



SHORT COMMUNICATION

# Evaluation of five primers and two opaque resins for bonding ceria-stabilized zirconia/alumina nanocomposite



Kohji Kamada <sup>a</sup>, Yohsuke Taira <sup>b\*</sup>, Ikuya Watanabe <sup>c</sup>,  
Takashi Sawase <sup>b</sup>

<sup>a</sup> Department of General Dentistry, Nagasaki University Hospital, Sakamoto, Nagasaki, Japan

<sup>b</sup> Department of Applied Prosthodontics, Graduate School of Biomedical Sciences, Nagasaki University, Sakamoto, Nagasaki, Japan

<sup>c</sup> Department of Dental and Biomedical Materials Science, Graduate School of Biomedical Sciences, Nagasaki University, Sakamoto, Nagasaki, Japan

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## KEYWORDS

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**Abstract** The purpose of this study was to evaluate the effect of five primers [Super-Bond C&B Monomer (SB), Clearfil Ceramic Primer, Alloy Primer, M.L. Primer, and AZ Primer] and two undercoating opaque resins [Super-Bond C&B (S-opaque) and Ceramage Pre-opaque (C-opaque)] on the bonding of a resin composite veneering material to a ceria-stabilized tetragonal zirconia polycrystals/alumina nanocomposite (Ce-TZP/Al<sub>2</sub>O<sub>3</sub>). Disk-shaped specimens of Ce-TZP/Al<sub>2</sub>O<sub>3</sub> were sandblasted with alumina and primed. The undercoating opaque resins and resin composites were subsequently applied to the specimen, and then light cured. After 5000 thermocycles at 4°C and 60°C, shear bond strengths were determined. Data were analyzed using analysis of variance, Tukey–Kramer honest significant difference test, and Student *t* test ( $n = 10$ ,  $\alpha = 0.05$ ). With the exception of SB/S-opaque, all S-opaque groups exhibited significantly higher bond strengths than C-opaque groups. The use of S-opaque resin is recommended when veneering frameworks made of Ce-TZP/Al<sub>2</sub>O<sub>3</sub>.

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\* Corresponding author. Department of Applied Prosthodontics, Graduate School of Biomedical Sciences, Nagasaki University, 1-7-1 Sakamoto, Nagasaki 852-8588, Japan.

E-mail address: [yohsuke@nagasaki-u.ac.jp](mailto:yohsuke@nagasaki-u.ac.jp) (Y. Taira).

## Introduction

With the development of computer-aided design and manufacturing (CAD/CAM) systems, tetragonal zirconia polycrystals (TZPs) have increasingly been used for crown restorations, dentures, and implant-supported superstructures. Recently, ceria-stabilized TZPs/alumina (Ce-TZP/ $\text{Al}_2\text{O}_3$ ) nanocomposites have been produced, and are commercially available as machinable ceramics for a CAD/CAM system (C-Pro System; Panasonic Health Care Co., Tokyo, Japan).<sup>1</sup> Compared with the more commonly used yttria-stabilized TZPs (Y-TZPs), Ce-TZP/ $\text{Al}_2\text{O}_3$  possesses higher mechanical strength and fracture toughness.<sup>2,3</sup>

Zirconia restorations can be veneered with glass ceramics or resin composites; however, chipping is a substantial problem for the veneering materials.<sup>4</sup> When compared with glass ceramics, resin veneers have the advantages of easy handling and no firing shrinkage. When minor defects in veneered zirconia restorations occur, they may be repaired with resin composite materials. Therefore, strong bonding between opaque resins and Ce-TZP/ $\text{Al}_2\text{O}_3$  frameworks is a prerequisite for the adequate maintenance of aesthetic restorations.

Bond strength between Y-TZP and luting cements is affected by surface treatment, cement type, and thermocycling.<sup>5</sup> In a previous study, silica coating significantly improved the bond strength of Y-TZP.<sup>6</sup> Some adhesion-promoting monomers, such as 10-methacryloyloxydecyl dihydrogen phosphate (MDP), 6-methacryloyloxyhexyl phosphonoacetate (6-MHPA), and 4-methacryloyloxyethyl trimellitate anhydride (4-META), have been recommended for Y-TZP.<sup>7</sup>

A self-curing resin that consists of 4-META, methyl methacrylate (MMA), and tributylborane (TBB) promotes adhesive bonding to metal alloys.<sup>8,9</sup> A 4-META/MMA–TBB resin exhibited higher bonding durability to a cobalt–chromium alloy than a light-curing opaque resin.<sup>9</sup> However, to the best of our knowledge, no information is available on bonding of 4-META/MMA–TBB resin to Ce-TZP/ $\text{Al}_2\text{O}_3$ . Although initiation of polymerization is an important factor for adhesive bonding,<sup>10</sup> little attention has been directed to the role of the polymerization initiator.

