Effect of etching with potassium hydrogen difluoride and ammonium hydrogen difluoride on bonding of a tri-*n*-butylborane initiated resin to zirconia

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The purpose of the current study was to evaluate the effect of etching with potassium hydrogen difluoride (KHF₂) and ammonium hydrogen difluoride (NH₄HF₂) on the bond strength of a self-polymerizing methyl methacrylate resin (MMA-TBB) bonded to zirconia. Zirconia disks were prepared using the following surface treatment: no treatment, alumina blasting, and etching with KHF₂ or NH₄HF₂. The specimens were bonded with the MMA-TBB. The shear bond (Ø=5 mm) strength was measured. The surface free energies of the specimens were determined by measuring contact angles. The KHF₂ and NH₄HF₂ groups exhibited higher shear bond strength and surface free energy than did the alumina blasting and no treatment groups. Compared with alumina blasting, etching with KHF₂ and NH₄HF₂ exhibited superior bonding ability of mechanical retention to zirconia.

Keywords: Ammonium hydrogen difluoride, Bonding, Potassium hydrogen difluoride, Tri-*n*-butylborane, Zirconia

INTRODUCTION

Zirconium dioxide (zirconia) has become more widely used for ceramic restorations and in clinical practice. Given its outstanding mechanical properties, chemical stability, biocompatibility, and aesthetics, zirconia is now widely used in restorations, fixed dental prostheses, and superstructures of implant-supported prostheses^{1,2}.

Regarding zirconia bonding, 10-methacryloyloxydecyl dihydrogen phosphate (MDP) monomer is known to chemically bond with the zirconia surface^{3,5}. Moreover, mechanical adhesion still remains the main prerequisite to achieve durable retention of zirconia restorations⁵⁻¹². Given the acid resistant properties of zirconia, etching with hydrofluoric acid, which is used for silica-based ceramic materials, is ineffective^{12,13}. In many laboratory^{5,7,9-12} and clinical^{14,15} studies, alumina blasting is used to increase the roughness of the zirconia surface instead of etching with hydrofluoric acid.

Recently, Ruyter *et al.* reported that etching with potassium hydrogen difluoride (KHF₂) and ammonium hydrogen difluoride (NH₄HF₂) was effective for zirconia¹⁶. However, that study did not strictly evaluate whether etching with KHF₂ and NH₄HF₂ yielded micromechanical interlocking because the primer and the luting agent used on zirconia surface contained a functional monomer that could influence the bond strength. Therefore, the consensus on etching with KHF₂ and NH₄HF₂ on zirconia remains unclear.

The purpose of the present study was to investigate

the effect of etching with KHF₂ and NH₄HF₂ on the bond strength of a self-polymerizing MMA resin bonded to zirconia. The MMA resin did not contain any functional monomers. The null hypothesis was that the shear bond strength would not be affected by each of the surface treatments.

MATERIALS AND METHODS

Materials

The materials used in this laboratory investigation are listed in Table 1. A total of 44 disk specimens (11.4 mm in diameter and 2.8 mm thickness) were fabricated with yttrium-oxide-partially-stabilized zirconia ceramics (Katana, Kuraray Noritake Dental, Tokyo, Japan) and used as the bonding substrate.

The following abrasive particles were used for alumina blasting: 50–70 µm alumina (Hi-Aluminas, Shofu, Kyoto, Japan).

Two chemical powders were used as the experimental etching agents: potassium hydrogen difluoride (KHF₂; Tokyo Chemical Ind., Tokyo, Japan) and ammonium hydrogen difluoride (NH₄HF₂; Sigma-Aldrich Japan, Tokyo, Japan). The melting point of KHF₂ is 239°C and that of NH₄HF₂ is 125°C.

