Evaluation of surface properties and shear bond strength of zirconia substructure after sandblasting and acid etching

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Keywords: zirconia, surface treatment, sandblasting, hot sulfuric acid, hydrofluoric acid, shear bond strength

Supplementary material for this article is available online

Abstract

To compare the effects of different surface treatment methods on the surface characteristics of yttria-stabilized tetragonal zirconia (Y-TZP) and relevant shear bond strength (SBS) between zirconia and composite resin. Forty-eight Y-TZP ceramics were randomly divided into four groups based on the specific surface treatments: Group C (blank treatment), Group Sand (sandblasting with 80 μm Al2O3 particles), Group HF (etched with 40% hydrofluoric acid for 10 min), and Group H2SO4 (etched with hot sulfuric acid for 10 min). Surface characteristics of the treated specimens, including morphology, roughness, wettability, chemical composition and crystalline structure were analyzed. SBS was tested by bonding ceramics to resin cement in the same group. Kruskal-Wallis test followed by pair wise comparison was conducted for statistical processing. A significance level of α = 0.05 was set. Three kinds of surface structures with different widths and heights in roughness were obtained, including micron-scale pit/peak size by sandblasting, nano-scale pit/peak size by hydrofluoric acid etching and middle submicron-scale pit/peak size by hot sulfuric acid etching. By comparison, the specimens of Group HF showed the most favorable wettability, the highest SBS and the lowest phase transformation than those of other groups. Therefore, HF etching was considered as a promising surface treatment to promote resin–zirconia bonding without excessive surface damage. The height, width, frequency and regularity of roughness altogether affected the shear strength.

1. Introduction

Y-TZP has become one of the most commonly used ceramic in prosthetic dentistry owing to its excellent esthetic performance, biocompatibility and mechanical properties (i.e. high strength and fracture toughness) [1, 2]. Also, great strides made on computer-aided design and computer-aided manufacturing (CAD/CAM) have broadened applications of Y-TZP ceramic in dentistry [3]. However, the main complications of zirconia, including chipping of porcelain veneer and loss of retention of prosthesis significantly restrict its clinical application [4]. Voidani et al [5] reported that the cementation space of zirconia crowns fabricated using CAD/CAM system is larger than that using the conventional dewaxing technique. Hence, an insufficient bond strength of the cement may lead to dislodgement of zirconia restorations [5]. Effective surface treatment methods aiming to increase the bond strength between the zirconia surface and the cement are necessarily required [6, 7].
HF acid (4%–10%) etching is typically utilized to improve the resin bonding of traditional ceramics although it is ineffective for Y-TZP at room temperature because of its high crystalline and silica-free structure [8]. Sandblasting with alumina particles followed by 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) containing primer is the most frequently cited surface treatment. The long-term reliability of zirconia, however, will be impaired because of sandblasting-induced micro-cracks on the surface [6, 9]. Various zirconia surface modification methods have emerged, such as tribochemical silica coating [2, 10, 11], laser treatment [9, 12, 13], the application of liner [4], selective infiltration etching [14, 15], plasma spraying [6, 7], surface fluorination [5], and the newly developed spraying and brushing technique [16]. These strengthening mechanisms involved in zirconia surface modification include either roughening surface to create micro-retentive structures or inducing chemical changes using silane coupling agents, and sometimes both [17]. However, their disadvantages should not be neglected, such as insufficient adhesion and being susceptible to thermal cycling, expensive equipment, complicated operation, and difficulty in standardization [4, 7, 11].

