Evaluation of shear bond strength between dual cure resin cement and zirconia ceramic after thermocycling treatment

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PURPOSE. This study was performed to evaluate shear bond strength (SBS) between three dual-cured resin cements and silica coated zirconia, before and after thermocycling treatment. **MATERIALS AND METHODS.** Sixty specimens were cut in 15 x 2.75 mm discs using zirconia. After air blasting of 50 μm alumina, samples were prepared by tribochemical silica coating with Rocatec™ plus. The specimens were divided into three groups according to the dual-cure resin cement used: (1) Calibra silane+Calibra®, (2) Monobond S+Multilink® N and (3) ESPN sil+RelyX™ Unicem Clicker. After the resin cement was bonded to the zirconia using a Teflon mold, photopolymerization was carried out. Only 10 specimens in each group were thermocycled 6,000 times. Depending on thermocycling treatment, each group was divided into two subgroups (n=10) and SBS was measured by applying force at the speed of 1 mm/min using a universal testing machine. To find out the differences in SBS according to the types of cements and thermocycling using the SPSS, two-way ANOVA was conducted and post-hoc analysis was performed by Turkey's test. **RESULTS.** In non-thermal aged groups, SBS of Multilink group (M1) was higher than that of Calibra (C1) and Unicem (U1) group ($P<.05$). Moreover, even after thermocycling treatment, SBS of Multilink group (M2) was higher than the other groups (C2 and U2). All three cements showed lower SBS after the thermocycling than before the treatments. But Multilink and Unicem had a significant difference ($P<.05$). **CONCLUSION.** In this experiment, Multilink showed the highest SBS before and after thermocycling. Also, bond strengths of all three cements decreased after thermocycling. ***[J Adv Prosthodont 2015;7:1-7]***

KEY WORDS: Y-TZP zirconia; Resin cement; Shear bond strength; Thermocycling treatment; Silica coating

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INTRODUCTION

In a field of dentistry, ceramic has been widely used because it provided a restoration without metallic component, good esthetics, stability of shade, bio-compatibility, high resistance to attrition and low thermo-conductibility.[1] Among ceramics, zirconia has properties such as high strength, transformation toughening, chemical and structural stability, and bio-compatibility; and these properties enabled ceramic prosthesis possible in posterior teeth area.[2-4] In recent days, advancement of CAD/CAM allowed even more use of zirconia.[5,6] Zirconia exists in three types of crystal states and it can be partially stabilized by adding oxidized metal to maintain its stable tetragonal state in room temperature. And this unique state is called partially stabilized zirconia (PSZ). If external force is applied to the PSZ, zirconia crystal undergoes phase variation in which its size increases and crack progression is inhibited that fracture toughness increases. All ceramic restorations that need high mechanical strength can be made as a result.

In terms of resin-cement bonding, all ceramic restoration has been attempted by acid-etching the inner surface and application of silane to achieve chemical bonding between silica based ceramic and resin.[7,8] However, there is a limitation to using resin cement because zirconia does not contain silica and has resistance to acid corrosion due to its highly-crystallized structure.[9-11]

A weak mechanochemical bond of resin cement and zirconia can have a significant effect on the prognosis, such as debonding in restorations and microleakage. For this reason, to obtain improved bonding strength, various surface treatment methods have been proposed. These include alumina air blasting and silica coating treatment, as in the Rocatec™ and CoJet™ systems (3M ESPE, Seefeld, Germany). Manufacturers recommend resin cements including 10-methacryloyloxy-decyl dihydrogenphosphate (MDP) monomer or phosphate monomer components, because it is possible to obtain increased bonding strength when using them. Resin cements including MDP show excellent bonding strength and remain stable even after thermocycling treatment and long-term storage in water.[12] Furthermore, phosphate monomers, such as phosphoric acid and methacrylated phosphoric ester, directly bond to zirconia and to teeth, so that better bonding strength can be obtained.[12] Many studies have reported that when resin cements including phosphate monomer after alumina air blasting were used, bonding strength increased.[2,13,14]

Chemical bonding through monomers can enhance bonding strength, but the bond strength decreases without effective maintenance after thermocycling treatment.[9,13] But, whether MDP monomer forms a chemical bond with zirconia or operates via micromechanical retention forces remains unclear.[15]

This study measured and compared shear bond strength to evaluate the influences of the monomer of resin cement and thermocycling treatment on bonding strength of zirconia and resin cements by selecting three dual-cured resin cements including different commercially available monomer components.

