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Original

Effect of thermocycling on the bond strength between dual-cured resin cements and zirconium-oxide ceramics

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Abstract: The present study evaluated the durability of bond strength between zirconia and 3 different resin cements. Thirty stabilized tetragonal zirconium-dioxide blocks were duplicated in dual-curing resin core build-up material specimens. Resin blocks were randomly luted to zirconium surfaces using 1) Clearfil Esthetic Cement (CLF), 2) RelyX Unicem Aplicap (RELX), or 3) Multilink Automix (MLA). After 24 h, half of the specimens from each of the 3 groups were loaded in tension until fracture (0.5 mm/min). The remaining half were tested after 6,000 thermal cycles (5 to 55°C). Data were analyzed using 2-way ANOVA and the Tukey test ($\alpha = 0.05$). Fractographic analysis was performed using a stereomicroscope. Tensile bond strength values were significantly affected by the luting agent system employed and by thermal aging ($P < 0.001$). The highest tensile bond strength values in non-thermal-aged groups were observed for specimens from the RELX and CLF groups. In contrast, in the thermal-aged groups, the highest tensile bond strength values were for the MLA and RELX groups. Moreover, while thermocycling significantly affected bond strengths in the RELX and CLF groups, the mean strength of the MLA group did not significantly change after aging. There was little difference in the distribution of failure modes in any group. (J Oral Sci 52, 425-430, 2010)

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Introduction

New high-performance non-etchable ceramics, such as alumina and zirconia, are becoming common in indirect restorations (1). Zirconium oxide all-ceramic materials have attractive properties, such as high strength (2,3) and biocompatibility (4), that permit their use as core materials for all-ceramic crowns (5) and fixed partial dentures (FPDs). These favorable mechanical properties are due to phase transformation toughening, which increases crack propagation resistance. The stress-induced phase transformation involves the transformation of metastable tetragonal grains to the monoclinic phase at the crack tip, which, in conjunction with volume expansion, induces compressive stresses (2,6). However, the surface stability of zirconia makes it difficult to establish durable chemical and mechanical bonds with this material (7,8). Hydrofluoric acid etching combined with silanization, which is used with other glass-ceramic materials, was not successful with acid-resistant and glass-free zirconia (9), and different surface treatments for surface zirconia frameworks have been proposed (10). A few luting agents, such as multi-step methacryloyloxydecyl dihydrogen phosphate (MDP) monomer-based resin cements, have demonstrated satisfactory bonding to zirconium-oxide ceramics (11-14). Unfortunately, there are insufficient data on the actual mechanism of the reaction of the MDP monomer. In addition, it is not known whether it establishes a true chemical bond with zirconia or whether it relies basically on micro-retention provided by particle abrasion (15).

There are also insufficient data on the long-term performance of MDP monomer-based resins and the effect of water hydrolysis on established bond strength (16,17). Self-adhesive cements have recently been marketed to simplify luting procedures (18). These single-step luting agents contain a resin matrix densely packed with multifunctional acid methacrylates that should ideally interact with the porcelain substrate (19,20). Nonetheless, there is little information in the literature on their bond strength to zirconia.

The aim of this study was to evaluate the durability of bond strength between zirconia and 3 different dual-cured resin cements, after aging by thermocycling (TC). The null hypotheses to be tested were that: 1) resin cement selection does not influence bond strength at cement-ceramic interfaces and 2) 6,000 cycles of TC do not affect adhesion to zirconium-oxide ceramic.

Materials and Methods

Thirty stabilized tetragonal zirconium-dioxide 5 × 5 × 5 mm specimens (Cad Cam Echo – batch no. 20080718 134615; Sweden & Martina S.p.A., Padova, Italy) were obtained from the manufacturer. The surfaces of each specimen were treated with a silica-coating process using an intraoral air abrasion device (Micerium, Avegno, Genova, Italy) filled with CoJet-Sand (30-μm SiO_x particles; 3M-ESPE, St. Paul, MN, USA) from a distance of approximately 10 mm at a pressure of 2.8 bar for 20 s (21). The remnants of sand particles were gently air-blown.