A self-polymerizing resin was selected as the luting material. This resin consisted of a partially oxidized tri-*n*-butylborane (TBB) initiator (Super-Bond Catalyst V, Sun Medical, Moriyama, Japan), methyl methacrylate (MMA; Tokyo Chemical Ind.), and polymethyl

Table 1 Materials assessed in this study

Material/Trade name	Manufacturer	Lot	Composition (%)
Adherend material			
Katana Zirconia	Kuraray Noritake Dental.	200218	ZrO ₂ 94.4%, Y ₂ O ₃ 5.4%
Particle abrasive			
Hi-Aluminas	Shofu	031401	50–70 µm alumina particles
Etching agent			
KHF ₂	Tokyo Chemical Ind.	PDMAOPO	KHF ₂ >99.0%
NH ₄ HF ₂	Sigma-Aldrich Japan	MKBS6955V	NH ₄ HF ₂ 95%
Luting material			
MMA	Tokyo Chemical Ind.	ZJ3WJIJ	MMA 99.8%
Super-Bond Ivory Opaque powder	Sun Medical	GT1	PolyMMA, titanium oxide
Super-Bond Catalyst V	Sun Medical	GG21F	TBB, TBB-O, hydrocarbon

MMA, methyl methacrylate; TBB, tri-*n*-butylborane; TBB-O, partially oxidized tri-*n*-butylborane

Fig. 1 The process from the specimen preparation to bonding.

methacrylate (PMMA; Super-Bond Opaque Ivory powder, Sun Medical).

Bonding specimen preparation and shear bond testing

The experimental design is presented in Fig. 1. The surface of all zirconia disks was wet-ground with 1500-grit silicon carbide abrasive paper (Wet or Dry Tri-M-ite, 3M, St. Paul, MN, USA) to create flat specimen surfaces of equal roughness. These disks were then cleaned with acetone for 10 min in an ultrasonic bath (SUC-110, Shofu), and dried with oil-free compressed air.

Zirconia disks were randomly assigned to four groups ($n=11$) according to the surface treatment preparation as follows:

Group NT: The zirconia surfaces were not treated (control).

Group AB: The zirconia surfaces were airborne-

particle abraded with 50–70 µm alumina particles for 10 s at a 0.28 MPa air-pressure at a distance of 20 mm. The bonding surface was then cleaned using compressed air for 15 s.

Groups KHF₂ and NH₄HF₂: All zirconia surfaces were powder-coated with KHF₂ or NH₄HF₂ in the amount of 70.0 (±15.0) mg. The specimens with KHF₂ were heated in a porcelain furnace (Esthemat stage 21, Shofu) to a temperature of 280°C. The specimens with NH₄HF₂ were also heated in the furnace to a temperature of 170°C. The bonding surface was then cleaned using a steam cleaner for 15 s followed by compressed air for 15 s.

The bonding area on the disk surface was defined using

a piece of double-coated adhesive tape with a circular hole 5 mm in diameter and approximately 50 μm in thickness. A stainless steel ring (SUS303, inner diameter 6 mm, height 2 mm, thickness 1 mm) was placed over the bonding area. The ring was filled with the MMA-TBB resin by means of the brush-dip technique.

After 30 min of bonding preparation, all specimens were stored in distilled water at 37°C for 24 h. The specimens were positioned in a steel mold and mounted in a shear bond test jig. The shear bond strength was determined using a mechanical testing device (Type 5567, Instron, Caton, MA, USA) with a 5-kN load cell at a crosshead speed of 0.5 mm/min.

Surface roughness measurements

The surface roughness of 11 samples per group after surface treatment protocols was measured. The arithmetical mean deviation of the roughness profile (R_a) was measured using a contact profilometer (Surfcom 1400A, Tokyo Seimitsu, Tokyo, Japan) along five lines by changing angles. The measurement conditions based on the Japanese Industrial Standards (JIS B 0633:2001) were conducted using a cut-off value of 0.8 mm and a transverse length of 4.0 mm.

