Bonding performance of self-adhesive luting agents to highly translucent zirconia ceramics

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Abstract

Purpose: The purpose of this study was to evaluate the long-term durability of the bonds between self-adhesive luting agents and yttria-stabilized partially stabilized zirconia (Y-PSZ) and the effect of phosphoric acid etching as a surface pre-treatment to Y-PSZ.

Materials and Methods: A total of 180 Y-PSZ disks were divided into two groups; the control group and the phosphoric acid etching group prior to the bonding with one of three self-adhesive luting agents; Panavia SA Cement Plus Automix (SAP), RelyX Unicem2 Automix (UC2), or Maxcem Elite Chroma (MXE). Bonded specimens were stored in distilled water, for 1 day, 30 days, or 150 days. After storage, the tensile bond strength was measured using a universal testing machine. The data were statistically analyzed using Welch’s t-test and Welch’s t-test with Bonferroni correction (α = 0.05). Results: The tensile bond strength of each luting agent measured more than 15 MPa after 1 day of immersion in distilled water with or without phosphoric acid etching. There were no significant differences between SAP and UC2 after 30 days and 150 days (p > 0.05) of immersion. SAP and UC2 showed significantly higher bond strength than MXE after 30 days and 150 days (p < 0.05) of immersion. There were no significant differences between with/without phosphoric acid etching in all groups (p > 0.05).

Conclusion: Durability of self-adhesive luting agent to Y-PSZ was material-dependent. A surface pre-treatment with phosphoric acid etching to Y-PSZ did not affect the bond strength of self-adhesive luting agent to Y-PSZ.

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Key Words: durability, phosphoric acid etching, self-adhesive luting agent, tensile bond strength, Y-PSZ, zirconia

Introduction

Ceramic dental restorations have become increasingly popular due to their good esthetics and biocompatibility as compared with porcelain-fused-to-metal (PFM) restorations [1]. Early generation zirconia, conventional yttria-stabilized tetragonal zirconia polycrystals (Y-TZP), have outstanding mechanical properties but exhibit an inherent opacity that makes its use less desirable when the esthetic appeal is essential [2]. Recently, yttria-stabilized partially stabilized zirconia (Y-PSZ) has been introduced in dentistry. Y-PSZ contains more Y:O₂-stabiliser than Y-TZP and this results in a significant amount of cubic zirconia phase [3], which makes Y-PSZ highly translucent and especially suitable for anterior esthetic crowns [2]. Y-PSZ is more hydrothermally stable but has lower levels of mechanical properties than Y-TZP [3].

In comparison with silica-based ceramics, zirconia-based ceramics present difficulty in forming reliable and durable bonds with luting agents [4]. Correct luting agent selection is a prerequisite for obtaining good bonding and success of indirect restorations. Luting agents are recommended for adhesive bonding in dentistry because of their low solubility in the oral environment, reduced microleakage at the restoration-tooth interface, and good optical properties [5]. Self-adhesive luting agents represent the latest and most simplified category of luting agents that is much easier to use than the rest. Therefore, these luting agents have rapidly gained popularity as luting agents for all types of ceramic restorations.

Before the seating procedure, phosphoric acid gel is widely used in clinical situations to remove contaminants from the inner surface of restorations. At present, little information is available regarding phosphoric acid etching as a surface pre-treatment to Y-PSZ for its use in conjunction with self-adhesive luting agent. Therefore, the purpose of this study was to evaluate the long-term durability of the bond between self-adhesive luting agents and Y-PSZ and the effect of phosphoric acid etching as a surface pre-treatment to Y-PSZ. The null hypotheses tested in this study were that (i) selection of self-adhesive luting agent does not affect the bond strength between self-adhesive luting agent and Y-PSZ, (ii) the length of the storage period does not affect the bond strength between self-adhesive luting agent and Y-PSZ, and (iii) a surface pre-treatment with phosphoric acid etching to Y-PSZ does not affect the bond strength of self-adhesive luting agent to Y-PSZ.