Each zirconium block was duplicated in a dual-curing resin core build-up material specimen (5 × 5 × 5 mm) (Clearfil DC Core Automix – batch no. 00042B; Kuraray Medical Inc., Tokyo, Japan) using a mold made of silicon impression material (Express, 3M-ESPE). Resin layers were incrementally condensed into the mold to fill it completely, and each layer was light-polymerized for 40 s (L. E. Demetron I, with a 1,200-mW/cm^2 output; Sybron/Kerr, Orange, CA, USA). After removing the polyethylene molds, each surface of the obtained specimens was subjected to an additional 20-second polymerization cycle. One resin block was fabricated for each zirconium block.

Three commercially available luting agent systems (Table 1) were used to bond zirconium blocks to resin composite blocks, to form 3 groups: the CLF group, RELX group, and MLA group, in which the luting agents used were Clearfil Esthetic Cement (Kuraray), Relyx Unicem Aplicap (3M-ESPE, Seefeld, Germany), and Multilink Automix (Ivoclar Vivadent, Schaan, Liechtenstein), respectively. Resin blocks were bonded to conditioned zirconium surfaces; materials were applied at a room temperature (RT) of 23.0 ± 1.0°C in accordance with the manufacturers' instructions. The operation mode and chemical composition of the tested materials are described in Table 1. Luting procedures were carried out under a constant load of 750 g in a special clamp at RT to standardize the exerted pressure. The seating force was applied for the first 5 min, during which the material was left to set in the self-curing modality. The bonded assemblies were held centrally between the 2 measuring arms of the vertically positioned digital micrometer. The luting cement thickness was maintained at approximately 100 μm. The micrometer arms were slowly adjusted to produce a reading that was 100-μm (mean) thicker than that initially recorded for the respective zirconium and resin specimens. During the dwell time, and before the resin luting agent completely polymerized, all excess material was carefully removed with a thin instrument used to place composite fillings. After the initial self-polymerization, 40 s of light irradiations from each side of the blocks were performed to ensure optimal polymerization.

After 24 h of storage in distilled water at 37°C, half of the specimens from each of the 3 groups were immediately tested for tensile bond strength. The other half of the bonded specimens underwent 6,000 thermal cycles in deionized water from 5°C to 55°C, with a 30-second dwelling time and a 5-second transfer between temperature baths (LTC100; LAM Technologies Electronic Equipment, Firenze, Italy).

The tensile bond strength test was evaluated using a computer-controlled universal testing machine (LMT 150; LAM Technologies Electronic Equipment): specimens were fixed to the machine by metal pliers and stressed to failure in tension at a cross-head speed of 0.5 mm/min. After testing, specimens were removed from the testing devices and the cross-sectional area of the fracture sites were measured with a digital caliper (series 500 Caliper; Mitutoyo America Corp, Aurora, Ill, USA) to calculate the ultimate tensile bond strength expressed in MPa. Statistical analysis was performed using SPSS Advanced Statistical 11.5 software for Windows (SPSS Inc., Chicago, IL, USA). The obtained values were statistically analyzed using 2-way ANOVA. Post-hoc multiple comparisons were performed using the Tukey test, with the significance level set at $\alpha = 0.05$.

The fractured specimens were evaluated by a single operator under a stereomicroscope (Olympus SZ-CTV, Olympus Co., Tokyo, Japan) at × 40 magnification to determine the mode of failure. Fracture patterns were categorized into 5 groups (22): type 1 – cement principally on resin specimen; type 2 – cement on resin and zirconium-dioxide specimens; type 3 – cement principally on