Surface free energy measurements

The surface free energies of 11 zirconia specimens from each treatment group were determined by measuring the contact angle of test liquids on the specimen surface. Standard test liquids with previously reported surface free energy parameters¹⁷⁾ were used. The selected liquids used were distilled water, 1-bromonaphthalen, and ethylene glycol. The equilibrium contact angle was measured by the sessile drop technique at 23 $\pm$ 2°C and 50 $\pm$ 10% relative humidity using a contact angle meter (Drop Master DM500, Kyowa Interface Science, Saitama, Japan). This apparatus was equipped with a charge-coupled device camera that could automatically measure the contact angle. The camera recorded the image of the liquid dropped on the specimen surface by a syringe to determine the contact angle. The surface free energy parameters were calculated using add-on software and the built-in interface measurement and analysis system (FAMAS, Kyowa Interface Science) based on the fundamental concepts of wetting¹⁸⁾.

Scanning electron microscopic observation

Surface observations of the specimens before and after the shear bond strength test were conducted by scanning electron microscopy (SEM). Specimens were dried in a vacuum desiccator and sputter-coated with osmium (HPC-1S, Vacuum Device, Mito, Japan) for 30 s. Examination of the sputter-coated surfaces were then undertaken using a SEM (S-4300, Hitachi High-Technologies, Tokyo, Japan) with an operating voltage of 15 kV.

X-ray diffraction (XRD) analysis

XRD was performed to identify the crystalline phases of the specimen surfaces treated with NT, KHF₂, and

NH₄HF₂ using X-ray diffractometry (Miniflex II, Rigaku, Tokyo, Japan) with an operating voltage of 15 mA and 30 kV. Diffraction output data were collected using Cu-K α radiation from 3 degrees $\leq 2\theta < 90$ degrees at a scanning speed of 2.0 degrees/min. Data were analyzed using computer software (PDXL, Rigaku) and the index of the International Center for Diffraction Data (ICDD, Newton Square, PA, USA).

Statistical analysis

The results of the shear bond strength, surface roughness, the contact angle, and the surface free energy parameter were statistically analyzed. The D'Agostino and Pearson omnibus test (GraphPad Prism 6.0, GraphPad software, La Jolla, CA, USA) and the Brown-Forsythe test (GraphPad Prism 6.0) were first conducted to determine whether a normal distribution was obtained.

Kruskal-Wallis test (GraphPad Prism 6.0) and Steel-Dwass multiple comparisons (Kyplot 5.0, KyensLab, Tokyo, Japan) were performed as nonparametric tests to evaluate the differences among each group because normality and/or dispersion were not distributed as indicated by the D'Agostino and Pearson omnibus test (GraphPad Prism 6.0) and the Brown-Forsythe test (GraphPad Prism 6.0). The statistical significance level was set at $\alpha=0.05$.

RESULTS

Shear bond strength

The results of the shear bond strength and statistical analysis are summarized in Table 2. The results of the shear bond strength test did not exhibit homoscedasticity according to the Brown-Forsythe test ($p < 0.05$). Therefore, the bond strength results were analyzed using the Kruskal-Wallis test and Steel-Dwass multiple comparisons. The p -value was less than 0.05 for all groups.

The median bond strengths varied from 0.4 to 4.2 MPa. NH₄HF₂ treatment exhibited the highest bond strength (category d), whilst NT resulted in the lowest bond strength (category a).

Surface roughness

Surface roughness (R_a) values are presented in Table 3. The Kruskal-Wallis test and Steel-Dwass multiple comparisons were applied to evaluate the roughness of surface treatments to zirconia because the data did not exhibit a normal distribution. The median R_a values were 0.04 μm for NT, 0.41 μm for AB, 0.08 μm for NH₄HF₂, and 0.09 μm for KHF₂. The R_a values differed significantly among all the conditions (categories a–d; $p < 0.05$). AB exhibited the highest surface roughness (category d), whereas NT exhibited the lowest surface roughness (category a).

