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Original

Effect of acidic primers on adhesive bonding of tri-*n*-butylborane initiated adhesive resin to alumina

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Abstract: The present study was conducted to evaluate the effect of acidic primers on adhesive bonding to sintered alumina. Alumina disk specimens were primed with one of the following acidic materials: Acryl Bond, All Bond II Primer B, Alloy Primer, Estenia Opaque Primer, Eye Sight Opaque Primer, M.L. Primer, MR. Bond, and Super-Bond Liquid. The disks were bonded with an adhesive resin (Super-Bond) initiated with a tri-*n*-butylborane (TBB) derivative, and bond strengths were determined. Average bond strength before thermocycling varied from 42.9 to 44.3 MPa, whereas post-thermocycling bond strength ranged from 22.0 to 42.8 MPa. Of the nine groups assessed, reduction of bond strength after thermocycling was not significant in three: Alloy Primer, Estenia Opaque Primer, and Eye Sight Opaque Primer. It can be concluded that phosphate-based primers are recommended for bonding sintered alumina with Super-Bond resin. (J Oral Sci 52, 571-576, 2010)

Keywords: alumina; acidic primer; bonding; tri-*n*-butylborane.

Introduction

Application of adhesive systems for seating ceramic restorations and fixed partial dentures (FPDs) has increased substantially. Aluminum oxide (alumina) has been used as a reinforcing component of dental feldspathic materials (1), and highly purified alumina has been introduced as a prefabricated coping material for a ceramic restorative system (2). It is of benefit to both patients and clinicians that alumina or alumina-based coping materials and abutment teeth can be bonded durably for an extended period for servicing of restorations and FPDs. Numerous papers have reported the effectiveness of adhesive systems for bonding alumina (3-16) and alumina-based materials (17-19). In a pioneering study of adhesive bonding of alumina and quartz, it was found that a carboxylic monomer was effective for bonding between alumina and an acrylic resin (3). Silane agents and/or surface preparations with silicon compounds have also been introduced for bonding alumina ceramic materials (3-6,8-11,13,14). Unlike silica-based materials, application of acidic compounds enhances bonding to alumina (3,6-16).

Although a number of adhesive systems for bonding ceramic restorations and FPDs are being introduced, only limited information is available about the bonding behavior of high-purity alumina, especially in relation to functional monomers in the bonding agents (3,15). The purpose of the present study was to evaluate the effect of acidic primers on bond strength of an acrylic resin joined to high-purity alumina.

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Materials and Methods

High-purity (99.7%) alumina sintered at 1,600°C for 5 days (Furuuchi Chemical Corp., Tokyo, Japan) was employed. Disk specimens of two sizes (10 and 8 mm in diameter by 3 mm thick) were prepared as the bonding substrates. Eight primers originally designed for priming casting alloys (Acryl Bond, AC; All Bond II Primer B, BP; Alloy Primer, AP; Estenia Opaque Primer, EP; Eye Sight Opaque Primer, EY; M.L. Primer, ML; MR. Bond, MR; and Super-Bond Liquid, SB) were assessed as bonding promoters. All the primers were a single liquid and contained at least one functional monomer. A self-polymerizing resin consisting of initiator, monomer liquid, and powder (Super-Bond, Sun Medical Co., Ltd., Moriyama, Japan) was selected as the luting agent. The initiator was partially oxidized tri-n-butylborane (TBB). The monomer liquid was methyl methacrylate (MMA) with 5% 4-methacryloyloxyethyl trimellitate anhydride (4-META). The powder was a finely pulverized poly(methyl methacrylate) (PMMA) with titanium dioxide pigment (Super-Bond Opaque Ivory powder). Information on the materials is summarized in Table 1.

A total of 144 pairs of specimens were wet-ground with a series of silicon-carbide (SiC) abrasive papers (400, 800, and 1,500 grit) and ultrasonically cleaned with acetone. The 144 disk pairs were divided into nine sets (eight primers and unprimed control, UP) of 16 specimen pairs. A piece of plastic tape with a circular hole 5 mm in diameter and 50 μm in thickness was positioned on the surface of the wide-diameter disk to define the area of the bond. Except for the control specimens (16 pairs), 128 disk pairs were primed with one of the eight primers, and air-dried. The 8- and 10-mm disks were bonded with the Super-Bond resin applied with the brush-dip technique. After bonding, a 5.0-N load was applied to the specimens for 30 minutes until setting of the resin material.