The purpose of this study was to investigate the shear bond strengths between Ce-TZP/ $\text{Al}_2\text{O}_3$  and a resin composite veneering material, with an emphasis on the significance of polymerization initiation. We tested the null hypothesis that neither primer nor 4-META/MMA–TBB resin improves bond strength.

## Material and methods

### Preparation of bonded specimens

The substrate material, primers, undercoating opaque resins, and veneering resin used in this study are presented in Table 1. A total 240 disk specimens of Ce-TZP/ $\text{Al}_2\text{O}_3$  (diameter: 10-mm; thickness: 2.5 mm) were ground using a 600-grit silicon carbide abrasive paper and ultrasonically cleaned with acetone for 10 minutes. The specimens were blasted with alumina (Hi-Aluminas; Shofu Inc., Kyoto, Japan) for 20 seconds using a sandblaster (Jet Blast III; J.

Morita Corp., Kyoto, Japan), and ultrasonically cleaned with acetone for 10 minutes. The air pressure used for sandblasting was 0.2 MPa. The disks were divided into 12 groups, each of which consisted of 20 specimens.

A 50- $\mu\text{m}$  thick piece of masking tape, with a circular hole of 5-mm diameter, was positioned on the surface of each specimen to delineate the bonding area. Primer and undercoating opaque resin were subsequently applied to the specimen. Super-Bond C&B (S-opaque; Sun Medical Co. Ltd., Morioka, Japan) is a TBB-initiated self-curing resin containing 4-META and MMA. Ceramage Pre-opaque (C-opaque; Shofu Inc.) was light polymerized for 60 seconds using a visible light-curing unit (Alpha-Light II; J. Morita Corp.), with a 360-W halogen lamp and two 27-W fluorescent lamps.

Ceramage Opaque (Shofu Inc.) was then applied to all 240 specimens and light polymerized for 180 seconds. After the procedures for each composite described above were completed, an acrylic ring (2.0 mm  $\times$  6.0 mm inside diameter) was placed on the specimen. The ring was then filled with a resin composite (Ceramage Body resin A3B; Shofu Inc.) and light cured for 240 seconds.

### Shear bond test

After the bonded specimens were stored at room temperature for 60 minutes, they were immersed in 37°C water for 24 hours. Half of the specimens (12 sets of 10 specimens) were tested for shear bond strength (designated “Thermocycle 0”). The remaining 12 sets of 10 specimens were thermocycled for 5000 cycles alternately between water baths held at 4°C and 60°C, with a 1-minute dwell time/bath. Each specimen was embedded in an acrylic resin mold and seated in a shear-testing device (ISO TR11405 jig; Wago Industrial Ltd., Nagasaki, Japan), which was used to apply a shearing load parallel to the bonded interface. Shear bond strengths were then determined using a universal testing machine (AGS-10kNG; Shimadzu Corp., Kyoto, Japan) at a crosshead speed of 0.5 mm/min.

### Failure mode observation

The debonded surfaces of all specimens were observed through an optical microscope (SMZ-10; Nikon Corp., Tokyo, Japan) at a magnification of 20 $\times$  to assess bond failure. Failure modes were categorized as *adhesive failure* (Ad), defined as failure at the undercoating opaque resin and Ce-TZP/ $\text{Al}_2\text{O}_3$  interface; *cohesive failure* (Co), defined as failure within the undercoating opaque resin; and *mixed failure* (Ad/Co), defined as adhesive failure at the undercoating opaque resin and Ce-TZP/ $\text{Al}_2\text{O}_3$  interface and cohesive failure within the undercoating opaque resin.

### Statistical analysis

The mean bond strength and the standard deviation for the 10 specimens were calculated for each group. Bond strength data were analyzed by two-way analysis of variance to determine the bond strength, and evaluate the interactions between different primers and undercoating opaque resins. The bond strengths were compared using a