Materials and Methods

The materials used in this study are listed in Table 1. One hundred and eighty fully sintered Y-PSZ disk-shaped specimens (Katana HT, Kuraray Noritake Dental, Tokyo, Japan) of 5 mm thickness 12 mm diameter were randomly divided into 18 groups (n = 10). All specimens were finished with 600-grit silicon carbide paper under running water and air-abraded using a blasting machine (Basic eco, Renfert, Hilzingen, Germany) with 0.3 MPa using 50 μm alumina particles (Cobra,
Renfert) for 20 s from a distance of 10 mm. Then they were ultrasonically cleaned in deionized water for 5 min and 99% ethanol for 2 min. The cleaned specimens were divided into two groups: the control (PA−) group and the phosphoric acid (PA+) group. The specimens in the PA+ group were treated with 40% phosphoric acid (K-etchant Gel, Kuraray Noritake Dental) for 20 s with a rubbing motion, left to stand for 10 s, rinsed with water for 20 s, and air-dried for 10 s. After the pretreatment, a plastic tape with a circular hole (4 mm in diameter and 100 μm in thickness) was placed on each of the specimens to demarcate the area for bonding.

Table 1 Materials used

| Material       | Code  | Manufacturer                     | Compositions                                                                 | Batch No.   |
|----------------|------|----------------------------------|------------------------------------------------------------------------------|-------------|
| Katana Zirconia HT | Zirconia | Kuraray Noritake Dental, Tokyo, Japan | ZrO₂, 90-95%; Y₂O₃, 5-8%; Others, <2%                                         | not available |
| Panavia SA Cement Plus Automix | SAP | Kuraray Noritake Dental | bis-GMA, TEGDMA, HEMA, 10-MDP, hydrophobic aromatic dimethacrylate, hydrophobic aliphatic dimethacrylate, sodium fluoride, silanated barium glass filler, silanated colloidal silica (70 wt% / 40 vol%) | 4E0205 |
| RelyX Unicem2 Automix | UC2 | 3M ESPE, St. Paul, MN, USA | Base Paste: methacrylate monomers containing phosphoric acid groups, methacrylate monomers, silanated fillers (70 wt% / 43 vol%), initiator components, stabilizers, rheological additives Catalyst Paste: methacrylate monomers, alkaline (basic) fillers, initiator components, stabilizers, pigments, rheological additives | 670650 |
| Maxcem Elite Chroma | MXE | Kerr Corporation, Orange, CA, USA | HEMA, GDM, UDMA, 1,1,3,3-tetramethylbutyl hydroperoxide TEGDMA, fluoroaluminosilicate glass, GPDM, barium glass filler, fumed silica (69 wt%) | 6325871 |
| K-etchant Gel | PA | Kuraray Noritake Dental | 40% phosphoric acid, water, colloidal silica, dye | CG0055 |
| Alloy Primer metal primer | | Kuraray Noritake Dental | VBATDT, 10-MDP, acetone | A40088 |

Stainless steel rods (8 mm diameter and 30 mm length) were used as an adherend. Stainless steel rods were finished with 600-grit silicon carbide papers and air-abraded in the same manner as Y-PSZ specimens. Then they were ultrasonically cleaned with water for 3 min. Stainless-steel rods were treated with metal primer (Alloy Primer, Kuraray Noritake Dental), and bonded to the Y-PSZ specimens with one of the three automix self-adhesive luting agents, Panavia SA Cement Plus Automix (SAP, Kuraray Noritake Dental), RelyX Unicem2 Automix (UC2, 3M ESPE, St. Paul, MN, USA), or Maxcem Elite Chroma (MXE, Kerr Corporation, Orange, CA, USA). Excess luting agent was removed from the bonding margin with a micro-brush and light-cured with an LED light-curing unit (VALO, Ultradent, South Jordan, UT, USA) at standard mode (1,000 mW/cm²) from each quarter for 10 s, that is, for 40 s in total. The bonded specimens were left at room temperature for 30 min. Then they were stored in deionized water at 37°C for 1 day, 30 days, or 150 days. The tensile bond strengths (TBS) were measured using a universal testing machine (Autograph AGS-J, Shimadzu, Kyoto, Japan) at a crosshead speed of 2 mm/min. Bond strength data were statistically analyzed by SPSS software (SPSS 22, IBM; Armonk, NY, USA) at a significance level of α = 0.05. Data distribution was evaluated primarily with the Shapiro-Wilk test, and equality of variance was evaluated with the Levene’s test. When the Shapiro-Wilk test showed a normal distribution and the Levene’s test did not show homogeneity of variances, then the data were analyzed with Welch's t-test to evaluate the differences between PA− and PA+, and Welch's t-test with Bonferroni correction to evaluate the differences among the luting agents and to evaluate the differences among the periods of storage.