The bonded specimens were next immersed in water at 37°C for 24 h. This state was defined as 0 thermocycle, and one half of the specimens (nine sets of eight pairs) were shear-tested at this stage. The remaining half of the specimens (nine sets of eight pairs) were subsequently thermocycled in water between 5°C and 55°C for 100,000 cycles with a 60-s dwell time per bath (Thermal Shock Tester TTS-1 LM, Thomas Kagaku Co. Ltd., Tokyo, Japan). Each specimen was positioned in a specimen holder and the shear bond strength was determined with a mechanical testing device (Type 5567, Instron Corp., Canton, MA, USA) at a cross-head speed of 0.5 mm per minute. The average shear bond strength and eight replications were calculated for each group.

The results were primarily analyzed by the Levene test for evaluation of equality of variance (SPSS 15.0, SPSS

Table 1 Materials assessed

Material	Abbr.	Manufacturer	Lot number	Composition (%)
Substrate material				
Sintered alumina		Furuuchi Chemical Corp., Tokyo., Japan		99.7 Al_2O_3, 0.08 SiO_2, 0.05 MgO
Primer				
Alloy Primer	AP	Kuraray Medical Inc., Tokyo, Japan	0264AA	MDP, VBATDT, Acetone
Eye Sight Opaque Primer	EY	Mutsumi Chemical Ind. Co., Ltd., Yokkaichi, Japan	A5Y	MP, Solvent
Estenia Opaque Primer	EP	Kuraray Medical Inc.	0150BA	MDP, Solvent
MR. Bond	MR	Tokuyama Dental Corp., Tokyo, Japan	0060Y7	MMA, MAC-10
M. L. Primer	ML	Shofu Inc., Kyoto, Japan	70726	10-MDDT, 6-MHPA, Acetone
Super-Bond Liquid	SB	Sun Medical Co., Ltd., Moriyama, Japan	RL3	4-META, MMA
All Bond II Primer B	BP	Bisco, Inc., Schaumburg, IL, USA	700007751	BPDM
Acryl Bond	AC	Shofu Inc.	110625	4-AETA, 2-HEMA, MMA
Luting agent				
Super-Bond Catalyst		Sun Medical Co., Ltd.	RL43	TBB
Super-Bond Liquid		Sun Medical Co., Ltd.	RL3	4-META, MMA
Super-Bond Opaque Powder		Sun Medical Co., Ltd.	RF1	PolyMMA (PMMA), TiO_2

MDP, 10-methacryloyloxydecyl dihydrogen phosphate; VBATDT, 6-(4-vinylbenzyl-*n*-propyl) amino-1,3,5-triazine-2,4-dithione; MP, methacrylate-phosphate; MMA, methyl methacrylate; MAC-10, 11-methacryloyloxy-1,1-undecane dicarboxylic acid; 10-MDDT, 10-methacryloyloxydecyl-6,6-dithiooctanoate; 6-MHPA, 6-methacryloyloxyhexyl phosphonoacetate; 4-META, 4-methacryloyloxyethyl trimellitate anhydride; BPDM, Adduct of 2-HEMA and 3,4,4',5'-biphenyl tetracarboxylic anhydride; 4-AETA, 4-acryloyloxyethyl trimellitate anhydride; 2-HEMA, 2-hydroxyethyl methacrylate; TBB, tri-*n*-butylborane

Table 2 Shear bond strength median, mean, and standard deviation in MPa

	0 thermocycle				100,000 thermocycles				
Primer	Median	IQR	Mean(SD)	Categories	Median	IQR	Mean(SD)	Categories	*P* value
AP	44.5	2.4	44.3(1.5)	a	45.2	8.9	42.8(4.5)	b c	$P = 0.96$
EY	43.4	1.4	43.1(1.1)	a	42.3	3.5	42.0(2.5)	b	$P = 0.39$
EP	44.5	1.5	44.2(1.1)	a	43.0	6.5	41.8(3.5)	b d	$P = 0.20$
MR	43.2	1.9	42.9(1.0)	a	37.0	7.8	37.1(4.4)	b e	$P = 0.03$*
ML	43.1	1.2	43.1(0.8)	a	37.9	9.0	36.5(5.9)	b f g h	$P < 0.01$*
UP	43.4	2.3	43.3(1.3)	a	35.0	4.5	35.8(3.0)	b f	$P < 0.01$*
SB	43.1	2.4	43.3(1.2)	a	35.5	6.6	34.4(3.6)	c d e f g	$P < 0.01$*
BP	44.6	3.6	44.1(2.3)	a	25.3	10.6	25.7(5.4)	e g h	$P < 0.01$*
AC	43.7	2.4	43.7(1.2)	a	21.2	5.7	22.0(4.5)	e h	$P < 0.01$*