Table 1 Summary of the materials and procedures used for cementation

Material (Group)	Composition	Application	Manufacturer
Clearfil Esthetic Cement (CLF)	*Clearfil Ceramic Primer*: 3-MPS; 10-MDP; ethanol. *ED Primer II A:* HEMA, MDP, water, accelerator. *ED Primer II B:* Methacrylate monomers, water, initiator, accelerator. *Paste A*: Bis-phenol A diglycidylmethacrylate; TEGDMA; methacrylate monomers; silanated glass filler; colloidal silica. *Paste B*: Bis-phenol A diglycidylmethacrylate; TEGDMA; methacrylate monomers; silanated glass filler; silanated silica; colloidal silica; benzoyl peroxide; CQ; pigments.	Apply K-etchant Gel (*batch no. 00389B*) on resin surfaces, leave for 5s, wash and dry. Apply ceramic primer (*batch no. 0001A*) on zirconium and resin surfaces and air-dry. Mix equal amounts of ED Primer II liquid A (*batch no. 00232A*) & B (*batch no. 00110A*), apply on resin surfaces, leave for 30 s and dry. Squeeze Paste A&B (*batch no. 0001AA*) from the dispenser syringe, apply, self-cure (5 min) and light-cure.	Kuraray Medical Inc., Tokyo, Japan
Rely X Unicem Aplicap (RELX)	*Espe-Sil:* 1-3-methacryloxypropyl trimethoxysilane, ethanol *RelyX Unicem:* Methacrylated phosphoric ester, dimethacrylate, acetate, stabilizer, initiators, glass powder, silica, substitute pyrimidine, calcium hydroxide, peroxy compound, pigment.	Apply Espe-Sil (*batch no. 225505*) on zirconium surfaces and air-dry. Mix luting agent (*batch no. 251058*) for 10 s (Rotomix, 3M ESPE). Apply, self-cure (5 min) and light-cure.	3M ESPE, Seefeld, Germany
Multilink Automix (MLA)	*Metal/Zirconia primer:* mixture of dimethacrylate, solvents, phosphonic acid acrylate, initiator, stabilizer. *Multilink Primer A*: aqueous solution of initiator. *Multilink Primer B:* HEMA, phosphonic acid, acrylic acid monomers. *Multilink Automix:* dimethacrylate, HEMA, barium glass, ytterbium trifluoride, spheroid mixed oxide.	Apply Metal/Zirconia primer (*batch no. L08583*) on zirconium surfaces and air-dry. Mix equal amounts of Multilink Primer liquid A (*batch no. L02975*) & B (*batch no. L04570*), apply on resin surfaces, leave for 15 s and dry. Squeeze Multilink Automix (*batch no. L07859*) from the dispenser syringe, apply, self-cure (5 min) and light-cure.	Ivoclar Vivadent, Schaan, Liechtenstein

Abbreviations: MDP: methacryloyloxydecyl dihydrogen phosphate; MPS: methacryloxypropyltrimethoxysilane; HEMA: 2-hydroxyethyl methacrylate; TEGDMA, triethylene glycol-dimethacrylate; CQ, camphorquinone.

zirconium-dioxide specimen; type 4 – fracture of resin specimen; type 5 – fracture of zirconium-dioxide specimen. The percentage of each fracture pattern was calculated for each group.

Results

The mean bond strengths of the tested groups are shown in Table 2. Two-way ANOVA showed that tensile bond strength values were significantly affected by the luting agent system employed and by thermal aging ($P < 0.001$). Both the null hypotheses tested were thus rejected.

The highest tensile bond strength value in the non-thermal-aged groups was for specimens from the RELX group, although there was no statistically significant difference between these specimens and those from the CLF group (Table 2). The MLA group had the lowest bond strength ($P < 0.05$) of the non-thermal-aged groups. In the thermal-aged groups, the tensile bond strength values for the MLA and RELX groups were significantly higher than that of the CLF group (Table 2). Moreover, while TC significantly affected the bond strength of the RELX and CLF groups, the mean strength of the MLA group was not

Table 2 Mean tensile bond strengths (MPa) and standard deviations (SD) in experimental groups

	CLF Group	RELX Group	MLA Group
Non-thermocycled	3.29^a (0.60)	3.56^a (0.43)	2.86^b (0.39)
Thermocycled	2.55^c (0.70)	2.74^b (0.77)	2.97^b (0.52)

Identical superscript letters indicate no significant difference ($P > 0.05$).

Table 3 Percentage distribution of failure modes

	CLF Group				RELX Group				MLA Group			
	1	2	3	4	1	2	3	4	1	2	3	4
Non-thermocycled	20	80	0	0	40	60	0	0	20	80	0	0
Thermocycled	20	60	20	0	20	60	20	0	0	80	0	20

Type 1 - cement principally on resin specimen; type 2 - cement on resin and zirconium-dioxide specimens; type 3 - cement principally on zirconium-dioxide specimen; type 4 - fracture of resin specimen. There were no type 5 failures.