**Table 1** Substrate material, primer, undercoating opaque resin, and veneering resin used in this study.

Name (abbreviation)	Component	Manufacturer	Batch No.
<b>Substrate material</b>			
NANOZR (Ce-TZP/Al <sub>2</sub> O <sub>3</sub> )	ZrO <sub>2</sub> , Al <sub>2</sub> O <sub>3</sub> , CeO <sub>2</sub> , others	Panasonic Health Care Co., Osaka, Japan	
<b>Primer</b>			
Clearfil Ceramic Primer (CP)	MDP, silane, ethanol	Kuraray Medical Co. Ltd., Osaka, Japan	00021C
Alloy Primer (AP)	MDP, VTD, acetone	Kuraray Medical Co. Ltd.	00413A
AZ Primer (AZ)	6-MHPA, acetone	Shofu Inc., Kyoto, Japan	031212
M.L. Primer (ML)	10-MDDT, 6-MHPA, acetone	Shofu Inc.	091156
Super-Bond C&B Monomer (SB)	4-META, MMA	Sun Medical Co. Ltd., Moriyama, Japan	FG1
<b>Undercoating opaque resin</b>			
Super-Bond C&B (S-opaque)	Powder: opaque ivory Monomer: 4-META, MMA Polymerization initiator: TBB	Sun Medical Co. Ltd.	EX1 FG1 EE1F
Ceramage Pre-opaque (C-opaque)	UDMA, 2-HEMA, aluminum silicate, glass powder, pigment, photoinitiator	Shofu Inc.	121139
<b>Veneering resin</b>			
Ceramage	Opaque A30: UDMA, 2-HEMA, aluminum silicate, glass powder, pigment, photoinitiator Body resin A3B: UDMA, 2-HEMA, urethane diacrylate, zirconium silicate, pigment, photoinitiator	Shofu Inc.	101150 121127

2-HEMA = 2-hydroxyethyl methacrylate; 4-META = 4-methacryloyloxyethyl trimellitate anhydride; 6-MHPA = 6-methacryloyloxyhexyl phosphonoacetate; 10-MDDT = 10-methacryloyloxydecyl-6,8-dithiooctanoate; Ce-TZP/Al<sub>2</sub>O<sub>3</sub> = ceria-stabilized tetragonal zirconia polycrystals/alumina nanocomposite; MDP = 10-methacryloyloxydecyl dihydrogen phosphate; MMA = methyl methacrylate; TBB = tributylborane; UDMA = urethane dimethacrylate; VTD = 6-(4-vinylbenzyl-*n*-propyl)amino-1,3,5-triazine-2,4-dithione-dithiol tautomer.

**Table 2** Shear bond strength and failure mode at Thermocycles 0 and 5000.

Group name	Mean (standard deviation), MPa		Failure mode (No. of specimens)	
	Thermocycle 0	5000	Thermocycle 0	5000
No-primer/S-opaque	20.6 (3.1) <sup>bcA</sup>	19.4 (3.3) <sup>aA</sup>	Ad/Co (10)	Ad/Co (10)
SB/S-opaque	17.2 (3.5) <sup>cdA</sup>	1.6 (1.2) <sup>bb</sup>	Ad/Co (10)	Ad (10)
CP/S-opaque	25.7 (3.2) <sup>aA</sup>	20.2 (3.9) <sup>ab</sup>	Ad/Co (10)	Ad/Co (10)
AP/S-opaque	23.5 (2.7) <sup>abA</sup>	16.9 (4.0) <sup>ab</sup>	Ad/Co (10)	Ad/Co (10)
AZ/S-opaque	22.9 (4.4) <sup>abA</sup>	17.9 (4.8) <sup>ab</sup>	Ad/Co (10)	Ad/Co (10)
ML/S-opaque	21.4 (3.9) <sup>ba</sup>	17.0 (5.0) <sup>ab</sup>	Ad/Co (10)	Ad/Co (10)
No-primer/C-opaque	7.5 (1.0) <sup>fa</sup>	0	Ad (10)	Ad (10)
SB/C-opaque	9.4 (2.2) <sup>fa</sup>	0.1 (0.2) <sup>bb</sup>	Ad (10)	Ad (10)
CP/C-opaque	13.5 (1.2) <sup>deA</sup>	0.3 (0.5) <sup>bb</sup>	Ad (10)	Ad (10)
AP/C-opaque	9.6 (1.2) <sup>efa</sup>	0.3 (0.7) <sup>bb</sup>	Ad (10)	Ad (10)
AZ/C-opaque	10.6 (1.7) <sup>efa</sup>	0.7 (0.7) <sup>bb</sup>	Ad (10)	Ad (10)
ML/C-opaque	10.0 (1.0) <sup>efa</sup>	0.3 (0.7) <sup>bb</sup>	Ad (10)	Ad (10)

The identical small letters in the same columns or capitals on each horizontal line in the same plane indicate that the values are not significantly different ( $P > 0.05$ ).