$n = 8$, IQR, Interquartile range. SD, Standard deviation. UP, Unprimed control. Identical letters indicated that the values are not significantly different ($P > 0.05$). *Significant difference between the pre- and post-thermocycling bond strengths ($P < 0.05$).

Inc., Chicago, IL, USA). The results were then analyzed by Kruskal-Wallis test (SPSS ver.15.0), followed by Steel-Dwass test (Kyplot 4.0, KyensLab Inc., Tokyo, Japan) at a significance level of $P < 0.05$. Differences between the pre- and post-thermocycling bond strengths for an identical priming condition were analyzed with the Mann-Whitney *U* test (SPSS ver.15.0).

After the shear testing, the debonded surfaces were observed through an optical microscope (8x; SZX9, Olympus Corp., Tokyo, Japan). The failure modes were classified into the following three categories: A, adhesive failure at the luting agent-alumina interface; C, cohesive failure within the luting agent; and CA, combination of cohesive and adhesive failures.

Table 3 Failure mode after the shear bond testing

Primer	0 thermocycle			100,000 thermocycles		
Failure mode	A	AC	C	A	AC	C
AP	6	4	0	6	2	0
EY	8	0	0	8	0	0
EP	6	2	0	8	0	0
MR	8	0	0	8	0	0
ML	7	1	0	8	0	0
UP	8	0	0	8	0	0
SB	8	0	0	8	0	0
BP	8	0	0	8	0	0
AC	8	0	0	8	0	0

UP, Unprimed control.
A, Adhesive failure at the aluminum oxide interface;
C, Cohesive failure within the luting agent;
AC, Combination of adhesive and cohesive failures.

Results

The Levene test run on the pre- and post-thermocycling groups did not show equality of variance for several groups. The Kruskal-Wallis test showed that χ^2 values were 10.520 for the pre-thermocycling group and 48.754 for the post-thermocycling group. The *P* value was 0.230 for pre-thermocycling bond strengths, whereas the *P* value was less than 0.05 for post-thermocyclintg bond strength. The post-thermocycling results were therefore analyzed by Steel-Dwass multiple comparisons. In addition, the differences between pre- and post-thermocycling bond strengths for an identical priming condition were analyzed by Mann-Whitney *U* test.

Results of shear bond testing are summarized in Table 2. Pre-thermocycling average bond strengths varied from a minimum of 42.9 MPa to a maximum of 44.3 MPa, and they were not significantly different from each other (category a). Post-thermocycling average bond strengths varied from 22.0 MPa to 42.8 MPa, and were categorized into seven groups (categories b-h). Among the post-thermocycling groups, six groups recorded the greatest bond strength (category b). Comparison between the pre- and post-thermocycling results revealed that the bond strength of three groups (AP, EY, and EP) was not significantly reduced by application of thermocycling ($P > 0.05$), whereas the bond strength of six groups (MR, ML, UP, SB, BP, and AC) was significantly reduced after thermocycling ($P < 0.05$).

Results of failure mode analysis are summarized in Table 3. None of the specimens showed cohesive failure within the experimental conditions employed. A combination of adhesive and cohesive failures was detected for

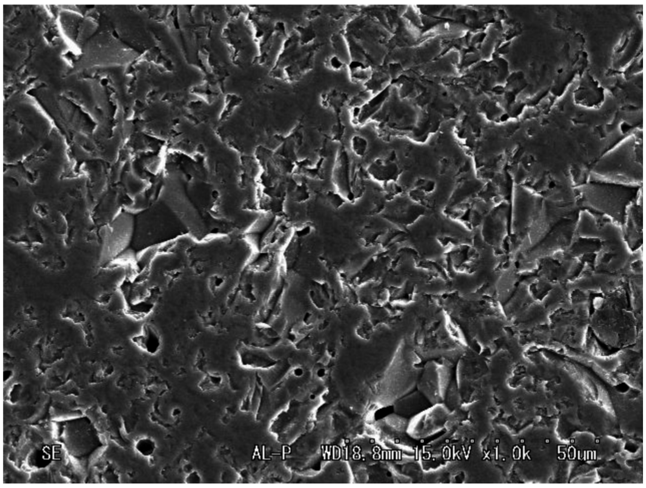

Fig. 1 Scanning electron micrograph of ground alumina.