Another new surface modification for Y-TZP, hot HCl/Fe2Cl3 etching, has been previously applied for conditioning the wings of Maryland bridges [18]. Compared with sandblasting, the zirconia, which is treated by hot chemical etching method for 10 min, particularly increases the bond strength between zirconia and resins [19]. Furthermore, composition changes of the etching solution result in differences of resultant bond strength on zirconia surface [17]. Hot acid etching with H2SO4/(NH4)2SO4 and HF/HNO3 is capable of creating excellent three-dimensional networks at a nano-scale, which significantly improves bond and bond durability of Y-TZP [2]. Similarly, Liu et al [17] demonstrated that 25-min application of 48% hydrofluoric acid solution at 100 °C increases resin-zirconia bond strength, without leading to a tetragonal to monoclinic (t-m) crystalline phase transformation. On the other hand, concentration or duration also plays an important role in the etching rate of acid solution [3]. Recent studies have found that zirconia can be etched by high-concentration acids at room temperature. It is reported that the application of 40% HF for 15 min significantly increases the roughness of the zirconia surface [20]. Therefore, surface treatment of zirconia with a traditional acid solution is a promising approach.

It is generally considered that for the current surface treatment techniques on Y-TZP, surface roughness height, namely the mean roughness (roughness average, Ra), is the most important factor affecting the bond strength between zirconia and polymer [21]. Other surface characteristics, such as surface roughness width, namely the size of pits and peaks, and their uniformity, however, are rarely analyzed.

The advantage of acid etching is that it uniformly roughens the surface of the material and exerts no stress on the material, thereby avoiding the risk of material delamination [22]. For establishing a simpler and more economical surface treatment, in the current study, three kinds of different surface characteristics in Y-TZP treated by common sandblasting and short term hydrofluoric acid etching, and self-developed hot sulfuric acid etching. Differences on the surface micro morphologies, profiles, hydrophilicity and SBS of resin cement to Y-TZP ceramics were compared. The null hypothesis was that different surface treatment techniques do not have any effect on the condition of zirconia surface, manifesting as no significant difference in the bond strengths.

2. Material and methods

2.1. Preparation of zirconia specimens and surface treatment

Considering a 20% volumetric shrinkage during the sintering process, pre-sintered Y-TZP blocks (12.5 × 12.5 × 3.75 mm) were fabricated using a cutting machine (BNA5090, Ningbo, China) from zirconia ceramic blanks (UPCERA ST, Shenzhen, China) and then sintered following the manufacturer’s recommendations (1530 °C, holding time: 2h). Forty-eight zirconia ceramic blocks with a final dimension of 10 × 10 × 3 mm (±0.01) were obtained. The materials used in the current study were summarized in table 1. One surface of each specimen was grinded consecutively with 400, 800 and 1200 grit silicon carbide (SiC) papers (ISO 9001:2000, KOREA) and finally polished with 3.0 and 1.0 μm diamond powder. After polishing, the specimens were rinsed with de-ionized water. These ceramic blocks were randomly divided into four groups (n = 12) using SPSS 23.0 (IBM, Armonk, New York, USA): Group C (control group): No further modification treatment. Group Sand: Ceramic surfaces were sandblasted using 80 μm aluminum oxide particles from a distance of approximately 10 mm at an angle of 45° for 20 s. The air pressure applied for the blasting was set at 0.2 MPa. Group HF: Zirconia blocks were etched in hydrofluoric acid solution (40% HF) for 10 min at an ambient temperature (22 ± 1 °C), rinsed thoroughly with de-ionized water for clearing the residual acid, and finally air-dried. Group H2SO4: Y-TZP plates were dipped in boiling sulphuric acid for 10 min, followed by washing and drying as above mentioned. The volume ratio of 98% concentrated sulphuric acid to water was 2: 1, and the measured peel point was 196.5 °C. To avoid disturbance of surface impurities on the surface testing, all
Table 1. Materials used in the current study (source: manufacturers).