MATERIALS AND METHODS

Zirconia block (Fulluster, HASS Co., Gangneung, Korea) made from tetragonal zirconia polycrystal (3Y-TZP: yttria-tetragonal zirconia polycrystal) containing 3 mol% Y_2O_3 was used as a specimen. Zirconia block was cut into a disk-shaped form using CAD/CAM, ground with a diamond wheel, polished with 1 μm diamond paste, and completed into a shape with diameter of 15 mm and thickness of 2.75 mm. 50 μm alumina particles were blasted for 10 seconds with 2.8 bar pressure away from 10 mm vertical distance and silica coating was done for 10 seconds with 2.8 bar pressure away from 10 mm vertical distance using Rocatec™ plus system (3M ESPE, Seefeld, Germany).

Among the widely used resin cements for cementation of zirconia restorations, three cements have different kinds of monomers. The Calibra® (Dentsply, Konstanz, Germany), Multilink® N (Ivoclar-vivadent, Schaan, Liechtenstein) and RelyX™ Unicem clicker™ (3M ESPE, Seefeld, Germany) cements were used (Table 1). Sixty specimens were divided into three groups depending on the type of resin cements. Each group was divided into two subgroups depending on thermocycling treatment. A total of six groups (C1, C2, M1, M2, U1, and U2), each with 10 specimens, were prepared (Table 2). After applying manufacture-recommended silane coupling agent to the surface of each specimen and drying for 1 minute, a cylindrical Teflon mold 6 mm in diameter and 4.5 mm in height was fixed using a metal jig.

At the manufacturer's suggestion, three types of dual-cured resin cements were mixed, placed in a mold and photopolymerized for 1 minute with 500 lx on the upper side of 2 mm vertically using a light-curing unit (Elipar FreeLight™ 2, 3M ESPE, St. Paul, MN, USA). After applying an oxygen-blocking agent, autopolymerization was carried out for 3 minutes. All procedures were done by the same person. The cements were stored in sterile distilled water at room temperature for 24 hours after the completion of polymerization (Fig. 1A).

After specimens were dried, the shear bond strength of the C1, M1 and U1 groups that did not undergo thermocy-

Table 1. Resin cements used in this study

Cement	Composition	Manufacturer
Calibra®	Barium boron fluoroalumino silicate glass, Bis-GMA, Dimethacrylate resin, Silica, Titanium dioxide	Dentsply, Konstanz, Germany
Multilink® N	DMA, HEMA, Ba-glass filler, Ytterbium fluoride, Spheroid mixed oxide, Phosphoric acid acrylate	Ivoclar-vivadent, Schaan, Liechtenstein
RelyX™ Unicem Clicker™	Methacrylated phosphoric ester, Dimethacrylate, Inorganic fillers, Fumed silica, Chemical and photoinitiator	3M ESPE, Seefeld, Germany

Table 2. Six groups used in this study

Group	Surface treatment	Silane coupling agent	Cement	Thermocycling
C1	Sandblast + Rocatec™	Calibra silane	Calibra®	no
C2				yes
M1		Monobond S	Multilink® N	no
M2				yes
U1		ESPE sil	RelyX™ Unicem Clicker	no
U2				yes

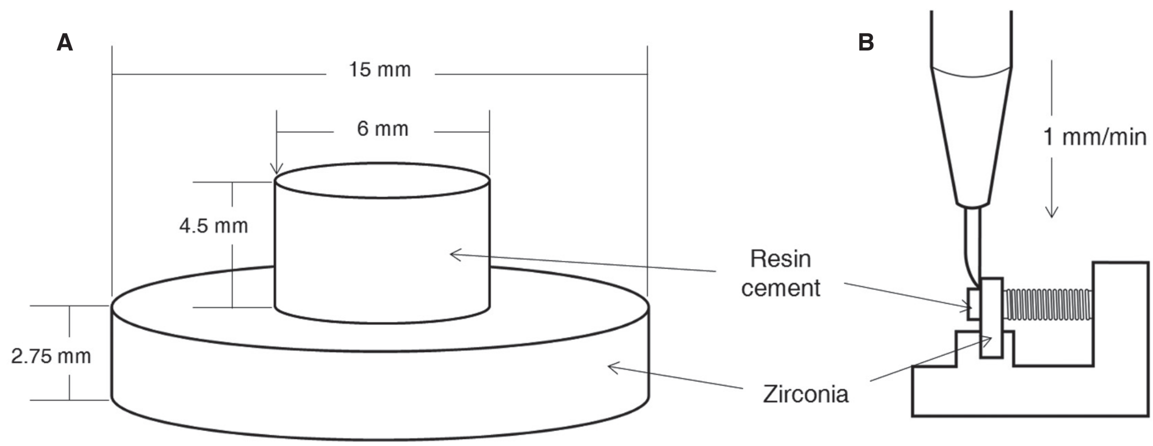

Fig. 1. The specimen (A) and the measurement of the shear bond strength (B) were illustrated by the schematic diagram.