Surface free energy measurement

The contact angles for the three test liquids are presented in Table 4. The surface free energy parameter is presented in Table 5. The contact angle and the surface

Table 2 Shear bond strength (MPa) of a tri-*n*-butylborane initiated resin to surface treated zirconia

	Mean (SD)	Median	IQR
NT	0.4 (0.2)	0.4 ^a	0.2
AB	1.5 (0.2)	1.5 ^b	0.3
KHF ₂	4.1 (0.9)	4.2 ^c	1.2
NH ₄ HF ₂	5.6 (1.1)	5.3 ^d	1.0

n=11; SD, Standard deviation; IQR, interquartile range; Steel-Dwass multiple comparison test was conducted. Different letters indicate that the values are significantly (*p*<0.05). NT, not treated; AB, alumina blasting; KHF₂, etching with KHF₂; NH₄HF₂, etching with NH₄HF₂

Table 3 Surface roughness (Ra) after surface treated zirconia

	Surface roughness (<i>Ra</i>) (μm)		
	Mean (SD)	Median	IQR
NT	0.04 (0.01)	0.04 ^a	0.02
AB	0.39 (0.05)	0.41 ^d	0.09
KHF ₂	0.09 (0.01)	0.09 ^c	0.01
NH ₄ HF ₂	0.07 (0.01)	0.08 ^b	0.02

n=11; SD, Standard deviation; IQR, interquartile range; Steel-Dwass multiple comparisons test was conducted. Different letters indicate that the values are significantly (*p*<0.05). NT, not treated; AB, alumina blasting; KHF₂, etching with KHF₂; NH₄HF₂, etching with NH₄HF₂

Table 4 Contact angles of three test liquids to surface treated zirconia

	Contact angles (°)		
	Distilled water	1-Bromnaphthalin	Diiodomethane
NT	76.0 (1.0) ^b	14.5 (2.1) ^d	40.0 (1.4) ^g
AB	87.9 (2.7) ^a	15.9 (2.2) ^d	42.9 (2.1) ^f
KHF ₂	11.2 (2.5) ^c	11.3 (2.9) ^e	26.1 (2.6) ^h
NH ₄ HF ₂	13.5 (2.5) ^c	9.9 (1.0) ^e	27.7 (2.5) ^h

n=11; Values are given as mean (standard deviation). Identical letters indicate that the values are not significantly (*p*>0.05). Steel-Dwass multiple comparisons test was conducted.

NT, not treated; AB, alumina blasting; KHF₂, etching with KHF₂; NH₄HF₂, etching with NH₄HF₂

Table 5 Surface free energy parameter (total free energy and their components) to surface treated zirconia

	Surface free energy parameter (mN m ⁻¹)			
	Total free energy	Dispersion force	Polar force	Hydrogen bonding force
NT	45.4 (0.6) ^b	43.2 (0.4) ^d	0.0 (0.0) ^f	2.2 (0.4) ^h
AB	42.4 (0.7) ^c	42.2 (0.7) ^d	0.0 (0.0) ^f	0.2 (0.2) ⁱ
KHF ₂	74.5 (2.6) ^a	42.3 (0.6) ^d	3.5 (1.5) ^e	28.7 (2.1) ^g
NH ₄ HF ₂	73.6 (2.5) ^a	42.7 (0.4) ^d	2.5 (1.2) ^e	28.4 (2.1) ^g

n=11; Values are given as mean (standard deviation). Identical letters indicate that the values are not significantly (*p*>0.05). Steel-Dwass multiple comparisons test was conducted.

NT, not treated; AB, alumina blasting; KHF₂, etching with KHF₂; NH₄HF₂, etching with NH₄HF₂

free energy parameter were analyzed using the Kruskal-Wallis test and Steel-Dwass multiple comparisons non-parametric tests, because the data did not exhibit a

normal distribution.

KHF₂ and NH₄HF₂ exhibited the lowest contact angles for all three test liquids (categories c, e, and h).