the AP, EP, and ML groups before thermocycling, and for the AP group after thermocycling. The remaining specimens were judged to show adhesive failure.

Figure 1 shows a scanning electron micrograph of the ground alumina surface before bonding. A complex relief pattern probably generated by sintering alumina can be seen. Figures 2-5 show the debonded surfaces of thermocycled alumina originally bonded with four adhesive systems. Figure 2 shows the appearance of adhesive failure at the alumina surface attributable to lack of resin remaining at the alumina surface. However, the micrograph indicates that fractured resin is still present inside the small voids. Figures 3 and 4 show debonded specimens in the AP and EY groups. Remnants of resin material can be detected. Figure 5 is the debonded surface of a specimen in the AC

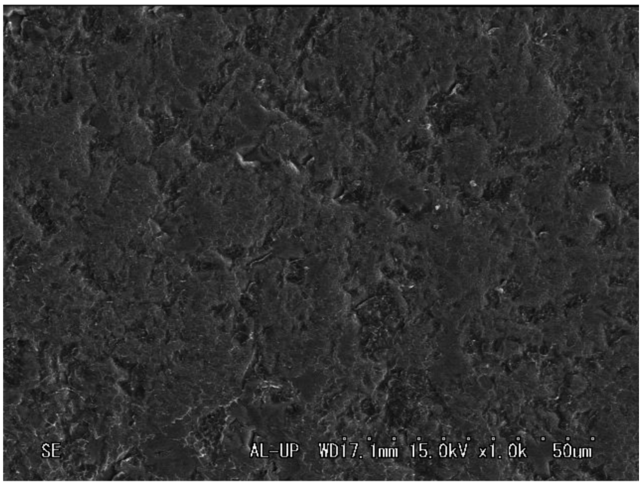

Fig. 2 Debonded surface of an unprimed thermocycled specimen.

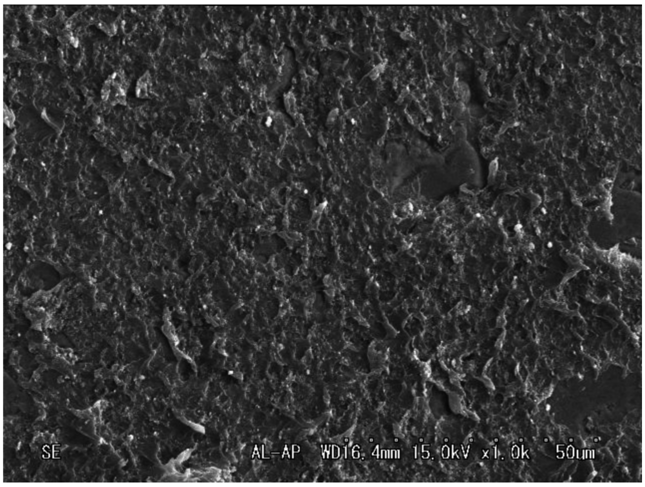

Fig. 3 Debonded surface of a thermocycled specimen primed with Alloy Primer.

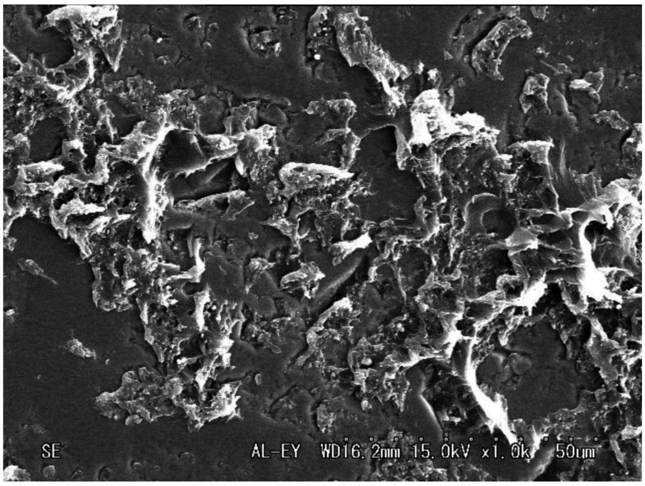

Fig. 4 Debonded surface of a thermocycled specimen primed with Eye Sight Opaque Primer.