| Material          | Brand name                  | Composition and performance                                                                 | Manufacture       |
|-------------------|-----------------------------|---------------------------------------------------------------------------------------------|-------------------|
| Composite resin   | Filtek™ Z350 XT Universal Restorative | bisGMA, UDMA, TEGDMA, PEGDMA and bis-EMA resins, silica filler (20 nm), zirconia filler (4 to 11 nm), zirconia/silica cluster filler Bending strength is not less than 50 MPa | 3M ESPE, St. Paul, USA |
| Flowable resin    | Filtek™ Z350 XT Flowable Restorative | bisGMA, TEGDMA and Procrylat resins, ytterbium trifluoride filler (0.1–5.0 microns), silica filler (20 nm, 75 nm), zirconia/silica cluster filler Three-point bending strength 300 MPa | 3M ESPE, St. Paul, USA |
| Zirconia          | ST zirconia                 | ZrO₂ + H₂O₂ + Y₂O₃ (≥99%), Y₂O₃ (4.5%–5.5%), Al₂O₃(<0.5%) Three-point bending strength 1200 MPa | UPCERA ST, Shenzhen, China |

Abbreviations: Bis-EMA, bisphenol A diglycidyl methacrylate ethoxylated; Bis-GMA, bisphenol A glycidyl dimethacrylate; PEGDMA, ethylene glycol dimethacrylate; TEGDMA, triethyleneglycol dimethacrylate; UDMA, urethane dimethacrylate.

Specimens were sequentially washed with 100% ethanol and de-ionized water in an ultrasonic cleaner for 15 min each, and finally dried under airflow.

2.2. Contact angle measurements
To evaluate the wettability of the surfaces to water, static contact angles were measured using a contact angle goniometer (LSA100, Lauda Scientific GmbH, Germany). A 4-μl droplet of de-ionized water was dripped onto the specimen surface at room temperature. After a settling time of 3 s, the image of the drop was taken by a charge-coupled device (CCD) camera. Meanwhile, the image processing software (SurfaceMeter™, version 1.2.1.9) automatically made six measurements, giving the left and right contact angles and their mean values. Measurements were performed on 3 samples randomly selected for each group (12 samples in total), one point per sample and averaged.

2.3. Atomic force microscopy (AFM)
To investigate surface roughness and topographical features of the ceramics, images of two ceramic surfaces per group were acquired using an atomic force microscope (Dimension ICON, Bruker, Germany). For each sample, we recorded five images, at a scan size of 5 × 5 μm and a resolution of 256 × 256 pixels, at a slow scan rate corresponding to 0.999 Hz. The images were taken in tapping mode in air and finally were manipulated for transformation from 2D into 3D by the matching AFM analysis software (NanoScope Analysis, v180r2sr3). The Ra values, namely the arithmetic mean of the absolute value of the contour offset within the sample length, were also calculated with the software.

2.4. X-ray diffraction (XRD)
Phase components were identified using X-ray diffractometer (XRD, D8-discover, Bruker-AXS, Germany). Diffraction data were collected within the 2θ range of 20°–70°. The peaks were read using MD1 Jade v6.0 to identify peaks and phases. Peak patterns were plotted by a set of line positions 2θ degree against intensity using the Origin Pro 2016.

2.5. Scanning electron microscopy (SEM), surface elemental analysis and porosity test
Sirion200 Field Emission Scanning Electron Microscope (FE-SEM, FEI, American) was conducted to investigate the surface morphology of specimens (n = 1), either with surface treatment or not. Prior to mounting on the stub of SEM, all specimens were sputter-coated with a layer of gold–palladium and then examined under different magnifications. An energy dispersive x-ray spectroscopy (EDS, OxfordAzter X-Max 80) coupled to the SEM was used to characterize the elemental chemical composition. The duration of acquiring EDS images was 60 s. One specimen was randomly selected from each of Group C, Group HF and Group H₂SO₄ for porosity test by mercury intrusion porosimetry (MIP, AutoPore IV 9500, micromeritics, USA).

