Effect of autoclave treatment on bonding strength of dental zirconia ceramics to resin cements

Hideo SATO,¹ Seiji BAN, Makiko HASHIGUCHI and Youichi YAMASAKI
Kagoshima University, Graduate School of Medical and Dental Sciences, 8-35-1 Sakuragaoka, Kagoshima 890-8544

The purpose of this study is to evaluate the bonding strengths between dental zirconia ceramics with surface treatments and resin cements. Two types of zirconia (NANOZR and Y-TZP) and six types of dental resin cements were used in this study. All zirconia specimens were treated as follows; sandblasted with alumina, annealed at 1100°C and stored in an autoclave at 134°C for 5 hours. Half of specimens after stored in the autoclave were dried in an oven at 150°C for 3 hours. Adhesive procedure of the zirconia and resin cements was undertaken according to each manufacturer’s direction. Shear bonding strengths between zirconia and resin cements were measured. The bonding strengths stored in the autoclave were higher compared with dried after autoclave treatment. XPS revealed that hydroxide or H₂O adsorbed on the outermost layer of the zirconia after autoclave treatment. It is extrapolated that adsorbed hydroxide enhanced the bonding reaction between zirconia and resin cement.

©2010 The Ceramic Society of Japan. All rights reserved.

Key-words : Zirconia, Dental resin cement, Autoclave treatment, XPS, Phosphoric ester

1. Introduction
Dental zirconia ceramics as restorative material has been widespread in conjunction with improvement of its mechanical properties, development of CAD/CAM system, increasing of aesthetic demand and concern about metallic hypersensitivity.¹,²,³ It is applied to various dental materials and devices; framework of crown and bridge, orthodontic bracket, implant fixture and superstructure. On zirconia-based frameworks for crown and bridge restorations, fabrication using CAD/CAM system is a standard routine.

After fabrication using CAD/CAM system and veneering feldspathic porcelain or composite resin, one or more surface treatments are typically performed in order to modify the surface geometry and property.

Sandblasting is one of the conventional surface treatment in dental practice. Several reports indicated that mechanical properties of zirconia changed by sandblasting and heat treatment because these induced phase transformation between tetragonal and monoclinic zirconia.²,³,⁴

On the other hand, low-temperature aging degradation (LTAD) at hydrothermal condition, especially at the case of yttria stabilized tetragonal zirconia polycrystals (Y-TZP), has been published.⁵ Autoclave treatment is commonly known as accelerating test for LTAD. Ban et al. reported that after long-time (240 hours) autoclave treatment, Ce-TZP/alumina nanocomposite (NANOZR) had not only excellent resistance to LTAD but also had higher biaxial flexure strength compared to Y-TZP.⁶ That result suggests a hypothesis that short-time autoclave treatment improve physical and chemical properties of thin layer at surface region whereas affect limited to the bulk.

Therefore the purpose of the present study was to evaluate the effect of autoclave treatments on the bonding strength of dental zirconia ceramics to resin cements.

[Received February 17, 2010; Accepted March 23, 2010]

2. Experimental procedure
2.1 Zirconia preparation
Two kinds of zirconia were used as substrate material listed in Table 1. NANOZR (Panasonic Electric Works, Osaka, Japan) powders were pressed to a cylindrical rod, 25 mm in diameter and 100 mm in length, using a cold isostatic pressing method. After peeling of the rod surface and firing at 1450°C for 2 hours, disc-shaped specimens, 7 and 14 mm in diameter and 2 mm in thickness, were prepared by cutting and grinding with a 400-grid diamond wheel. To compare with conventional yttria stabilized tetragonal zirconia polycrystals (Y-TZP, Tosoh, Tokyo, Japan), its powders were also pressed using the same method, fired at 1350°C for 6 hours, and sliced to disc-shaped specimens, 7 and 14 mm in diameter and 2 mm in thickness, by the same method.

2.2 Surface treatment
After grinding with 1000-grid diamond paper, the zirconia disks were sandblasted with a device (Hi-Blaster Ovaljet, Shofu, Kyoto, Japan) by 70μm Al₂O₃ powder at 0.3 MPa for 10 sec. After ultrasonic cleaning in distilled water, heat treatment was performed at 1100°C for 10 min in air (Cerafusion VPF, Jelenko, MA, USA) to form homogeneous tetragonal ZrO₂. Then, All disks were stored with distilled water in an autoclave (SN200, Yamato, Tokyo, Japan) at 134°C and 0.2 MPa for 5 hours. Half of the disks were dried in an oven (DKM300, Yamato, Tokyo, Japan) at 150°C for 3 hours.

2.3 Bonding procedure and shear bonding test
Six types of dental resin cements used in this study were listed in Table 2. As bonding procedure of the resin cements was undertaken according to each manufacturer’s direction, the large zirconia disk and the small one was bonded by the dispensed resin cement. After soaking at 37°C in distilled water for 24 hours, some specimens were soaked alternatively in water at 5°C and 55°C for 5,000 thermal-cycling. Shear bonding strengths (ten

¹ Corresponding author: H. Sato; E-mail: hideo-sato@ms.kagoshima-u.ac.jp
specimens in each condition) between two zirconia and six resin cements were measured using an universal testing machine at cross-head speed of 0.5 mm/min.

2.4 Surface characterization

Microscopic observation was conducted on two types of zirconia using a field emission probe microanalyzer (JXA-8530FA, JEOL, Tokyo, Japan). It was operated at an accelerating voltage of 15 kV to investigate the surface geometry. To observe the effects of surface treatments on NANOZR and Y-TZP surfaces, heat treatment and autoclave treatment were performed, respectively.