AB resulted in the highest contact angles in distilled water (category a) and diiodomethane (category f). NT and AB exhibited the highest contact angles in 1-bromnaphthalin (category d).

The highest total free energy values were noted for KHF_2 and NH_4HF_2 (category a), whereas the lowest value was noted for AB (category c). Dispersion force parameters of each condition were not significantly different (category d; $p>0.05$). Regarding polar force, KHF_2 and NH_4HF_2 (category e) exhibited significantly higher values than NT and AB (category f). Hydrogen bonding forces of KHF_2 and NH_4HF_2 resulted in the highest values (category g) and that of AB exhibited the lowest value (category i).

Electron microscopy observations

Figure 2 presents the SEM images of each treated

zirconia surface and zirconia disks wet-ground with #1500 SiC abrasive paper followed by heating in a furnace at a temperature of 170 or 280°C. The ground and/or heated zirconia surfaces (Figs. 2a–c) exhibited scratches generated by the abrasive paper. These structures do not change regardless of heating in a furnace. The zirconia surfaces after AB treatments (Fig. 2d) demonstrated notched and roughened surface irregularities. The zirconia surfaces after KHF_2 and NH_4HF_2 (Figs. 2e and f) exhibited a rough morphology similar to fine grains with random porosities.

Figure 3 presents representative debonded surfaces after shear bond testing. The no treated zirconia surface (Figs. 3a and b) exhibited adhesive failure similar to that noted in Figs. 2a–c. The abraded zirconia surface (Figs. 3c and d) exhibited adhesive failure similar to that noted in Fig. 2d. Etched zirconia surfaces (Figs. 3b–d)

Fig. 2 Zirconia surfaces: (a) wet-ground with #1,500 SiC abrasive paper (NT, $\times 1,000$), (b) NT heated at 280°C ($\times 1,000$), (c) NT heated at 170°C ($\times 1,000$), (d) alumina blasting (AB, $\times 1,000$), (e) etching with KHF_2 (KHF_2 , $\times 1,000$), and (f) etching with NH_4HF_2 (NH_4HF_2 , $\times 1,000$).

Fig. 3 Debonded surfaces: (a) wet-ground with #1,500 SiC abrasive paper (NT, $\times 1,000$), (b) wet-ground with #1,500 SiC abrasive paper (NT, $\times 3,000$), (c) alumina blasting (AB, $\times 1,000$), (d) alumina blasting (AB, $\times 3,000$), (e) etching with KHF_2 (KHF_2 , $\times 1,000$), (f) etching with KHF_2 (KHF_2 , $\times 3,000$), (g) etching with NH_4HF_2 (NH_4HF_2 , $\times 1,000$), and (h) etching with NH_4HF_2 (NH_4HF_2 , $\times 3,000$).

Fig. 4 The XRD patterns of the zirconia specimens: (a) wet-ground with #1,500 SiC abrasive paper (NT), (b) etching with KHF_2 , and (c) etching with NH_4HF_2 .

exhibited the presence of resin remnants and resulted in a combination of adhesive and cohesive failures.

XRD analysis

Figure 4 presents the XRD patterns of non-treated zirconia and zirconia treated with KHF_2 and NH_4HF_2 . The NT specimen (Fig. 4a) presents a typical XRD pattern of zirconia. The XRD patterns of KHF_2 and NH_4HF_2 (Figs. 4b and c) were detected and exhibited a peak of zirconium fluoride hydrate oxide.

DISCUSSION

This study evaluated the effects of etching with KHF_2 and NH_4HF_2 on bonding to zirconia with a MMA-TBB self-polymerizing resin. The protocol of this study did not contain chemical surface treatment using a priming agent because the effects of mechanical retention by etching with KHF_2 and NH_4HF_2 must be assessed without any potentially confounding parameters that may provide skewed or incorrect results. Hence, a luting agent that did not contain any functional monomer was used. The results of this study demonstrated that the surface treatments of alumina blasting and etching influenced the shear bond strength. Thus, the null hypothesis was rejected.