2.6. Preparation of bonding specimens
A nylon mold (inner diameter: 6 mm, height: 2 mm) was placed in a glass tank of equal height, followed by the placement of the composite resin material (Z350 XT, 3M ESPE, St. Paul, USA) in the mold with a filler and compaction. The upper end was flattened with the cover of the tank and light-cured for 2 s by a dental curing light (Elipar Free-light 2, 3M ESPE, USA) with an output power of 1200 mW cm⁻². Then, forty-one pre-polymerized composite resins (diameter: 6 mm, height: 2 mm) were produced. Considering that platinum residue on the surface of zirconia may affect the shear strength after SEM observation, the zirconia block (one per group) was excluded. MIP is a destructive technique. Therefore, zirconia blocks after the porosity test were
also discarded. Finally, 10 zirconia (11 for Group Sand) ceramic blocks per group were ultrasonically cleaned again as described above to remove possible contamination. A resin cylinder was bonded to each zirconia surface with a layer of light-cured flowable resin (Z350 XT, 3M ESPE, St. Paul, USA). Subsequently, a piece of lead weighing 50g was placed over the resin cylinder for 2 min aiming to obtain equal cement thickness in all ceramics. The center gravity of zirconia, resin column should be consistent to that of the lead. Excess cement was immediately removed with a microbrush and the specimens were eventually light-polymerized from four directions along the interface with an interval of 20 s. The procedure of bonding specimen fabricating was shown in figure 1.

2.7. Shear bond strength test
After 12 h of chemical polymerization, the bonding specimens were individually embedded in a polyvinyl chloride (PVC) tube with autopolymerizing acrylic resin and they were submitted to a shear strength test using a universal Testing Machine (Instron 3365, ElectroPlus, USA). As shown in figure 2, the test was performed at 1 mm min⁻¹ crosshead speed, and the shear force parallel to the zirconia-composite interface until fracture occurred was applied. The SBS was calculated by dividing the failure load (N) by the bond area (mm²). Following the testing, all debonded zirconia ceramic surfaces were observed using a ZOOM 645S camera stereoscopic microscopy at 10× magnification, and fracture pattern was classified as adhesive failure (complete exposure of

Figure 1. A process of fabricating bonding specimen (a) Experimental equipment: glass tank, glass cover, nylon mold and filler (b) Composite resin filling (c) Initial curing with an LED curing light (d) Pre-polymerized resin cylinders (e) Final curing (d) Bonding specimen.

Figure 2. Shear bond testing (A) The test method (B) Test fixture (a) Shear tool (b) Composite resin cylinder (c) Zirconia (d) Acrylic resin (e) PVC tube.
the ceramic surface without residual resin cement), cohesive failure (a fracture inside the resin column or resin cement), and mixed failure (partial exposure of the ceramic surface with residual composite resin or resin cement).

2.8. Statistical analysis
SPSS 23.0 (IBM, Armonk, New York, USA) was used for statistical analysis. Figures were depicted using the OriginPro Version 2019b (OriginLab Corporation, Northampton, MA, USA). Measurement data were subjected to analysis of normal distribution. Non-normally distributed data were expressed as mean (Q25, Q75), and compared using Kruskal-Wallis test. Multiple differences were conducted using pairwise comparison. Two-tailed p < 0.05 was considered as statistically significant.

3. Results

3.1. Contact angle (CA)
Images of the contact angles on different surfaces and statistical results were presented in figure 3. All surface treatments of the ceramics increased their hydrophilicity. The mean contact angle values of the water droplets were slightly dropped to 35.950 (25.600, 56.200) after sandblasting and 22.500 (18.375, 29.525) after sulfuric acid treatment. The average value of the control group was 48.600 (48.300, 67.200). The lowest contact angle 18.250 (13.425, 19.725) was observed following HF etching (P < 0.05).

3.2. AFM and surface roughness
Representative 2D and 3D images obtained through the AFM analysis of specimens subjected to different surface-conditioning methods were depicted in figure 4. The control group showed a relatively smooth surface with a small quantity of irregular granular protrusions and pits scattered on the surface of the zirconia ceramic (figure 4(a)). In sandblasted specimens (figure 4(b)), large irregular protrusions and irregular wide pit were visible, which were possibly caused by the impact and abrasion of the sand. By comparison, specimens in Group HF (figure 4(c)) and Group H2SO4 (figure 4(d)) presented more uniform pits and peak distribution, whilst Group HF displayed acicular features.