cling was measured using a universal test machine (Model 4021, Instron Co, Norwood, MA, USA). Regarding shearing force, a force was applied at a crosshead speed of 1 mm/min and shear bond strength was calculated by dividing a maximum load until the resin cement cylinder separated from the zirconia surface by the cross-sectional area (Fig. 1B). The conversion formula is:

$$S = L/A$$

S: shear bond strength (MPa)
L: load at failure ($kg \cdot m/s^2$)
A: adhesive area (mm^2)

To evaluate the changes of bonding strength according to aging, the shear bond strength of C2, M2 and U2 groups that underwent thermocycling treatment 6,000 times at 5ºC and 55ºC for 20 seconds was measured under the same conditions described above. It was impossible to measure the shear bond strength of C2 group because after thermocycling treatment, resin cements spontaneously debonded from the two specimens. These specimens were excluded.

Surfaces that had been polished, alumina air blasted and silica coated using Rocatec™ were observed using scanning electron microscopy (SEM) (JSM-6400, JEOL Co., Tokyo, Japan). The surface of specimens was observed using the same microscope to permit comparison of the failure pattern.

To compare the bonding strength between the resin cement and zirconia according to the types of resin cements and thermocycling treatment, two-way ANOVA was performed after normality test using SPSS statistical program (SPSS 20.0 for Window, SPSS Inc., Chicago, IL, USA), and post-hoc analysis was done using Turkey's test. All statistical significance was assayed at 95%.

RESULTS

Results and analysis on shear bond strengths were shown in Table 3 and Fig. 2. Table 4 summarizes the results of the two-way ANOVA. Three cements were stored in distilled water for 24 hours after bonding, and then shear bond strengths were measured. Before thermocycling treatment, the result showed that the bond strength was 17.71 ± 1.37 MPa in Multilink (the highest), 11.78 ± 1.82 MPa in RelyX Unicem, 2.66 ± 0.25 MPa in Calibra (the lowest), and discrepancy between these values was statistically significant

(P<.05). Also, after thermocycling treatment, shear strength of Multilink, Unicem and Calibra showed discrepancies of significance in a respective order (P<.05).

As a result of analysis on changing of shear bond strength before and after thermocycling treatment, RelyX Unicem showed the highest change, followed by Multilink and Calibra. Shear bond strength of all three cements before and after thermocycling treatment decreased but, Multilink and RelyX unicem showed significant differences (P<.05). In C2 group, resin cements of two specimens were separated automatically.

In a result of observation on the surface of specimen after fracture, Calibra showed 100% adhesive failure before and after thermocycling treatment, and Multilink and Unicem showed adhesive failure and mixed failure, combined. Cohesive failure was not shown in any of specimens (Fig. 3).

Fig. 4A, Fig. 4B, Fig. 4C respectively shows polished surface of each zirconia, surface after alumina air blasting, and surface after silica Rocatec™ silica coating; and Fig. 4D, Fig. 4E, Fig. 4F show SEM views on surfaces of Calibra, Multilink, and Unicem after shear bond strength experiment respectively.

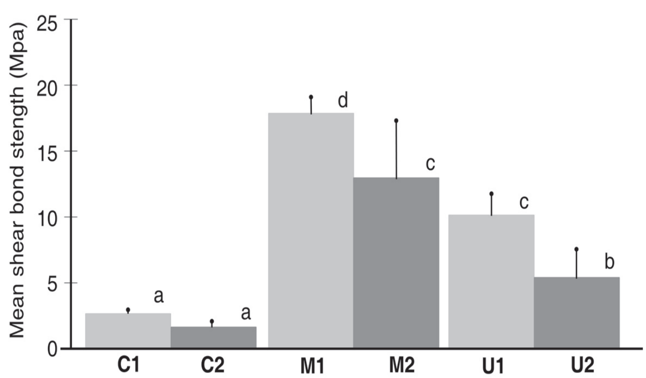

Fig. 2. Mean shear bond strength of resin cements before and after thermocycling was shown. Same lowercase letters were not statistically significant (P<.05).