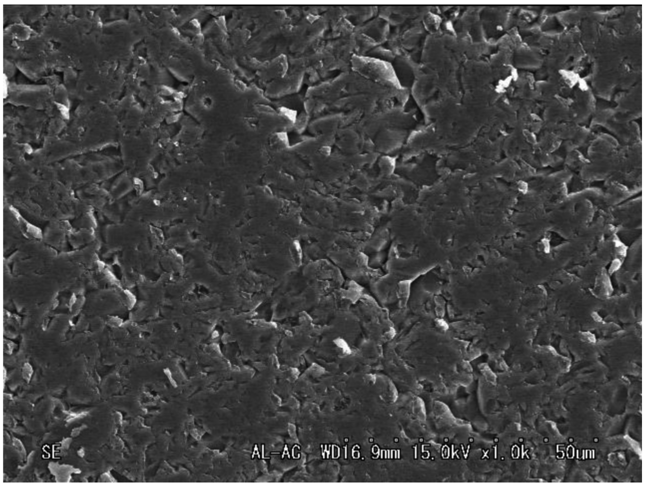

Fig. 5 Debonded surface of a thermocycled specimen primed with Acryl Bond.

group. The surface has an appearance similar to that of the ground alumina specimen.

Discussion

This study evaluated the bonding characteristics of sintered alumina using acidic primers and a TBB-initiated Super-Bond resin. An alumina substrate was used without mechanical surface preparation because the purpose of the study was to evaluate the effect of acidic functional monomers on chemical bonding rather than the effect of mechanical retention. However, sintered alumina exhibited a fused crystalline structure with multiple voids (Fig. 1). As a result, the surface may be mechanically retentive.

This study used Super-Bond resin as the luting agent. This resin did not contain a tertiary amine reducing agent. This composition made it possible to evaluate the effect of acidic functional monomers in the primers or luting agents. Super-Bond resin contains carboxylic 4-META monomer in the liquid component. Due to its carboxylic structure, 4-META may positively influence the strength of bonding of TBB-initiated resin to alumina. The authors therefore primarily evaluated the effect of acidic monomers on the bond strength to alumina of TBB-initiated resin without 4-META (15). The results showed that effect of 4-META was ranked as moderate among the eight primers. The authors used eight acidic primers and Super-Bond resin considering the possibility of combined application of acidic primers and the Super-Bond resin.

The results (Table 2) demonstrated that the phosphate primers (AP, EY, and EP) had better bond performance than the others, although the statistical categories overlapped. This was probably due to the difference in bonding ability between the phosphate monomer and other acidic monomers. Other studies have demonstrated the effectiveness of MDP monomer for bonding dental base metal alloys (20-22) and zirconia (23-24). Base metal alloys and zirconia are usually covered with a metal oxide layer. Considering the fact that MDP is effective for bonding base metals or metal oxides, it is not contradictory to the experimental result that MDP monomer is useful for bonding alumina, because alumina is also an oxide of aluminum metal.

Sen et al. (18) reported that the Panavia luting agent, based on MDP, showed higher bond strength than the 4-META-based Super-Bond resin for bonding In-Ceram glass-infiltrated alumina. At least three factors can be considered when evaluating the difference between Panavia and Super-Bond materials: the matrix system, the initiator, and the functional monomer. The present experiment unified the luting resin and the initiator, and the remaining factor, the functional monomer, was evaluated using eight primers. It was found that phosphate primers demonstrated reliable bonding performance without a reduction in bond strength after thermocycling. This supports the hypothesis that phosphate-based monomer is a suitable compound for priming alumina, within the limitations of the present experimental conditions.

It is important for clinicians to employ a compatible bonding system, taking into consideration the relationship between the functional monomer and the substrate composition. It can be concluded that the use of acidic primers containing hydrophobic phosphate is recommended for bonding sintered alumina with the TBB-initiated Super-Bond resin.

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