Compared with the control group, sandblasting and H2SO4 etching significantly increased the surface roughness of ZrO2, as illustrated in figures 4(e) and (f). The surface roughness height and average roughness (Ra) were counted from ten different areas per specimen. Statistically, Group H2SO4 had the highest roughness height, followed by Group Sand, and the roughness height of Group HF was much lower than that of the other two groups due to the formation of a very fine nano-scale pit/peak size.

Besides the roughness height, a significant difference was detected in these surface texture as AFM images revealed (figures 4(a)–(d)), which was supported by their roughness profile curves of two diagonal sections. Based on the roughness profile curves under the 2D and 3D AFM images, an obvious difference in the roughness width, namely the pit size, was identified between Group Sand and Group H2SO4, corresponding to micron-
3.3. X-ray diffraction analysis

The XRD scans of the four surfaces either with the surface treatment or not were illustrated in figure 5. Typical peaks of the monoclinic ZrO₂ phase were clearly identified from Groups Sand, HF and H₂SO₄ at 2θ of 28.275°. The volume percentage of the monoclinic phase crystal formed on the surface gradually increased in Group HF (9.8%), Group H₂SO₄ (12.63%), and Group Sand (14.2%). The surfaces showed a peak at 2θ of 30.3° as well, which was characterized for the tetragonal phase of ZrO₂ and further specific peaks for the tetragonal phase could be identified.

3.4. Morphology and porosity analysis

SEM findings revealed a homogeneous and flat surface in the control group without any surface treatment of zirconia. However, small pits could be seen under a high magnification, which may be derived from sintering defects (figure 6(a)). Sandblasting-treated specimens had surfaces covered with notched grooves in different lengths, forming a certain degree of peak-to-valley coarsening. However, the grain undulations were flat and did not show obvious pores under a high-power field (figure 6(b)). HF-etched specimens were homogeneous and presented a relatively smooth surface under a low magnification, but there were a large number of small gaps formed among grains in high-magnification images (figure 6(c)). The surface of the zirconia treated with sulfuric acid exhibited a fine and loose sandy beach structure and polishing traces could also be observed. The high-magnification SEM images provided valuable information concerning the porous structure combined with loose crystal particles (figure 6(d)). The results from MIP showed that the specimen etched by sulfuric acid
generated bigger pores (87.8 nm) and higher porosity (8.52%) compared with those of HF etching (76.4 nm, 7.87%), but a lower total pore area (0.352 m² g⁻¹) was obtained in comparison to that of HF etching (0.486 m² g⁻¹). The blank treated zirconia was relatively dense with porosity at 1.08%, and the pore diameter was failed to be measured by MIP. Therefore, this technique was only applied as a comparative tool for porosity assessment. EDS analysis showed the presence of alumina (Al) peaks in the sandblasted samples, fluorine (F) in
the HF-etched specimens, and the underlying chemical element of zirconia and oxygen for all groups (figures 6(a)–(d)).

3.5. Shear bond strength of resin cement

According to the box-plot diagram results (figure 7), surface treatments of zirconia significantly improved the SBS compared with the control (P < 0.01). Furthermore, the surface treatment with acid solutions demonstrated higher mean SBS values (P < 0.01) compared with the sandblasting-treated specimens. The highest SBS was noted in Group HF. However, no statistically significant differences were noted between the HF and H2SO4 group (P > 0.05).

3.6. Fracture pattern analysis

The distribution of fracture pattern was shown in table 2. Mixed failure was predominantly observed in Group HF, while adhesion failure was prevalent in the other groups. The number of mixed failure cases increased with the lift of SBS, but no cohesive failure was observed in all studied groups. The representative micrographs of fracture pattern were presented in figure 8.

