

Effect of Artificial Saliva and pH on Shear Bond Strength of Resin Cements to Zirconia-Based Ceramic

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Abstract - The aim of the present study was to evaluate the effect of media with different pH on shear and strength of resin cements to zirconia-based ceramics. Sixty rectangularly shaped specimens made of a zirconia based ceramic (Cercon, Dentsply) were prepared, air-blasted with 110 μ m aluminum oxide particles (Al_2O_3) and randomly assigned into three groups ($n=30$). A universal resin composite (Filtek Z250, 3M/ESPE) was bonded to each specimen using one of the following three cements: Calibra (Dentsply), Panavia F2 (kurary) and Unicem (3M/ESPE). Specimens were thermal cycled and stored in one of the following three media for two weeks: water at pH=7, saliva at pH=7 and saliva at pH= 3.5. The mean shear bond strength of each group was analyzed using the Kruskal-Wallis test ($\alpha=0.05$). The modes of failure were recorded using a stereomicroscope. All specimens in the Calibra groups showed premature debonding. No significant difference was found between the two other cements or different media. The failure modes in the two latter cements were predominantly adhesive. Despite the adverse effect of acidic media on the properties of restorative materials, the media did not significantly influence the bond strength of MDP-containing resin cement and a self-adhesive cement to a zirconia- based ceramic.

KEYWORDS: zirconia, shear bond strength, resin cement, artificial saliva, pH

INTRODUCTION

Since the introduction of yttrium partially stabilized tetragonal zirconia polycrystalline (Y-TZP) to dentistry in the 1990s, the interest in this high strength ceramic has grown¹. Zirconia is the highest ranking among all other available dental ceramics in terms of fracture toughness (approximately 10 MPa/m^{0.5}) and flexural strength (approximately 1000 MPa)². The high fracture resistance of zirconia is based on a phenomenon known as “transformation toughening”. It involves stress-induced phase transformation of tetragonal zirconia to the monoclinic phase (t $\rightarrow$ m) at room temperature. This results in a 4-5% volume change, subsequently developing compressive stress and crack tip shielding, hindering its propagation³.

These unique mechanical properties as well as favorable optical behavior result in a wide range of clinical applications in implant dentistry and restorative procedures such as crowns and conventional fixed partial dentures (FPD) for replacing posterior teeth⁴. A success rate of 97.8 % was reported for anterior and posterior zirconia FPDs over a period of 5 years⁵. Marginal discrepancy, recurrent caries and fracture of veneering ceramic were the predominate types of complications^{6,7}. Clinically, fractured veneers can be restored either in the lab or intraorally. Another application of adhesive cements is for luting the restoration itself. It has been demonstrated that using adhesive resin cements instead of conventional cements results in improved marginal integrity and retention⁸.

The basic mechanism of bonding to ceramic systems relies on enhanced micromechanical retention by selective etching using hydrofluoric acid, increased surface wettability and chemical bonding using silane agents. However, the bonding mechanism and efficiency is not clearly known in non-silica-based all-ceramic systems such as zirconium oxide ceramic. It has been shown in previous studies that air abrasion plays an important role in improving the bond strength of resin cements to zirconia⁹⁻¹¹. Luting cements have been reported as another variable when bonding to metal oxide ceramics. In general, cements that employ 10-methacroyxydecyl dihydrogen phosphate (10-MDP) as functional monomers and self-adhesive cements showed better results compared with conventional Bis-GMA-based cements¹²⁻¹⁷.

Regardless of conditioning methods or luting cements, the durability of the bond strength has been questioned due to data showing that bond strength decreases by half or one-third after a period of storage in a wet environment and/or thermocycling¹⁵⁻¹⁹. Therefore, in the evaluation of restorative materials, it has been suggested that it is necessary to simulate relevant intraoral conditions such as the presence of saliva and pH that could influence the material properties²⁰. Therefore, the present study was conducted to examine the effect of storage media on the bond strength of different cements to zirconia ceramic. The null hypothesis was that storage media and cement types have no effect on the bond strength to a zirconia ceramic.

MATERIALS AND METHODS

Sixty rectangularly shaped (15×10×3 mm) specimens were made of presintered zirconia CAD/CAM blocks (Cercon, Dentsply, Konstanz, Germany) and polished with 600 grit abrasive paper. Surface treatment was performed perpen-

