Preliminary studies on the effects of in-situ synthesized polycrystalline particulates on the bonding strength of resin to zirconia ceramic surface

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Abstract

Objectives—To develop a novel zirconia surface modification method to improve the shear bond strength of resin cement. **Methods** Yttrium-stabilized tetragonal zirconia (Y-TZP) discs (~~16 mm in diameter, 1.5 mm in thickness~~) were cut from prefabricated ceramic blocks and polished ~~with water proof silicone carbide paper until 1200#~~ **through 1200-grit SiC abrasive**. Based on the immersion time of zirconia disc in HF solution, zirconia samples were divided into four groups: ~~C, without immersion treatment; I₃, I₅ and I₇, immersed in the HF solution for 30 s, 50 s and 70 s, respectively (n=11).~~ Then, **put** samples to CaCl₂ solution (~~0.1 mol/L~~) for 90 s, dipped in NaOH solution from 20 °C to 80 °C in a water bath, kept at 80 °C for 2 h. After final sintering (~~1450 °C~~), surface appearance and chemical components were characterized with scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and x-ray diffraction (XRD), respectively. The surface roughness of discs was measured as well. Shear bond strength of zirconia to resin cement was tested and the failure mode was analyzed. Three point bending tests were done to determine the flexural strength of samples. The statistical analysis was also done for all above data. **Results**—ZrO₂ polycrystalline particulates were in situ synthesized on the surface of zirconia substrates. The Ra values of the four groups were 0.27±0.05 μm, 0.89±0.34 μm, 1.04±0.41 μm and 1.41±0.38 μm, respectively. The treated group was statistically significant different from the control group (p<0.05). Three point

bending strength values of the four groups were 7.88 ± 1.94 MPa, 11.87 ± 3.7 MPa, 17.84 ± 6.21 MPa and 16.27 ± 5.87 MPa, respectively, and those of I_5 and I_7 were statistically different from that of C ($P < 0.05$). The failure mode was mainly adhesive in group C and mixed in I_5 . Three point bending strength values of the four groups were 730.21 ± 56.91 MPa, 689.81 ± 73.75 MPa, 704.25 ± 91.44 MPa and 702.28 ± 86.05 MPa, respectively, without statistically significant difference between each other ($p > 0.05$).

~~**Significance** In-situ synthesized polycrystalline particulates on zirconium ceramic surface can effectively improve the bonding strength of resin, avoid micro cracks and maintain the mechanical strength of ceramics.~~

In the conclusion, in-situ synthesized polycrystalline particulates on zirconium ceramic surface can effectively improve the bonding strength of resin, avoid micro cracks and maintain the mechanical strength of ceramics.

Keywords: Zirconia; in-situ synthesis; polycrystalline particulates; surface; mechanical strength

1. Introduction

Because of superb properties of yttria-stabilized tetragonal zirconia polycrystalline (Y-TZP) ceramics, including flexural strength, chemical stability, biocompatibility and tooth-like color, they have already been applied in dentistry for all-ceramic crowns, long-span bridges, posts and cores [1-5] and even implants [6,7]. In zirconia restorations, the adhesive bonding of resin cement to ceramic substrates and teeth is one key to its clinical success [8], which mainly depends on micromechanical and chemical environments [9,10]. Up to present, many effective surface treatment techniques [11,12] have been used to improve the bond strength of resin to zirconia ceramics, such as surface air abrasion [13-15], diamond burs abrasion [16], silicoating [17] and selective infiltration etching [18]. Other studies have also shown that laser could improve the bond strength of resin to zirconia ceramics [19-21].

However, microscopic cracks have been found in some studies because of these surface treatments and accelerate tetragonal-to-monoclinic (t→m) phase transformation [19,21-25]. On the other hand, the character of chemical stabilization of Y-TZP reduces the efficiency of adhesive characteristics [26-28].

In this study, a novel in-situ method was developed to improve the shear bond strength between resin cement and Y-TZP, avoid micro cracks and maintain the mechanical strength of ceramics.

2. Materials and Methods

2.1 Specimen preparation and treatments

Prefabricated ceramic blocks (High transparent material, Nissin-Metec China Co., Ltd., China) were cut with a diamond saw (Isomet 4000 Linear Precision Saw, Buehler, USA) into discs (16 mm diameter, 1.5 mm thickness) with copious water. Similarly, three-point bending bars (25×5×1.5 mm) were prepared. The specimen surface was polished ~~with water proof silicone carbide paper until 1200#~~ through 1200-grit SiC abrasive. Substrates were ultrasonically cleaned in deionized water to remove surface debris prior to use, and then randomly divided into four groups: C as control, I₃, I₅ and I₇ as experimental groups. The experimental groups were immersed in HF acid solution for 30 s, 50 s, and 70 s, respectively (Table 1). After samples were immersed to 0.1 mol/L CaCl₂ solution for 90 s, they were dipped in 1 mol/L NaOH solution which was heated from 20°C to 80°C in a water bath. After held at 80°C for 2 h, all samples were sintered in the sintering furnace (ZSK 1700, Cassini (Beijing) Electric Co., LTD., China), with the heating speed of 5°C/min to 1450 °C. After 2 h at 1450 °C, all samples were cleaned in deionized water for 10 min.