4. Discussion

Since zirconium oxide ceramics are not silica-based and cannot establish chemical silica-silane bonds, their bond strengths are not reliable and adequate [9]. This study investigated the influences of three different surface treatments on surface properties and the strength of bonding between zirconia and resin cement. The null hypothesis formulated in this study should be rejected, since all tested treatments were capable of altering surface roughness and morphology, and significantly increased the SBS in comparison to those of the control group.

Sandblasting was selected as the positive control for this study because it is the most commonly cited method to improve the adhesion of zirconia [19]. On the one hand, sandblasting creates a rough surface and improves surface characteristics, including surface energy and wettability [6, 23]. On the other hand, sandblasting puts a
high stress on the zirconia surface, resulting in the formation of micro-cracks on the zirconia ceramic surface and t-m phase transformation [2, 23]. XRD analysis (figure 5) showed the highest crystal phase transition on the surface of zirconia in Group Sand. The t-m phase transition is usually accompanied by 3%–5% volume expansion, and a compressive stress layer is formed on the surface of the material, which can increase the flexural strength of the material through preventing expansion and extension of cracks, that is, transformation toughing. However, the flexural strength of the zirconia ceramic is reduced once the monoclinic phase transition exceeds a certain limit [6, 21, 24]. It depends on the particle size of blasting alumina, blasting pressure, blasting time and distance, etc [24]. Sandblasting with alumina particles at 0.2 MPa for 20 s and the powder size of 110 μm is recommended by Naichuan et al for improving the bonding between the zirconia and indirect composite resin [23]. Matani et al believed that sandblasting of alumina particles larger than 80 μm would cause damage to zirconia [25]. Yukiko et al found that surface roughness of zirconia continuously increases after sandblasting with 75-, 100-, and 150-μm aluminum oxide, but there are no significant differences in the shear bond strength [26]. In summary, this experiment used 80-μm alumina to blast for 20 s at 0.2 MPa. As seen by SEM, sandblasting forms grooves with sharp edges of varying sizes, which can cause a stress concentration on the surface of zirconia and thus damage the long-term clinical success of zirconia [27]. Consistently, sandblasting creates only a modest amount of undercuts on the zirconia surface because of its hardness, and a sufficient micromechanical bonding with the resin cement is failed to obtain [10]. Our findings uncovered that SBS values in Group Sand were merely higher than those of the control group while lower than the acid groups. Hence, sandblasting in combination with the use of MDP-containing luting resins is recommended for a better chemical and mechanical bonding [6, 9, 10, 19]. In addition, the presence of aluminum element after sandblasting, as confirmed by EDS analysis in figure 6, was consistent to the finding by Jardim et al that the abrasive particles debris may have a negative influence on the zirconia/resin cement bond [15].

Acid etching of zirconia can be conducted by strong acids such as nitric acid, hydrofluoric acid, and sulfuric acid [2]. Through calculation, the mass fraction of sulfuric acid used in this experiment was about 77%, which belonged to the category of concentrated sulfuric acid. During hot acid etching, a lower temperature in comparison to laser etching or selective infiltration etching, and a smaller internal stress in comparison to sandblasting or grinding may attribute to its lower monoclinic phase transition than that of sandblasting [2, 19]. SEM and AFM analysis showed that, compared with sandblasting, hot acid etching obtained a better rough structure and a higher Ra value. A loose porous structure was also observed, as shown in figure 6(d), which may be responsible for the higher SBS than that in Group Sand. Our results were consistent with previous studies that the hot etching solution significantly enlarges the inter-grain space and increases the surface roughness by removing the less-arranged and high energy peripheral atoms on the zirconia surface. Etching rate may be affected by solution movement over the ceramic, the concentration, the application time and the temperature [14, 19]. High temperature facilitates the removal of zirconia grains [17]. The pore evolution process ultimately depends on the Damkohler number of acid flow and reaction [28]. Although the surface roughness of zirconia continues to increase after 10-, 30-, and 60-minutes hot etching [14]. Canan et al observed that 10-min etching of zirconia surface produces greater bond strength values compared with 30-min etching. Therefore, 10-min acid etching was conducted in this experiment.