After debonding, fractured specimens were observed with an optical microscope (SMZ100, Nikon, Tokyo, Japan) at ×8 magnification. The fractured specimens were classified into the following two types: A, adhesive failure at the interface between Y-PSZ and luting agent; and B, cohesive failure in luting agent and mixed failure.

Results
The TBS test results are shown in Table 2. Within the same luting agent and the same PA condition, there were significant differences among 1 day and 30 days, and 1 day and 150 days storage periods in all groups (p < 0.05). However, the
differences between 30 days and 150 days periods were not significant in any of the groups \( (p > 0.05) \). Within the same period and the same PA conditions, there were no significant differences between UC2 and MXE after 1 day, and between SAP and UC2 after 30 days and 150 days of storage \( (p > 0.05) \). There were no significant differences between PA− and PA+ in all groups \( (p > 0.05) \).

Representative fracture mode images are shown in Fig. 1. In the SAP groups, only type B was observed regardless of the PA status and storage period. In the UC2 groups, both type A and type B were observed regardless of their PA status and storage period. In the MXE groups, both type A and type B were observed regardless of their PA status after 1 day. Only type A was observed regardless of its PA status after 30 days and 150 days.

**Table 2** Tensile bond strength in MPa and the fracture mode distribution (Type A / Type B)

| Luting agent | PA | 1 day       | 30 days      | 150 days     |
|--------------|----|-------------|--------------|--------------|
| SAP          | –  | 21.60 ± 4.65 (0/10) | 8.64 ± 1.41c (0/10) | 9.20 ± 3.20ad (0/10) |
|              | +  | 18.30 ± 6.04a (0/10) | 10.03 ± 3.34bd (0/10) | 9.90 ± 2.08bf (0/10) |
| UC2          | –  | 15.13 ± 4.72b (4/6) | 8.12 ± 2.33c (2/8) | 9.72 ± 3.21ef (2/8) |
|              | +  | 17.45 ± 5.04a (2/8) | 6.73 ± 1.69ad (5/5) | 7.05 ± 2.47df (3/7) |
| MXE          | –  | 18.54 ± 11.56b (4/6) | 0.32 ± 0.01e (10/0) | 0.37 ± 0.02e (10/0) |
|              | +  | 17.70 ± 10.78b (2/8) | 0.34 ± 0.02f (10/0) | 0.32 ± 0.02e (10/0) |

All values are the mean ± SD. When the PA condition and the period are same, the values with the same capital superscript letters indicate no significant differences among the luting agents \( (p > 0.05) \). Same small superscript letters indicate no significant differences within the row \( (p > 0.05) \). Type A, adhesive failure at the interface between Y-PSZ and luting agent. Type B, cohesive failure in luting agent and mixed failure.

**Discussion**

The acidic functional monomers play a key role in self-adhesive luting agents. Molecular structure of functional monomers strongly influences the chemical interaction and bonding performance of luting agents with zirconia ceramics [6]. Each of the self-adhesive luting agents used in the present study contains specific acidic phosphate monomers. SAP contains 10-methacryloyloxydecyl dihydrogen phosphate (MDP), a phosphate methacrylate adhesive monomer, which has originally developed to bond to tooth structure and metal oxide restorative material. Research have shown that MDP promotes adhesion to zirconia through the chemical interaction between the phosphate ester group of MDP and the hydroxyl groups in the zirconia surface [7-9]. The chemical bond between MDP and bisphenol-A-diglycidyl-methacrylate (bis-GMA) composite resins is established by the methacrylate group of MDP and the composite resin matrix of the luting agent. The MDP molecule increases the bond strength by converting a hydrophilic surface to a hydrophobic one and by forming phosphoric acid salts between the composite and zirconia [10]. Additionally, the MDP molecule forms a hydrogen bond between of MDP and zirconia [10,11]. The combination of airborne particle abrasion and MDP monomer contained either in the adhesive primer or in the luting agent itself is the recommended method of bonding to zirconia [12-15]. In PA- group, SAP showed higher bond strength than UC2 and MXE after 1 day of storage in the present study. After 30 days and 150 days of storage, the SAP groups showed lower bond strength than after 1 day. However, all specimens of SAP group did not show adhesive failure at the interface between zirconia and luting agent. This result was in line with...
the previous study [16]. Accumulation of MDP on the zirconia surface probably improved adhesion and degree of conversion of luting agent [6].