2.2 Surface characterization of specimens

Scanning electron microscope (Phenom-world Co., LTD., Netherlands, SEM) was used to evaluate the surface morphology changes of zirconia, which were treated with different methods. The average surface roughness (Ra) and topography were measured with a surface-texture and contour measuring instrument (JB-4C, Shanghai Taiming Optical Instrument Co., Ltd., China) and the cut-off value was set at 0.8 mm and the traversing length of stylus (tip radius of 2 μm) was 4 mm. The average values were calculated from measurements done at 3 different points. 3D Roughness Reconstruction (Phenom proX scanning electron microscopy, Phenom-World B.V., Holland) was done to confirm the similarity of depth and width of scratches in one specimen of each group. In addition, interfaces between polycrystalline particulates and zirconia discs were observed with SEM.

The composition of zirconia surfaces was investigated with energy dispersive spectrometry (EDS). The specimen of group C and I₃ were examined by X-ray Diffraction (XRD 7000 X-ray diffractometer, Shimadzu, Japan) with Cu α radiation ($\lambda=1.5406 \text{ \AA}$). The experimental conditions were the following: 2θ range of 20–80 ° at 2 °/step and 6 s photon counting time per step. The relative mass fraction of monoclinic phase (X_m) on the zirconia surfaces was calculated according to Garvie and Nicholson's formula:

$$X_m = \frac{I_m(\bar{1}11) + I_m(111)}{I_m(\bar{1}11) + I_m(111) + I_t(101)}$$

where X_m is the relative amount of monoclinic phase, $I_m(\bar{1}11)$ is the intensity of monoclinic peak at 28.2 °, $I_m(111)$ is the intensity of monoclinic peak at 31.5 °, and $I_t(101)$ is the intensity of tetragonal peak at 30.2 °.

2.3 Shear bond of zirconia/resin composite

All discs were ultrasonically cleaned in deionized water for 10 min, dried with

clean air flow and kept in a desiccator. Self-adhesive resin cement (Valux™ Plus, 3M ESPE, USA) was properly made into resinous column (5 mm in diameter, 4 mm in thickness) with stainless steel mold. Before bonding, a single transparent polyethylene tape with a diameter of 4 mm was fixed on the specimen surface. Composite resin bonding material (Variolink N Ceramic Primer, Ivoclar Vivadent AG, Liechtenstein) was properly applied to bond zirconia specimen and resinous column according to the manufacturer's instruction, cured from the lateral side for 20 s with a light curing unit (Elipar™ 2500, 3M ESPE, USA) under the weight of 20 N force. All discs were then kept at 37 °C for 24 h. Each specimen was embedded in an acrylic mold with methyl methacrylate resin and subjected to bonding tests. Shear bond tests were performed on a universal testing machine (AG-X Plus, Shimadzu Co., LTD., Shimadzu, Japan) at a crosshead speed of 0.5 mm/min until the separation of the resinous column from the zirconia-based ceramic. A force was applied to the specimen so that the shear load was exerted adjacent to and directly to the bonding interface. The average shear bond strength was calculated from 10 data. Each shear bond strength data was calculated according to the formula:

$$\sigma=F/S$$

where σ is shear bond strength (MPa), F is maximum load shear force (N), and S is bonded area (mm²).

2.4 Failure mode analysis

The failure between the zirconia and resin stub was defined as 'adhesive'. The failure within either the zirconia or resin stub was defined as 'cohesive'. The term 'mixed' failure was used to describe the combination of these two failure types. The fractured surfaces were observed with scanning electron microscope under 1000×magnification.

2.5 Three point bending tests

Three point bending test were performed on a universal testing machine at a crosshead speed of 0.5 mm/min until the fracture of specimen. The average three point bending strength was calculated from 10 data. Each three point bending strength was obtained according to the formula:

$$\sigma = 3Fl/2wb^2$$

where σ is three-point bending strength (MPa), F is breaking load (N), l is the test span (mm), w is the width of specimen (mm), and b is the thickness of specimen (mm).

