The role of functional phosphoric acid ester monomers in the surface treatment of yttria-stabilized tetragonal zirconia polycrystals

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This study aimed to evaluate the bond strength of a resin cement to yttria-stabilized tetragonal zirconia polycrystals (Y-TZPs) treated with three different phosphate functional monomers containing primers by measuring the water contact angle. Seventy Y-TZP discs were divided into seven experimental groups ($n=10$), including an untreated (control) group. Specimens were treated with one of the following monomers: MDP (MD), GPDM (GP), and Phenyl-P (PP). After primer application and air drying, half the treated specimens were ultrasonically cleaned in ethanol for 2 min (MD-e, GP-e, and PP-e), and contact angles were measured. The tensile bond strength test was performed after storage for 24 h in 37°C water. The contact angle on the MD-e surface (64°) was significantly higher than that on the Con, GP-e, and PP-e surfaces (51°–52°). The application of the MDP-containing primer resulted in significantly higher bond strength between Y-TZP ceramics and a resin cement.

Keywords: Phosphoric functional monomer, Yttria-stabilized tetragonal zirconia, Tensile bond strength, Contact angle, Adhesion

INTRODUCTION

In recent years, yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) ceramics have become increasingly popular in dentistry due to their superior optical properties, biocompatibility, and mechanical properties than other conventional all-ceramic materials¹. Y-TZP ceramics have been used as a metal-free alternative for conventional dental materials for various dental clinical applications such as abutments for implants, crowns, and fixed partial prostheses². However, a significant drawback of these ceramics is their limited ability to adhere to resin cements because of their glass-free polycrystalline microstructure³. Moreover, traditional silane coupling agents used with silica-based ceramics are ineffective with zirconia⁴ due to the lack of silica in Y-TZP ceramics.

To overcome this problem, several methods that improve the bonding performance between resin cement and Y-TZP ceramics have been reported. Particle air abrasion using Al_2O_3 has been reported to provide effective initial bond strength through micromechanical interlocking, although spontaneous failure may occur following storage for a period of time^{5,6}. A tribochemical silica coating (Rocatec and Cojet, 3M ESPE, St. Paul, MN, USA) can be created by abrasion with airborne silica-coated aluminum particles that result in the formation of a silica layer on the roughened Y-TZP surfaces due to high-speed impact^{7,8}. This silica layer then allows silanization with a silane coupling agent (γ -MPTS) to produce a chemical bonding, which significantly enhances the bond strength between a treated substrate and resin cement⁹. However, several studies have also

reported that water storage and thermal cycling result in a decrease in the bond strength between silica-coated Y-TZP surfaces and resin cements¹⁰.

Recently, adhesive strategies that combine chemical and mechanical pre-treatment have been developed. Kern and Wegner⁷ reported that sandblasting with Al_2O_3 and resin cements containing 10-methacryloyloxydecyl dihydrogenphosphate (MDP) as a monomer is essential to achieve strong and durable bonding to zirconia ceramics. Therefore, air abrasion at 0.2–0.3 MPa combined with MDP-containing primer/cement is the most popular method for achievement of a strong and reliable bond between Y-TZP and resin-based cements^{11,12}. However, there are a limited number of studies that focus on the effects of acidic phosphate monomers on the Y-TZP surface after the application.

Therefore, the purpose of this study was to measure the water contact angle formed on a Y-TZP ceramic surface and to examine the role of functional phosphoric acid ester monomers on the bond strength of a resin cement.

MATERIALS AND METHODS

Experiment 1 —Contact angle measurement

The materials used are listed in Table 1. Seventy Y-TZP discs (Lava, 3M ESPE) were fabricated according to the manufacturer's instructions. The surfaces of the specimens were wet-polished using #600-grid SiC paper and was then cleaned with deionized water for 5 min and 99% ethanol for 2 min. They were then randomly divided into seven experimental groups (Fig. 1), including one control (left untreated; Con group). The experimental specimens were treated with three different phosphate functional monomers [MDP (MD),

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Table 1 Composition of the materials used in this study

Material	Manufacturer	Composition
Lava Zirconia Blocks	3M ESPE	zirconium dioxide, yttrium oxide, aluminum oxide, hafnium dioxide
Clearfil Esthetic Cement	Kuraray Noritake Dental	A paste: surface treatment glass filler, surface treatment barium glass filler, silica-based microfiller, dimethacrylate monomer, chemical polymerization catalyst, etc. B paste: surface treatment glass filler, surface treatment barium glass filler, chemical polymerization catalyst, silica-based microfiller, dimethacrylate monomer, photopolymerization catalyst, etc.
Experimental Primer	Kuraray Noritake Dental	MDP primer: 5% 10-methacryloyloxydecyl dihydrogen phosphate in ethanol GPDM primer: 5% glycerol phosphate dimethacrylate in ethanol Phenyl-P primer: 5% methacrylic acid 2-(phenoxyphosphonyloxy)ethyl ester in ethanol
MDP		$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}-\text{O}-(\text{CH}_2)_{10}-\text{O}-\text{P}(\text{OH})_2$
GPDM		$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}-\text{O}-\text{CH}_2-\text{CH}(\text{O}-\text{P}(\text{OH})_2)-\text{CH}_2-\text{O}-\text{CO}-\text{C}(\text{CH}_3)=\text{CH}_2$
Phenyl-P		$\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{P}(\text{OH})_2-\text{O}-\text{C}_6\text{H}_5$

Fig. 1 Schematic illustration of the methodology of specimen preparation for contact angle measurement.