UC2 has the characteristic of self-etching phosphorylated methacrylate that is designed to bond directly to both enamel and dentin. With two phosphate groups and at least two double-bonded carbon atoms, good bond strength with zirconia and adequate cross-linking to the resin matrix are achieved [17]. Self-adhesive luting agents have a low pH, and the acidic groups join with calcium hydroxyapatite to form a stable bond between the methacrylate network and tooth [18]. UC2 has been reported to have stable physical properties, i.e., water sorption, solubility, flexural strength, and pH-neutralization behavior [19]. Therefore, UC2 showed comparable TBS to SAP after 30 days and 150 days regardless of PA.

Although MXE group showed more than 15 MPa after 1 day of storage, the bond strength TBS of MXE dropped dramatically after 30 days and 150 days of storage. MXE contains glycerol-phosphate dimethacrylate (GPDM) which is one of the first chemical compounds proposed to bond to human dentin [20]. GPDM has one phosphate acidic functional group and two polymerizable methacryloyl groups [6,21]. A previous study reported that chemical interactions of GPDM with zirconia ceramic surfaces do not exhibit ordered arrangement due to steric hindrance [6].

GDM and tetramethylbutyl hydroperoxide in MXE may be responsible for water uptake and stress build-up associated with hydroscopic expansion. GDM has relatively higher hydrophilicity and water sorption [22] than other methacrylate monomers contained in SAP and UC2. Consequently, MXE was more prone to hydrolytic degradation. Thus, after 30 days and 150 days of storage MXE groups showed extremely low bond strength and a high rate of adhesive failure at the interface between zirconia and luting agent.

Differences in chemical and physical properties of self-adhesive luting agents may affect the bonding mechanism and bonding durability to zirconia ceramic [23,24]. According to what is stated above, the first and second null hypotheses were rejected, which means the selection of self-adhesive luting agent and storage period affected the bond strength of self-adhesive luting agent to Y-PSZ.

In the present study, a surface pre-treatment with phosphoric acid etching to Y-PSZ did not affect the bond strength in all groups. Thus, the third null hypothesis was accepted. In a clinical situation, contamination of the inner surface of restorations by saliva, blood, or silicone indicators during the try-in procedure of restoration is unavoidable [25]. Contamination deteriorates the bonding of the restoration, but this problem could be solved by using various surface cleaning methods. As for the mechanical cleaning method, alumina blasting is one of the effective methods to clean saliva contaminated restorations [26-28]. Airborne-particle abrasion cleans the bonding surface and increases roughness, surface area, and surface energy and therefore the wettability of zirconia surfaces [29,30]. Moreover, airborne-particle abrasion may generate on the zirconia surfaces the hydroxyl groups that facilitate the chemical reaction with phosphate monomer containing self-adhesive luting agent [30,31]. As for chemical cleaning methods, the use of a product composed of a supersaturated solution of zirconia particles in sodium hydroxide was recommended [32,33].

Several studies revealed that although PA removes organic residues from salivary contamination [26], PA might change the surface energy at the zirconia surface and, thereby, reduce the bonding properties [26,27,34,35]. Applying PA to surfaces of zirconia leaves a phosphorous residue that impairs the bond strength to luting agent [26,28,36]. The reason for the inconsistency of results between the previous studies and the present study was not clear, surface pretreatment with phosphoric acid etching did not improve the bond strength of any self-adhesive luting agents.

Within the limitation of this study, it can be concluded that the durability of self-adhesive luting agent to Y-PSZ was material-dependent. Also, a surface pre-treatment with phosphoric acid etching to Y-PSZ did not affect the bond strength of self-adhesive luting agent to Y-PSZ.

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Conflicts of Interest
None of the authors have any conflict of interest to declare.

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