Ad = adhesive failure at the undercoating opaque resin-Ce-TZP/Al<sub>2</sub>O<sub>3</sub> interface; Ad/Co = mixed failure (adhesive failure at the undercoating opaque resin-Ce-TZP/Al<sub>2</sub>O<sub>3</sub> interface and cohesive failure within the undercoating opaque resin); AP = Alloy Primer; AZ = AZ Primer; CP = Clearfil Ceramic Primer; ML = M.L. Primer; SB = Super-Bond C&B Monomer.

Tukey–Kramer honest significant difference test or Student *t* test, with *P* values < 0.05 considered statistically significant. Failure mode data were analyzed by Chi-square test, with a significance level of 0.05.

## Results

Analysis of variance results indicated that bond strength was significantly influenced by the primer and the undercoating opaque, and that their interactions were significant. At Thermocycle 0, three groups using S-opaque [Clearfil Ceramic Primer (CP)/S-opaque, Alloy Primer (AP)/S-opaque, and AZ Primer (AZ)/S-opaque] exhibited the highest bond strengths, followed by M.L. Primer (ML)/S-opaque, no-primer/S-opaque, Super-Bond C&B Monomer (SB)/S-opaque, and CP/C-opaque (Table 2). The remaining five groups using C-opaque (no-primer/C-opaque, SB/C-opaque, AP/C-opaque, AZ/C-opaque, and ML/C-opaque) resulted in the lowest bond strengths.

After 5000 thermocycles, all S-opaque groups except SB/S-opaque exhibited significantly higher bond strengths, compared with all C-opaque groups. With the exception of no-primer/S-opaque, the bond strength in each group was significantly decreased during the 5000 thermocycles. No significant difference was found among the four primers (CP, AP, AZ, and ML) for either undercoating opaque resin.

Chi-square tests indicated that the failure mode was significantly influenced by the undercoating opaque resin ( $\chi^2 = 120$ , *P* < 0.0001), but not by the primer ( $\chi^2 = 0$ , *P* > 0.99) at Thermocycle 0. After 5000 thermocycles, both of the undercoating opaque resin ( $\chi^2 = 85.7$ , *P* < 0.0001) and the primer ( $\chi^2 = 17.1$ , *P* = 0.0042) affected the failure mode significantly.

With the exception of SB/S-opaque, the specimens using S-opaque (no-primer/S-opaque, CP/S-opaque, AP/S-opaque, AZ/S-opaque, and ML/S-opaque) exhibited Ad/Co. Although all specimens of SB/S-opaque showed Ad/Co before thermocycling, the failure modes completely shifted to Ad after thermocycling. By contrast, the failure mode observed in all groups using C-opaque (no-primer/C-opaque, CP/C-opaque, AP/C-opaque, AZ/C-opaque, and ML/C-opaque) was Ad before and after thermocycling.

## Discussion

Analysis of variance indicated that bond strengths were significantly influenced by the primer, undercoating opaque resin, and thermocycling. Therefore, the null hypothesis was rejected.

Comparisons between the no-primer group and four primed groups (CP, AP, AZ, and ML) suggested that the effects of 6-MHPA are equivalent to MDP, irrespective of the presence of 6-(4-vinylbenzyl-*n*-propyl)amino-1,3,5-triazine-2,4-dithione-dithiol tautomer or 10-methacryloyloxydecyl 6,8-dithiooctanoate. Although SB contained 4-META and MMA, the results of no-primer/S-opaque and SB/S-opaque indicate that the group primed with SB weakened the

bonding of S-opaque (4-META/MMA–TBB resin). This may be due to the lack of TBB in the SB primer.

The polymerization initiator system and its effect on polymerization shrinkage is an important factor for adhesive bonding. When using a light-curing system, light irradiation of the resin surface initiates polymerization from the upper surface, so that the contraction stress weakens the adhesive force.<sup>10</sup> Therefore, we speculate that the contraction stress generated by the self-curing system using TBB is comparatively smaller, which assists chemical bonding between the functional monomer (6-MHPA or MDP) and Ce-TZP/Al<sub>2</sub>O<sub>3</sub>.

In conclusion, the undercoating opaque resins used, rather than the primers containing functional monomer, affected the bond strength before and after thermocycling. The self-curing S-opaque produced greater bond strengths between the resin composite veneering material and Ce-TZP/Al<sub>2</sub>O<sub>3</sub>, compared with the light-curing C-opaque. 4-META/MMA–TBB opaque resins are therefore an effective option for veneering frameworks made of Ce-TZP/Al<sub>2</sub>O<sub>3</sub> materials.

## Conflicts of interest

The authors have no conflicts of interest relevant to this article.

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