressive to the Y-TZP surface. SEM images demonstrated no significant change in the surface topography of Y-TZP plates after the plasma treatment, which suggested non-thermal plasma treatment would not result in substantial change in physical and morphological properties of Y-TZP restorations. This is important in ceramic veneer restorations since these types of dental restorations are very delicate and precise, which are used mainly for esthetic purposes.

The plasma treatments investigated in the current study resulted in significant improvement of shear bonding strengths. The mean shear bonding strength obtained from five-minute plasma treatment was equivalent to that obtained by the conventional clinical protocol of HF etching and silane coupling-agent coating on lithium silicate plates, which is considered the gold standard for ceramic bonding. In this study, we investigated the possible mechanism of plasma treatment to improve bond strength between enamel and zirconia ceramic. Our study showed that plasma treatment resulted in significantly lower contact angle, indicative of increased hydrophilicity of zirconia surface. Thus, these surfaces have much better wettability for dental bonding. Moreover, SEM images demonstrated considerable qualitative differences in the surface topography of Y-TZP plates coated with silane-agent after the plasma treatments. Silane-agent spread widely and uniformly after plasma treatment. Plasma treatment also results in higher silicon content in the surface of Y-TZP

coated with silane-agent. All these analyses suggest that plasma treatment significantly increase the hydrophilicity of the Y-TZP surface and makes it more wettable for silane and dental adhesives. An increase in the plasma treatment time could induce a higher number of hydrophilic polar groups on the surface. It suggested the possibility that the bonding strength might continue to improve by increasing plasma treatment time. The analysis of fracture mode showed that the fracture was most cohesive or mixed after plasma treatment, which indicates a significant decrease in adhesive failure. This finding is consistent with that of a previous report of surface treatment of feldspathic ceramic using non-thermal atmospheric plasma [19]. The failure mode results also showed that adhesive failures mostly occurred between resin cement and Y-TZP plate. This might suggest that, even when higher bonding strength to zirconia is obtained, this bond is not as strong as that between enamel and cement material. In the current study, only the immediate bonding strength (measured 24 hours after cementation) was tested. The long term bond strength at months after cementation is not known. Further study on the structural analysis of plasma adhesion using ACPB and its durability under various conditions such as water storage, thermocycling and mechanical loading is needed to better understand the adhesion mechanism.

5. Conclusion

Due to the unique combination of simple design, relatively low capital and operational cost, the utilization of non-toxic gases, operating at near room temperature, and the absence of harmful residues, the non-thermal plasma may be a cost-effective method to modify the surface of zirconia ceramic material to improve bonding strength for both clinical and dental laboratory use, in particular for zirconia veneer procedures.

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Fig 1. Shear bond strength according to surface treatments: negative control, two-minute plasma, five-minute plasma, and positive control. Different letters indicate a statistically significant difference in shear bond strength.

Fig 2.

Fracture mode distribution according to surface treatments: negative control, two-minute plasma, five-minute plasma, and positive control. Mode A: adhesive failure at the interface between the ceramic and resin cement or between the resin cement and the enamel interface. Mode B: cohesive failure within the ceramic, within the resin cement or within the enamel only. Mode C: mixed failure for adhesive and cohesive failure at the same site.

Fig 3.

3a and 3b: Cohesive failure after plasma treatment with an oblique fracture. Z-zirconia, R-resin cement, and E-enamel. 3c and 3d: SEM images (1000x) of ceramic surfaces. 3c: Y-TZP surface untreated; 3d: Y-TZP surface after plasma treatment. No significant morphological differences were observed between the Y-TZP plates after plasma treatment and no plasma treatment. 3e and 3f: Contact angles of untreated control specimen (3e) and 2-min treated specimen (3f)

Fig4.

SEM images (original magnification 40X (a c e) and 400X (b d f)) of Y-TZP surfaces, silanization with silane-agent. Note differences in silane-agent distribution between images (4a and 4b: no plasma treatment; 4c and 4d: 2 min treatment with plasma; 4e and 4f: 5 min treatment with plasma), Untreated Y-TZP surface coated with silane-agent showed gathering of silane-agent as the arrow points. And silane-agent spread widely and equally with the increase of plasma treatment time.

Fig5.

EDS analysis of Y-TZP surface coated with silane-agent. Note that the silicon content was higher for the silica-coated specimens after plasma treatment (5b) than for those specimens without plasma treatment (5a).

Shear bond strength (SBS) and fracture mode distribution according to surface treatment

Table 1

	Ceramic surface treatment	Mean shear bond strength (MPa)	Range of shear bond strength (MPa)	percent increase	Fracture Mode (%)		
					A	M	C
Negative control	none	14.79±4.47 ^a	10.30–19.52	0	80%	0	20%
Experimental group 1	2 minute exposure to plasma	24.34±4.95 ^b	15.89–32.20	64.6%	40%	20%	40%
Experimental group 2	5 minute exposure to plasma	27.89±3.31 ^{bc}	22.73–33.01	88.6%	30%	40%	30%
Positive control	HF and silane coating to lithium silicate	31.97±4.75 ^c	26.17–37.38	114.7%	40%	20%	40%