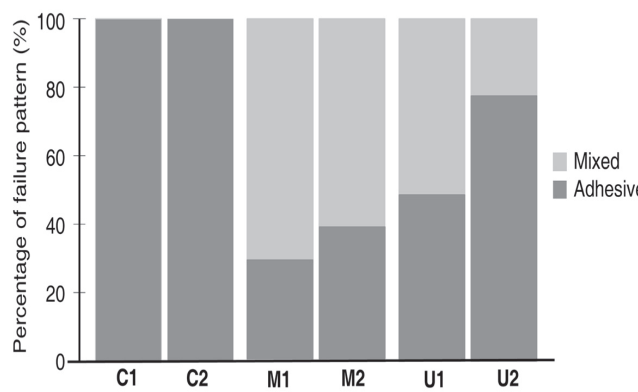

Fig. 3. Mean percentage of failure patterns after shear bond strength test.

Table 3. Shear bond strength (SD) of experimental groups

Group	n	Mean maximum force (kg·m/s^2)	Shear bond strength (MPa)	Amount of change (MPa)
C1	10	75.18 (7.10)	2.66 (0.25)	-1.09
C2	8	44.29 (10.66)	1.57 (0.38)	
M1	10	500.61 (38.82)	17.71 (1.37)	-4.75
M2	10	366.25 (125.50)	12.96 (4.44)	
U1	10	333.04 (51.53)	11.78 (1.82)	-6.37
U2	10	152.82 (52.59)	5.41 (1.86)	

Table 4. The results of two-way ANOVA test with type of metal and galvanic corrosion

Source of variation	Sum of squares	*df*	Mean square	F	*P*
Corrected model	1966.364	5	393.273	79.525	<.001
Type of cement	1649.212	2	824.606	166.746	<.001
Thermocycling	239.095	1	239.095	48.348	<.001
Type of cement * Thermocycling	68.137	2	34.068	6.889	.002
Error	257.155	52	4.945		
Corrected total	2223.519	57			

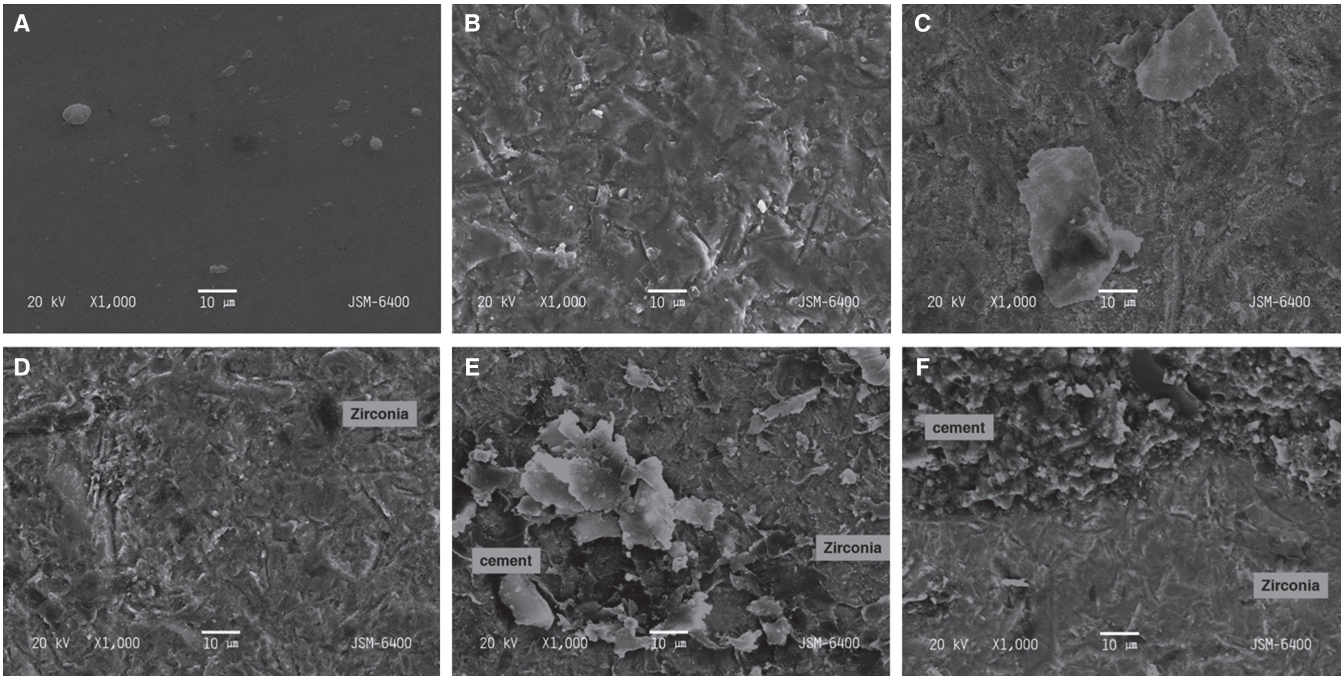

Fig. 4. Scanning electron microscope images of zirconia surface were shown (magnification ×1,000). A: polished with 1 µm diamond paste, B: 50 µm Al_2O_3 sandblasting, C: Silica coating with Rocatec™ plus, D: Adhesive failure mode of zirconia surface (Calibra), E: Mixed failure mode of zirconia surface (Multilink N), F: Mixed failure mode of zirconia surface (RelyX Unicem).