GPDM (GP), and Phenyl-P (PP)] containing primers (experimental primer, 5% in ethanol, Kuraray Noritake Dental, Tokyo, Japan) for 10 s. After primer application and air drying with forceful air, half the specimens treated with the primers were ultrasonically cleaned in ethanol for 2 min to remove unreacted functional monomers (MD-e, GP-e, and PP-e). Thereafter, a deionized water droplet was placed on the surface of each specimen ($n=10$), and the contact angle was measured using a contact angle measuring device (VCA OPTIMA-XE, Techscience, Koshigaya, Japan). Each measurement was repeated at least three times, and the mean value was reported. Data were statistically analyzed using Dunnett's T3 test with Bonferroni correction and 95% confidence intervals.

Experiment 2—Tensile bond strength test

Seventy Y-TZP discs were prepared in the same manner as mentioned above, sandblasted with aluminum oxide (50 μm , 0.2 MPa, 10 s, 10 mm distance), and cleaned with deionized water for 5 min and ethanol for 2 min (Fig. 2). After surface cleaning with 40% phosphoric acid gel (K-etchant, Kuraray Noritake Dental), the specimens were randomly divided into seven experimental groups (Con group or pre-treated with the three different phosphate functional monomers containing primers mentioned above) for 10 s. After primer application and air drying with forceful air, half the primer treated specimens were ultrasonically cleaned in ethanol for 2 min to remove unreacted functional monomers (MD-e, GP-e, and PP-e). A piece of aluminum tape with a circular hole of 4 mm diameter and 100 μm thickness was placed on the specimen surface to demarcate the

Fig. 2 Schematic illustration of the methodology of specimen preparation for the tensile bond strength test.

Table 2 Means and standard deviations of contact angles (°) of all groups ($n=10$)

	MD	GP	PP	Con
Ethanol cleaning (–)	n.d.*	24.2±5.6	33.6±2.7	51.2±3.2 ^a
Ethanol cleaning (+)	65.4±3.5	54.9±5.0 ^a	49.9±4.0 ^a	—

Means followed by the same superscript letter are not statistically different ($p>0.05$).

* not detected due to water droplet spread out

bonding area. An MDP-free dual-cured resin cement (Clearfil Esthetic Cement, Kuraray Noritake Dental) was applied to the treated surface as a handle with the help of a metal primer-treated stainless steel rod for the subsequent tensile bond testing and was then light cured with a halogen light (Optilux 501, 600 mW/cm², Demetron, Danbury, CT, USA) for 40 s. The specimens were stored at room temperature for 1 h, followed by water at 37°C for 24 h. Tensile bond strengths were measured using a universal testing machine (Autograph AGS-J, Shimadzu, Kyoto, Japan) at a crosshead speed of 2 mm/min. Data were statistically analyzed using Dunnett's T3 test with Bonferroni correction and 95% confidence intervals. After tensile bond strength testing, the failure mode was examined under a light microscope (OCS 912042, Olympus, Tokyo, Japan). Failure modes were classified into the following two categories: adhesive failure between ceramics and resin cements and mixed failure including cohesive failure within resin cements. Data were analyzed using the chi-square test with Bonferroni correction and 95% confidence intervals.

RESULTS

Experiment 1—Contact angle measurement

The contact angle on the MD surface could not be measured due to the spreading of the water droplet. Table 2 shows the contact angles of each group. The GP and PP groups exhibited significantly lower contact angles than the Con group ($p<0.05$); however, these differences ceased to exist after ethanol ultrasonic cleaning ($p>0.05$). The contact angle on the MD-e surface (65.4°) was significantly higher than that of the Con, GP-e, or PP-e groups.

Experiment 2—Tensile bond strength test

The results of the tensile bond strength test are summarized in Table 3. MD and MD-e exhibited the highest tensile bond strengths among the tested groups, being significantly higher than that of the PP, PP-e, and Con groups ($p<0.05$). Ethanol ultrasonic cleaning after primer application tended to improve the tensile bond strength of each monomer, but these differences were not

Table 3 Means and standard deviations of tensile bond strength (MPa) for all groups ($n=10$)

	MD	GP	PP	Con
Ethanol cleaning (–)	12.5±3.9 ^a	9.1±3.8 ^{ac}	4.9±1.6 ^{bc}	4.5±1.2 ^{bc}
Ethanol cleaning (+)	13.8±3.8 ^a	11.7±4.8 ^{ac}	7.2±2.7 ^{bc}	—

Means followed by the same superscript letters are not significantly different ($p>0.05$).