The XPS measurements were performed on an X-ray Photoelectron Spectrometer (ESCA-1000, Shima-dzu, Kyoto, Japan). The present X-ray source was Mg Kα (1253.6 eV) radiation. The spectra of Zr 3d and O 1s were acquired with the pass energy of 32 eV and a step of 0.125 eV per channel. All recorded lines were calibrated to the C 1s line.

3. Results and discussion

Figure 1 shows the shear bonding strengths between zirconia with surface treatments and six resin cements after soaked in distilled water at 37°C for 24 hours as initial bonding strengths. Almost bonding strengths, except one, of both zirconia with stored in an autoclave, were higher than those with dried after autoclave. The bonding strengths of both zirconia with RXA cement were lower compared to other cements. Figure 2 shows the shear bonding strengths between zirconia with autoclave treatment and resin cements before and after thermal-cycling. The bonding strengths of some resin cements after thermal-cycling decreased compared before that. The Weibull failure probability lines are shown in Fig. 3. The inclinations among resin cements with zirconia after autoclave treatment are similar. The Weibull distribution for the autoclave treatment groups has a narrower distribution compared that for the dry treatment groups. These results indicate that the autoclave treatment is effective for the increasing of the initial bonding strength.

Figure 4 shows the SEM images of both zirconia with surface treatments. The surface geometry of both zirconia are almost similar patterns between surface treatments. Figure 5 shows Zr 3d and O 1s spectra obtained from the zirconia surface with surface treatments. Slightly broader O 1s peaks at the about 531 eV at the outermost layer were observed with autoclave treatment. These results indicate that autoclave treatment enhances the zirconia surface to adsorb the hydroxide. Moreover adsorbed hydroxide on the zirconia surface improve the surface properties, which may subsequently promote the adhesive reaction at the interface between zirconia surface and resin cement. Although the initial bonding strengths with autoclave treatment of RXU cement decreased compared with dry treatment, there were no significant differences between

---

**Table 1. Zirconia used in this study**

<table>
<thead>
<tr>
<th>Code</th>
<th>Material</th>
<th>Composition</th>
<th>Sintering Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>NANOZR</td>
<td>MACZ-100, Panasonic Electric Works, Osaka, Japan</td>
<td>10 mol% CeO₂-ZrO₂, 30 vol% Al₂O₃</td>
<td>1450°C, 2 hr</td>
</tr>
<tr>
<td>Y-TZP</td>
<td>TZ-3YB-E, Tohos, Yamaguchi, Japan</td>
<td>3 mol% Y₂O₃-ZrO₂</td>
<td>1350°C, 6 hr</td>
</tr>
</tbody>
</table>

---

**Table 2. Resin cements used in this study**

<table>
<thead>
<tr>
<th>Code</th>
<th>Manufacturer</th>
<th>Composition</th>
<th>Dispensing</th>
</tr>
</thead>
<tbody>
<tr>
<td>RC</td>
<td>Shofu</td>
<td>Fluoroaluminosilicate glass, UDMA⁴, TEGDMA⁵, 4-AET⁶, HEMA⁷, 6-MHPA⁸</td>
<td>Automix</td>
</tr>
<tr>
<td>GCA</td>
<td>GC</td>
<td>Fluoroaluminosilicate glass, methacrylated ester, phosphoric esters, SiO₂</td>
<td>Automix</td>
</tr>
<tr>
<td>RXA</td>
<td>3M ESPE</td>
<td>MMA⁹, dimethacrylate, acetate, glass powder, silica</td>
<td>Hand mixed</td>
</tr>
<tr>
<td>CSL</td>
<td>Kuraray medical</td>
<td>Bis-GMA¹⁰, TEGDMA, MDP¹¹, barium glass, silica</td>
<td>Hand mixed</td>
</tr>
<tr>
<td>GL</td>
<td>GC</td>
<td>Fluoroaluminosilicate glass, methacrylated ester, phosphoric esters, SiO₂</td>
<td>Hand mixed</td>
</tr>
<tr>
<td>RXU</td>
<td>3M ESPE</td>
<td>MMA, dimethacrylate, acetate, glass powder, silica, phosphoric esters</td>
<td>Hand mixed</td>
</tr>
</tbody>
</table>

1) urethane dimethacrylate; 2) triethyleneglycol dimethacrylate; 3) 4-acryloyloxyethyltrimellitic acid; 4) 2-hydroxyethyl methacrylate; 5) 6-methacryloxyhexylphosphonaacetate; 6) methyl methacrylate; 7) bisphenol A diglycidyl ether dimethacrylate; 8) 10-methacryloxyloxydecyl dihydrogen phosphate
surface treatments. However autoclave treatment for 5 hours may limitedly affect to the zirconia surface region. Hence autoclave treatment may effect to improve the initial bonding strengths between zirconia and resin cements.

**Figure 6** shows the schematic illustration at the adhesive layer between zirconia and resin cements. From the results of shear bonding strengths, the strengths of RXA cements were lower than that of others. These resin cements except RXA include the phosphoric ester or similar monomer, therefore it is extrapolated,
indicating in the illustration, that these monomers and adsorbed hydroxide probably play roles as functional agents for the adhesive reaction between zirconia and resin cements. On the other hand, as the result after thermal-cycling, several kinds of specimens, long-term durability of the bonding strengths were decreased. It is perhaps caused that polynelization of several cements increased, where the other cements that the hydrolysis of the resin matrix by the water increased and the strain occurred by the difficulties of the coefficient of the thermal expansion into the hot and cold water.

The future study to develop the surface treatment for improving the durability is needed.

Acknowledgement This work was supported by Grant-in-Aid for Young Scientists (B) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), KAKENHI (No. 21791912 for H. S. and No. 20791435 for M. H.), Japan.

References