2.6 Statistical analysis

Results were expressed as mean $\pm$ SD. Statistical assessments were carried out with one-way analysis of variance and Turkey's HSD pairwise multiple comparisons. And the value of $p < 0.05$ was considered to be statistically significant.

3. Results

3.1 Surface characterization

From SEM images shown in Fig. 1, regular polycrystalline particulates were found on the zirconia matrix surface. With the increase of immersion time in HF, polycrystalline particulate distribution density became more connected closely. As shown in Fig. 2 of SEM section surface image of sample I₅, polycrystalline particulates grew in situ on the surface and stuck the zirconia substrates together. As shown in Fig. 3 of EDS spot scanning of I₅, the chemical composition of all polycrystalline particulates only had Zr and O.

XRD result of group C (red) was mainly from rectangular crystalline phase ZrO_2 , group I_5 (blue) with rectangular and monoclinic crystalline phase ZrO_2 (Fig. 4).

Fig. 5 shows the mean and standard deviation values of surface-roughness of the matched and experimental groups. Compared with C group ($0.27 \pm 0.05 \mu\text{m}$), mean R_a values of these experimental groups were $0.89 \pm 0.34 \mu\text{m}$, $1.04 \pm 0.41 \mu\text{m}$ and $1.41 \pm 0.38 \mu\text{m}$, respectively. The control C was significantly different from I_3 , I_5 and I_7 ($p < 0.05$).

The representative images of 3-D were shown in Fig. 6. Differences of specimen surfaces were verified from reconstructed 3-dimensional images. I_3 , I_5 and I_7 showed irregular outlines. With the increase of immersion time, the polycrystal particulates were more connected closely.

3.2 Shear bond tests

Shear bond strength values of these four groups were shown in Fig. 7. The values of C, I_3 , I_5 and I_7 were $7.88 \pm 1.94 \text{ MPa}$, $11.87 \pm 3.7 \text{ MPa}$, $17.84 \pm 6.21 \text{ MPa}$ and $16.27 \pm 5.87 \text{ MPa}$ respectively, and the shear bond strengths of I_5 and I_7 were statistically significant, compared with that of C. The shear bond strength of I_5 was also the largest.

3.3 Failure mode analysis

Failure types and distribution were presented in Table 2. The main failure modes were found to be exhibited adhesive and mixed types. Especially, in group C, it was almost entirely adhesive failure type. Cohesive failure within zirconia occurred only in the three treatment groups, and typical mixed type from I_5 was shown in Fig. 8, in which matrix side had residual resin binder and ZrO_2 polycrystalline particulates. Resin side had fractured ZrO_2 polycrystalline particulates and pits. Zirconia matrix cohesive damage also occurred between zirconia and zirconia polycrystalline particulates in I_7 .

3.4 Three point bending tests

Three point bending values of these four groups were shown in Fig. 9, with mechanical strengths of 730.21 ± 56.91 Mpa, 689.81 ± 73.75 Mpa, 704.25 ± 91.44 Mpa and 702.28 ± 86.05 Mpa, respectively. And there was no significant difference ($p > 0.05$). It seemed that the treatment had limited effect on the mechanical strength of zirconia matrix.

4. Discussion

The chemical stability of Y-TZP ceramics in acid and alkali solution depends on its dense sintering, whereas the crystal phase is decided by its dense sintering temperature. Zirconia ceramic can be etched in hydrofluoric acid without being densely sintered [29]. The rate and level of reaction have relations with concentration of hydrofluoric acid at room temperature, atmospheric pressure, reaction time and temperature and so on. However, dense sintering makes etching ineffective in hydrofluoric acid and hydrochloric acid at room temperature and pressure with the same influence on quality and surface of zirconia matrix [30].

Chemical reactions in this study were shown in Eq. 1. HF reacted with ZrO_2 on the surface of pre-sintered zirconia to produce ZrF_4 , the ZrF_4 reacted with CaCl_2 to produce ZrOCl_2 , ZrOCl_2 reacted with NaOH in the water heating to produce $\text{Zr}(\text{OH})_4$, the $\text{Zr}(\text{OH})_4$ decomposed at the high temperature (1450°C) into ZrO_2 and H_2O , and thus the ZrO_2 polycrystalline particulates was in-situ synthesized on the zirconia substrates.

Eq. 1

Eq. 2

Eq. 3

Eq. 4

Equations Chemical equations in this study.