Table 4 Failure mode distribution in all groups (adhesive failure/cohesive and mixed failure, $n=10$)

	MD	GP	PP	Con
Ethanol cleaning (–)	0/10 [*]	10/0	10/0	10/0
Ethanol cleaning (+)	5/5	10/0	10/0	—

* represents a statistically significant difference in distribution ($p<0.05$) as seen in chi-square test.

statistically significant. The failure mode distribution is summarized in Table 4. All specimens, except MD and MD-e, exhibited adhesive failure between the ceramic and resin cement. Half the MD-e and all MD specimens exhibited cohesive or mixed failure within the resin cement. The chi-square test indicated that MD ($p<0.05$) was significantly different.

DISCUSSION

To achieve durable bonding with zirconia-based ceramics, surface cleaning to remove contamination (oil, saliva protein, *etc.*), surface roughening to achieve mechanical interlocking, and improvement of surface wettability using phosphate functional monomers are essential before the application of resin cements. Dental resin cements that do not contain any phosphate functional monomers exhibit hydrophobic characteristics due to the nature of their monomers. The wettability of luting cements is one of the factors that predicts adhesive properties between resin cements and adherends. The monolayer chemically bonded phosphate functional monomers create relatively low surface energy in zirconia ceramics, leading to a higher contact angle¹³. Therefore, measuring the contact angle of a water droplet serves as a convenient indicator of the surface modification of zirconia ceramics with phosphate functional monomers.

In this study, the contact angle of the Con group was 51.2°, and this was in agreement with a previous study that used the same material surface¹⁴ (52.7°). MD-e exhibited a significantly higher contact angle than the GP-e, PP-e, and Con groups and significantly higher tensile bond strength than the PP-e and Con groups. MDP is one of the most frequently used phosphate functional monomers and was originally designed to enhance bond strength to tooth substrate and non-precious metal alloys. Similar to the interaction of phosphoric functional monomers with

hydroxyapatite^{15,16}, a chemical interaction is believed to occur between the functional monomer and the hydroxyl group of metal ions on the ceramic surface¹⁷. Kern *et al.*¹⁸ reported that a combination of alumina particle air abrasion and priming with MDP-containing primers provided durable, long-term bonding to dental zirconia ceramics. MD exhibited the highest bond strength among all treated specimens, regardless of whether the primer-treated surface had undergone ethanol cleaning. These adhesive monomers are believed to possess the ability to chemically adsorb onto metal oxide surfaces, resulting in secondary forces such as van der Waals forces or hydrogen bonds at the resin-zirconia interface¹⁹. These adsorbed monomers are arranged in a single layer with the hydrophobic methacryloyloxy group on the surface, resulting in an improvement in the surface wettability of zirconia ceramic surfaces to resin cements.

The groups that did not undergo ethanol ultrasonic cleaning after primer application exhibited lower contact angles, regardless of the choice of phosphoric functional monomer. Ethanol evaporates from the primer on the ceramic surface while air dry, unreacted monomer must have accumulated and left unevenly on the surface. Phosphate functional monomers possess both hydrophilic and hydrophobic characteristics, and the initial dentin bond strength is influenced by the length and hydrophilicity of their spacer chains²⁰. Thus, in the absence of ethanol cleaning, the hydrophilic parts of the phosphoric functional monomers were scattered on the surface, resulting in lower contact angles than those of the Con group.

Ethanol cleaning resulted in the contact angles of GP-e and PP-e significantly differing from that of the Con group, and they also exhibited higher tensile bond strength. Chemical interactions of GPDM and Phenyl-P with zirconia ceramic surfaces do not exhibit ordered arrangement due to steric hindrance, resulting in adhesive failure between the ceramic and resin

cement. Cohesive failure within the resin cement was observed in the MD and MD-e groups, with a better bonding performance, despite the fact that they exhibited completely different surface characteristics. The balanced molecular structure of MDP makes its soluble in water and dimethacrylate monomers²⁰. In the MD group, MDP accumulated after primer application and air drying may have dissolved into and polymerized with the dimethacrylate monomers in the resin cement. The degree of conversion of a resin can be affected by the functional monomer²¹. The degree of conversion of resin cement may have been affected by contamination with accumulated MDP left on the surface in the MD group which, along with improved adhesion, may have resulted in the higher frequency of cohesive failure observed in this group. These results suggest that the molecular structure of phosphoric functional monomers strongly influences the chemical interaction and bonding performance of resin cements with zirconia ceramics. Further investigations focusing on long-term bond durability and the mechanism of chemical interaction between zirconia ceramics and functional monomers are necessary.

CONCLUSIONS

Within the limitations of this study, the following conclusions were drawn:

a) MDP-containing primers exhibited the best bonding performance among all tested phosphoric functional monomers and b) their chemical interaction ability was strongly influenced by the molecular structure.

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