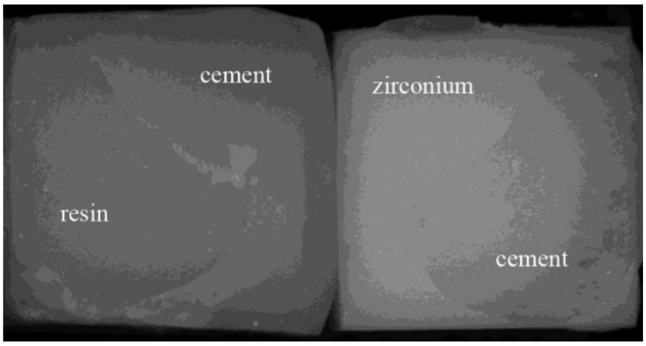

Fig. 1 Representative micrograph of a type 2 failure. The cement is evident both on resin and zirconium-dioxide specimens.

significantly different after the aging process.

The distribution of failure modes for each experimental group is summarized in Table 3. There was little difference among and within groups; mixed failure (type 2) was most common (Fig. 1); some type 1, 3, and 4 failures were also recorded. There were no cohesive failures in zirconium.

Discussion

Zirconium-oxide ceramics resist fracture loads and have optimal strength *in vitro* (2,23), but their use requires a reliable bond with the luting agent. The aim of this study was to evaluate the success of bonding between zirconia and 3 recently introduced cement types, and to assess durability after thermal aging. Zirconia-pretreated surfaces were not bonded to human dentin but to composite specimens. Because the purpose of the investigation was to analyze the cement-ceramic interface, the microstructural variations of natural tooth tissues, which could result in ambiguous results, were avoided (24,25).

In the non-aged groups, the bond strengths of the RELX and CLF groups were significantly higher than that of the MLA group. After thermocycling, the tensile bond strength values of the MLA and RELX groups were significantly higher than that of the CLF group. Moreover, thermocycling significantly decreased bond strength in the RELX and CLF groups. These varying results may be due to differences in monomer composition, initiator, and solvent between the 3 types of dual-cured resin cements. As reported by Oyagüe et al. (25), the adhesive potential of the CLF monomer 10-MDP to densely sintered zirconia, which results in the formation of a strong polymolecular film, may depend on the presence of a zirconium-oxide passive coating on the ceramic surface (25). The strength of the bond between phosphate monomer-containing CLF and zirconia highlights the capability of acidic functional monomers to react with the substrate (26,27). The functional monomer 10-MDP has been rated as relatively hydrolytic-stable (28) due to the presence of a decamethylene chain (22). However, Oyagüe et al. noted a statistically significant decline in bond strength of MDP-containing resin cement after 6 months of water storage when luting to either untreated or sandblasted zirconia surfaces; in contrast, no significant bond strength variability was seen for this type of resin cement after 6 months of water exposure when luting to silica-coated zirconia surfaces (25). In the present study, the influence of TC significantly affected bond strength in the RELX and CLF groups, despite the fact that a silica-coating process was chosen for treatment of the zirconium surfaces.

Long-term water storage and thermal cycling are the conditions most often used to test the durability of resin bonds. Both tests are considered clinically relevant aging parameters (29-31). In previous studies, long-term water storage was combined with TC at regular intervals to test the durability of bonds (32,33); however, this combination does not permit separate evaluation of the effect of each parameter on bond strength. The present work only investigated the effect of TC on bond strength. The observation period was too short to provide information on the long-term stability of the ceramic bond, as water saturation of the bonding interface was not achieved during this period (11,34). Due to the relatively short observation time, our findings must be interpreted with care. Nevertheless, in studies with a much longer aging time (150 days of water storage with 37,500 TC), there was only a slight, nonsignificant, decrease in the bond strength of a phosphate monomer-containing luting agent to different non-acid-etchable all-ceramic materials (glass-infiltrated alumina, zirconia, and alumina) (32,33).

In conclusion, this study showed that resin-ceramic interfacial longevity depends on cement selection, and that thermocycling plays a significant role in some cements in the degradation of resin cement/zirconia ceramic bonds.

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