In the SEM images, the regular geometry polycrystalline particulate structures were observed on the treated zirconia surface. EDS analysis showed the chemical composition of the polycrystalline particulates only included zirconium and oxygen, and XRD confirmed they were monoclinic zirconia. The zirconia polycrystalline particulate could significantly increase surface roughness of the ceramic, which offered a large number of micro-mechanical lock junction structures in the bonding, to significantly enhance the retention, which further proved that the increase of bond strength was mainly due to surface roughness and micro-mechanical lock knot [17,23]. Furthermore, the zirconia polycrystalline particulate had a good junction with the matrix with no obvious boundary (Fig. 2).

Because HF reacted with ZrO_2 to produce more ZrF_4 , with the increase of immersion time in HF, polycrystalline particulates became more connected closely. With more ZrF_4 , more polycrystalline particulates would be produced, resulting in the roughed surface (Figs. 5 and 6).

To estimate bond strength, there are many methods such as shear bond tests, bending tests, and tensile tests with push-out tests to be used. In this study, shear bond tests were chosen due to not only many reports [31,32] in the same experimental category, but also severe testing method. The specimens of in-situ synthesized polycrystalline particulates had larger surface roughness as shown in Fig. 5, leading to greater shear bond strength than those of group C. The relation between surface roughness and shear bond strength was not a linear relationship [33] because

excessive rough surface might lead to stress concentration to consequently weaken the interfacial bonding between zirconia and resin.

The failure mode results suggested that all groups mainly had adhesive and mixed failure types. Cohesive failure within zirconia occurred only in the three treatment groups, probably because the overmuch polycrystalline particulate distribution density reduced the mechanical strength. While, in control group C, the failure type was adhesive type due to the relatively smooth surface, chemical inertness of zirconia [34,35] and no inherent glass content in the matrix of zirconia. In group I₅, main failure mode was mixed type, because the proper polycrystalline particulates distribution density had the retention effect and the particulates also improved the surface roughness of the zirconia substrates (Fig. 8). In some area of the experimental groups, the connection area between polycrystalline particulates and zirconia matrix was small, which was not enough to resist shear force, therefore zirconia matrix cohesive damage happened.

Three point bending values were relatively lower in the treatment groups, but they were not significantly different. Hydrofluoric acid could reduce specimen thickness before dense sintering, resulting in a decreased mechanical strength, another reason might be due to that the immersion treatment to change the structure of the pre-sintered zirconia.

5. Conclusions

In this study, all experimental results showed that in-situ synthesized polycrystalline particulates on zirconia ceramic surface was a very powerful method to increase surface roughness and successfully improved the bonding strength between zirconia and resin, with advantages of low cost, short processing time and no hidden cracks. However, further studies are still needed to explore the variables in size, quantity, distribution of in-situ synthesized ZrO₂ polycrystalline particulates and vitro cell experiments of osteoblasts.

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Appendices

Figure captions

Fig. 1. SEM images of groups C, I₃, I₅ and I₇.

Fig. 2. SEM image of I₅ section surface.

Fig. 3. EDS results of group I₅.

Fig. 4. XRD patterns of groups C (red) and I₅ (blue).

Fig. 5. Sample roughness after surface treatment. C-control C; I₃-group I₃; I₅-group I₅; I₇-group I₇. Vertical bars indicate standard deviation and identical letters indicate their difference is not significant (P < 0.05).

Fig. 6. Representative 3-D images of groups C, I₃, I₅ and I₇.

Fig. 7. Shear bond strength after surface treatment. C-control C; I₃-group I₃; I₅-group I₅; I₇-group I₇. Vertical bars indicate standard deviation and identical letters indicate their difference is not significant (P < 0.05).

Fig. 8. Shear bond tests: A-zirconia matrix side, B-resin stub side.

Fig. 9. Three point bending after surface treatment. C-control C; I₃-group I₃; I₅-group I₅; I₇-group I₇. Vertical bars indicate the standard deviation. These four groups are not significantly different (p > 0.05).

Table captions

Table 1. Surface treatments for zirconia samples

Table 2. Failure types of the four groups (after 24 hours)

Equations

Chemical equations in this study.

Eq. 1

Eq. 2

Eq. 3

Eq. 4

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Table 1. Surface treatments for zirconia samples

Group	N	Immersion time in HF(s)	Immersion time in CaCl ₂ (s)	Immersion time in NaOH(h)
C	10	-	-	-
I ₃	10	30	90	2
I ₅	10	50	90	2
I ₇	10	70	90	2

Table 2. Failure types of the four groups (after 24 hours)

Group	Mode of failure		
	Adhesive	Mixed	Cohesive
C	9	1	0
I ₃	7	2	1
I ₅	2	7	1
I ₇	5	3	2

Graphical abstract

In-situ synthesized polycrystalline particulates on zirconium ceramic surface can effectively improve the bonding strength of resin, avoid micro cracks and maintain the mechanical strength of ceramics.