Quentin et al concluded that 40% HF is the most appropriate concentration for conditioning zirconia at ambient temperature, because it forms the fastest and most uniform etching [29]. In all HF-treated groups, a phase conversion to the monoclinic form owing to the low temperature degradation (LTD) phenomenon occurring in the wet state, consistent with the current research results, is observed by Ju-Hyoung et al [3]. Conversely, Xie et al [30] claimed that chemical degradation caused by immersion in HF acid, instead of LTD, worsens physical properties and surface roughness of Y-TZP. Similarly, Zr-F bonds on the HF-etched zirconia are also detected by Lee et al [8], implying that the formation of fluoride phase enhances the reactivity of the
surface. However, Han et al [1] did not detect the presence of fluorine on the surface of zirconium with EDS. In this experiment, fluorine was not always detected and the elemental composition was slightly different at each time point, which may be explained by its small content, different scanning fields and sensitivities of the detection instrument [1, 29]. The AFM and SEM images revealed that both acid solutions create uniformly distributed microretentions, which are different from air-abrasion created ones, thus resulting in an increase in bond strength between resin and zirconia regardless of the application of MDP-containing resins or primers [8]. Since our experiments only focused on micromechanical retention of etching, resin cement was directly applied to conditioned zirconia ceramic without the involvement of any primers.

Appropriate wetting and an adequate surface area are essential for obtaining satisfactory adhesion of restorations with resins [9]. A negative significant correlation is verified between the contact angle and the SBS test [12], which is consistent with our findings. An increase in the surface roughness is not parallel to an increase in mechanical bond strength [16, 26]. In addition, an excessive roughness may lead to a surface damage [17]. Weilin et al [31] proposed a mathematical model to predict the asperity effect on adhesion. Their data showed that the interfacial toughness gradually increases with the asperity rising, after which a further increase in roughness, conversely, dramatically decreases. Their findings can partially support our experimental results. In the present research, the Ra values of HF and H2SO4 were 21.64 nm (nano scale) and 165.33 nm (submicron scale), respectively, which were the asperity degree. However, their average SBS values were 333.45 MPa and 231.04 MPa, respectively, with the different order. The roughness height in Group H2SO4 was close to that in Group Sand, but the SBS was significantly higher than that of Group Sand. These results indicated that not only roughness height, but also the roughness width, frequency and regularity are of significance in the bonding force [15]. After HF etching, fine and uniform nano-scale pits were formed and the surface area was enlarged, which were conducive to the formation of high SBS values. Therefore, such a shallow surface architecture may be desirable in that it increased adhesion without forming deep and excessive surface damage that can weaken the treated zirconia [8].

Due to the low cost and ease procedures, the SBS test was selected for measuring the bond strength. However, a large standard deviation caused by an inhomogeneous stress distribution limited our study [6, 19]. The mixed type of failure also showed that cement was basically left at the edge of the bonding interface, indicating that the stress was more concentrated at the central area of interface between zirconia and resin. Although the HF etching provides the highest SBS values, it meets the minimum clinical bonding of 10 to 13 MPa [9]. Strategies to enhance adhesion, such as prolonging application duration of HF etching, accelerating acid etching and combined application of resins or primers containing functional monomer, are necessary. In addition, the effect of roughness on bonding needs to be further studied.

5. Conclusion

Hot concentrated sulfuric acid alone can etch zirconia and form a porous structure favorable for bonding. HF etching creates a nano roughness surface that significantly increases SBS and surface hydrophilicity, with the minimal damage to zirconia. Therefore, HF etching is a promising method for conditioning zirconia surfaces. Not only the roughness height, but also the roughness width value, as well as frequency and regularity affect the bonding strength.

Acknowledgments

This research was funded by the International Science and Technology Cooperation Program of China (2018YFE0194100), the Science and Technology Commission Program of Nanjing (201605011), and the ‘Southeast University and Nanjing Medical University Cooperative Research Project’ (2242018K3DN03).

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