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dicularly to the ceramic surface using air abrasion with 110 μm aluminum oxide particles applied for 20 seconds at a distance of 10 mm and a pressure of 0.4 MPa and cleaned in an ultrasonic unit (Prosonic 300, Sultan Health care, Englewood, NJ USA) with 96% ethanol for 3 minutes. The specimens were randomly assigned to three groups according to the different cement types ($n=30$). Plastic tubes (3.2 mm in diameter and 3 mm in height, (Tygon, Norton Performance Plastic Co, Cleveland, OH, USA) were used to fabricate composite resin cylinders (Z250, lot 3LBJ, Shade A2, 3M ESPE, St Paul, MN, USA). The plastic tubes were filled incrementally with composite resin, and each layer was light polymerized using a light unit (Coltolux 75, Coltene/Whaledent, Cuyahoga Falls, Ohio, USA) for 60 s at 600 mW/cm² and a distance of 1.0 mm. The plastic tubes were removed carefully using a scalpel. Experimental groups were prepared by cementing the composite resin cylinder to the ceramic specimens using the following three cements according to the manufacturer's instructions: Panavia F2 (lot 0255AB, Kurary, Osaka, Japan, Group PAN), Calibra (lot 050412, Denstply/Caulk, Milford, DE, USA, Group CAL), and RelyX Unicem (lot 8GAL, 3M/ESPE, group UNC) (table 1). Each specimen was under constant force of 1 kg for 60 seconds before exposure to light from three directions. Specimens of each group were further divided into 3 ($n=10$) and stored in one of the following three media for two weeks: distilled water at 37 °C and pH=7.5, artificial saliva pH of 3.5 and artificial saliva with pH of 7.0. The standard formula of NF S91-141 was used in preparing artificial saliva. All specimens were subjected to thermal cycling for 1000 cycles between 5 °C and 55 °C with a dwelling time of 15 seconds.

The shear bond test was carried out using a universal testing machine (Zwick Roell Z050, Ulm, Germany) with a cross head speed of 0.5 mm/min. In order to similarly align the specimens to the blade of testing machine, an alignment jig was fabricated, and the force at failure was recorded. Bond strength was calculated by dividing the recorded force in newtons by the bonded area in square millimeters. Because the data were found to be non-normally distributed, mean differences in the shear bond strength of specimens were statistically analyzed using a non-parametric Krsukal-Wallis test at a significance level of $\alpha=0.05$. Fractured specimens were examined for mode of failures using a stereomicroscope and magnification of 40x (Zeiss OPM1; Carl Zeiss, Oberkochen, Germany). Mode of failures were assigned as adhesive, cohesive or mixed.

RESULTS

The means and standard deviations of bond strength of the tested groups with different cements in three media are shown in Table 1. The maximum and minimum bond strength values were 23.49 MPa (found in the PAN 3.5 group) and 5.65 MPa (found in the PAN 7.0 group), respectively.

All specimens in the CAL groups were prematurely deboned before the bond strength test. Therefore, these specimens were removed from the analysis. No significant differences were found between the two other test groups and storage media ($P>0.05$). Modes of failure for the specimens are shown in Table 2. Except for the CAL groups, there was no significant difference in types of failure with the two other cements.

Table 1. Bond strength values of tested specimens in three media.

<i>cements</i>	<i>medium</i>	<i>Minimum (MPa)</i>	<i>Maximum (MPa)</i>	<i>Mean $\pm$ Std</i>
Panavia F2	W	8.62	23.72	12.43(4.48)
	S7	5.65	11.63	9.06(1.83)
	S3.5	7.55	23.49	13.3(4.42)
Unicem	W	7.37	16.96	13.81(2.86)
	S7	8.68	20.74	15.34(2.30)
	S3.5	9.32	23.77	11.39(5.34)
Calibra	W	.00	.68	.07(.22)
	S7	.00	.99	.10(.03)
	S3.5	.00	.00	.00

W= water, S7=Saliva, pH 7, and S3.5=Saliva, pH3.5

Table 2. Frequency of failure modes.

<i>Medium</i>	<i>Water</i>			<i>Saliva pH =7</i>			<i>Saliva pH=3.5</i>		
<i>Failure mode</i>	A	M	C	A	M	C	A	M	C
Panavia F2	3	5	2	6	4	0	3	6	1
Unicem	5	5	0	4	4	2	2	5	3

A= adhesive, M=mixed, C=Cohesive

DISCUSSION

Several recent studies have investigated bonding of resin composite and resin luting agents to zirconia ceramics. Despite differences in hypotheses and methodologies, the results of many of these studies were consistent. It was demonstrated that employment of the combination of airborne particle abrasion and MDP-containing resin or self-adhesive cement resulted in more durable and higher bond strengths¹²⁻¹⁷. To this end, we included an MDP-containing resin cement (Panavia F2), a self-adhesive cement (Unicem) and a conventional Bis-GMA based cement.

In the present study, water storage and thermal cycling were included as aging parameters. While strong evidence justify using thermal cycling in studies on the adhesive bond strength to zirconia, the effect of different thermal cycling protocols was compared in few reports²¹. Therefore, such evaluation about the thermal cycling regimen is difficult and the choice is made arbitrary. Regarding the wide range of 500 to 50,000 cycles that has been applied in the studies²², 1000 cycles was chosen in the present study which is safely more than the recommendation of ISO TR 11450 standards²³.