DISCUSSION

In order to increase bond strength of ceramic restorations, mechanical or chemical method could be used. There are mechanical methods such as acid-etching, alumina air blasting, etc., and chemical methods such as application of silane and various adhesive monomers. There are difficulties in establishing reliable protocols because there are many variables such as blasting pressure when air blasting, time, diameter, and section form of blasted particles.[14] Because Y-TZP ceramic is acid-resistant and does not contain silica component, it is important to understand physical properties and reciprocal action of material in order to use it properly to gain a stable bonding with resin cement.

Külünk *et al.*[16] stated that 30-50 µm or 110 µm alumina particles were effective in making appropriate roughness structure. On the other hand, Tsuo *et al.*[15] reported that there were no difference in initial bond strengths by sizes of alumina particles and bond strengths decreased after thermocycling treatment. Phark *et al.*[17] stated that there was no difference in bond strengths by the sizes of particles and stable adhesive force was maintained after thermocycling treatment as well.

Therefore, it is considered that it is not the size of the particle but the micro-roughness of the surface is important in bond strength, and in some reports, it is also said that air blasting particles could decrease the strength of zirconia causing failures.[18] Based on these, 50 µm alumina particles were used in this experiment, and micro-roughness of the surface was confirmed by SEM observation after air blasting.

Silica coating can also be attempted as chemical method to increase bond strength between resin cement and zirconia. Silica-coated layer which is formed in zirconia improves the bond strength by reacting with silane coupling agent and forming chemical bonding with resin cement.[19-21] Silane reacts with hydroxyl radical of silica that is coated on zirconia surface and forms siloxane networks through a chemical bonding and also forms a bonding with metacrylate monomer of the resin. However, there is also a report that silica coating is not so effective because permeation of silica is not sufficient due to its high density.[4]

It was reported that using resin cement which contains phosphate monomer makes bond strength of zirconia higher. This is because adhesive monomer not only forms bonding with silane but also forms a chemical bonding with hydroxyl radical of zirconia surface.[22] Adhesive monomers of resin cements used for this experiment were Bis-GMA of Calibra, phosphoric acid acrylate of Multilink, and methacrylate phosphoric ester of RelyX Unicem.

It is known that using Bis-GMA series cement after silane application shows high bond strength, but it was reported that bond strength decreased after thermocycling treatment.[23,24] Bonding of Bis-GMA resin cement after silica coating produced high bonding strength, which was not stable for a long period.[22,24] The explanation is that because air-blasting, unlike a metal, does not form a sufficient undercut so that sufficient chemical bond cannot be obtained through silica coating.[2] The rationale likely also applies to Calibra including Bis-GMA, which showed the lowest binding forces; two specimens showed spontaneous debonding.

Bond strength of Multilink was higher than that of Unicem before and after thermocycling treatment. Based on this, it is thought that phosphoric acid acrylate monomer shows more stable bonding with hydroxyl radical of zirconia surface than methacrylate phosphoric ester monomer and similar results were shown in experiments of D'Amario *et al*.[25] in 2010.

It is important for the bonding strength of resin cements to be maintained even after a long-term aging process. Thermocycling treatments were performed to compare bonding strength according to aging. Regardless of the types of cements, the shear bonding strength tended to decrease in all groups after thermocycling. This was because all three types of cements were enhanced in their binding forces through chemical bonds at first, with these bonds subsequently weakening due to degeneration of material through thermocycling treatments.

In this study, as a result of bonding three kinds of dual cure resin cements on zirconia surface and measuring their shear bond strengths, resin cement containing phosphate series monomer showed higher shear bond strength than resin cement containing Bis-GMA monomer. Additionally, it is thought that experiments on bond strengths using various surface treatments on zirconia and various kinds of cements will be necessary.

CONCLUSION

Shear bond strength was measured to determine the influences of the type of resin cements and thermocycling treatment on the bonding strength between resin cement and zirconia.

The types of resin cements and thermocycling treatment had a significant effect on bonding strength between zirconia and resin cement. The bonding strength of resin cement including phosphoric acid acrylate was significantly higher than resin cements including other monomer. The bonding strength between resin cement and zirconia tended to reduce after thermocycling treatment.

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