No significant differences were observed for the mean bond strength of Panavia F2 and Unicem regardless of the storage media used. It is noteworthy that in a study of different aging condition on zirconia ceramic, MDP-congaing composite resin (Panavia) showed more stable, water resisted interface than conventional bis-GMA cements and did not show significant decrease after 35000 thermal cycles¹⁸. 10,000 thermal cycling also did not change the ranking of the MDP-containing luting cements with compared to other conventional resin cements¹⁹.

High performance of these cements has also been reported in other investigations, which will be discussed. A Dual polymerizing bis-GMA composite resin cement (Calibra) showed premature debonding before any testing. Despite the dissimilarity in the present test variable and design, this finding confirmed previous studies on the subject of bond strength of the cement types to the zirconia ceramic^{1,13,15,18,19,24}. The lack of an adhesive functional monomer and absence of an interfacial hydrophobic layer, which may lead to water penetration and hydrolysis of bonded interfaces, could be a contributing factor in the lower performance of this cement.

The present study was intended to evaluate the bond strength of different cement types to zirconia in artificial saliva with different pH levels. No significant differences were found between different pH values. Acidic solutions (pH 3-4) have been shown to facilitate corrosion (degradation) on several silica based ceramics that contain alkaline ions in flux²⁵. In those ceramics, corrosion occurs as a consequence of an exchange of H⁺ from the medium with alkaline ions from the porcelain²⁶.

However, polycrystalline ceramics such as zirconia and alumina demonstrated improved chemical durability in acidic medium²⁷. Partially stabilized zirconia (Y-TZP) is a zirconia alloy doped by 3% moles yttrium, which creates one oxygen vacancy for every two yttrium ions²⁸. Interaction of OH⁻ ions with oxygen vacancies may only occur at high pH values (>13). This exchange could produce tensile stress which acclerlates t→m transformation and

low thermal degradation of the zirconia surface^{29,30}. Fortunately, that high level of pH is less likely to occur in the oral environment. Another contributing factor for the result observed in the present study is that the bonded interface could protect the ceramic from direct exposure to the medium. As mentioned earlier, MDP-containing cements achieved higher bonds with suitable durability *in vitro*. The current evidence suggests that the phosphate ester group of the adhesive monomer bonds directly to metal oxides and hydroxyl groups on the ceramic surface. Moreover, the long hydrophobic carbonyl chains in Panavia F2 make the bonded interface hydrolytically most stable^{14,15}. On the other hand, the exact mechanism of Unicem self-adhesive cement adhesion to zirconia ceramic is not well understood. Nevertheless, following the setting process, the continued acid/base reaction between multiple acidic functional monomers and the basic fillers results in a hydrophobic matrix, and less water sorption and ion transportation is expected³¹. A study on the solubility of resin cements and the effect of pH on resin degradation also indicated that they are more resistant than cements with hydrophilic monomers³².

Because the composition of the corrosion medium affects the degradation of ceramic materials, artificial saliva was prepared as a test medium to simulate normal oral conditions. However, there are several important differences between the test medium and the *in vivo* condtions. A constant pH was used in the present storage medium, whereas oral pH is known to vary according to the acid production of bacterial plaques, ingested food, brushing, salivary secretion and saliva buffering²⁰. In additon, the biofilm present on most surfaces in the oral cavity could affect chemical reactions³³. This needs to be further studied, and direct extrapolation of the results of the present study to clinical situations must be done cautiously.

The shear bond test has been criticized for inducing non-homogenous stress on the bonded interface, leading to either higher bond strength or errornous interpretation of data³⁴. It has been further rationalized by more cohesive failure in the shear bond test, which is not realistic³⁵. Despite the aforementioned facts, the shear bond test is still among the most common test methods used for measuring bond strength between resin composites and ceramics. It is suggested for use because it avoids the difficulties in preparing specimens when bond strenth is evaluated in high strength ceramics such as zirconia. With high strength ceramics, cutting the specimens could cause defects in the bonded interface and consequently result in faulty results³⁶.

Therefore, SBS was utilized in the present study because the specimens can be prepared with less risk of premature fracture, and SBS may provide information on overall bond stregnth. At the same time, its reliability has been demonstrated in other studies.¹ Despite the claim that the specimen size and preparation could affect the results, the bond stregnth values obtained in the present study were in the range of previous studies and considered sufficient values for the real situation.¹⁹ In additon, none of the failure modes were cohesive in the ceramics, adding to the validity of the test methodology³⁵.

Although two weeks storage in the medium was regarded as sufficient for the bonded interface to reach to a saturation level, chemical interaction in the presence of a variable

pH proved to be more complex and may require longer periods of storage, and continuous pH monitoring is recommended in future studies.

CONCLUSION

Within the limitations of the present study, Panavia F2 and Unicem demonstrated satisfactory performance in media with different pH. Calibra failed in bonding to Cercon ceramic and is not recommended for this purpose.

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