Alumina blasting makes the zirconia surface rough and causes zirconia to bond in combination with the primer containing MDP^{5,7,9-12}. In the current study, AB exhibited increased bond strength compared with NT. Furthermore, the surface roughness R_a of AB was significantly higher than that of the other groups. Therefore, it is assumed that alumina blasting of the

zirconia surface increases the surface roughness and produces micromechanical interlocks, thereby improving the bond strength. This finding is consistent with previous studies^{5,7,9-12}.

KHF_2 and NH_4HF_2 were chosen in anticipation of the effect by chemically etching, unlike alumina blasting as mechanical surface treatment. The shear bond strengths of KHF_2 and NH_4HF_2 were significantly higher than those of AB and NT. In addition, surface roughness values were higher for KHF_2 and NH_4HF_2 treated surfaces than for NT. These results suggest that etching with KHF_2 and NH_4HF_2 can roughen the zirconia surface, and surface roughness is one of the factors that improves the bond strength. Compared with AB, KHF_2 and NH_4HF_2 exhibited increased bond strength, but lower roughness values. These results indicate that the wettability modified by the surface treatments may influence on the bonding ability.

The wettability of the zirconia surface that is related to surface free energy of the solid and the surface tension of the liquid, characterizes the bonding ability of the solid¹⁹⁻²¹. The surface free energy of zirconia is determined by means of the contact angle on the surface using the liquids with already known surface free energy values¹⁷. In general, when the liquid forms a lower contact angle on the solid, the surface free energy of the solid tends to be higher and exhibits more favorable wettability for bonding²². In this study, compared with NT and AB, KHF_2 and NH_4HF_2 exhibited significantly higher surface free energy values. Therefore, it is suggested that etching with KHF_2 and NH_4HF_2 modifies the surface free energy of the zirconia surface and contributes to increased bond strength. A similar phenomenon was noted in the bonding to leucite glass ceramic. Several studies assessing leucite glass ceramic reported that compared with alumina abrasion, etching with hydrofluoric acid resulted in increased bond strength, but reduced roughness^{23,24}. Nonetheless, Oh *et al.* found that the contact angle of leucite glass ceramic etched with hydrofluoric acid was lower than that abraded with alumina particles²⁵. Recent and previous findings indicate that the surface roughness and the surface free energy are not correlated in ceramic bond strength.

In the SEM images, it was observed that etching with KHF_2 and NH_4HF_2 changed the scratch patterns (Fig. 2a) to porosities and an aggregation of fine grains (Figs. 2e and f). Because the zirconia surface etched with KHF_2 and NH_4HF_2 exhibits a similar morphology to pre-sintered zirconia polished followed by sintering in SEM images²⁶, etching with KHF_2 and NH_4HF_2 exposed the original zirconia grains. The effect of only heating to zirconia can be denied because the structures of the ground and/or heated zirconia surfaces (Figs. 2a–c) do not change regardless of heating in a furnace. In addition, the XRD analysis results indicated that etching with KHF_2 and NH_4HF_2 chemically changed zirconia into fluoride compounds. Ruyter *et al.* reported that these fluoride compounds as the etched surface product were assumed to be $\text{K}_2(\text{ZrF}_6)$ by fourier transform infrared absorption

spectroscopic analysis¹⁶⁾. These are results that dissolved zirconia and molted $\text{KHF}_2/\text{NH}_4\text{HF}_2$ caused chemical reaction, resulting in sediments containing ZrF_4 ²⁷⁾. The presence of porosities and surface irregularities the grains provided a better surface for interlocking with a luting material, which then improved the bond strength compared with the different surface irregularities generated by the alumina blasting. In a previous study on bonding to porcelain, Kato *et al.* demonstrated that the undercuts created by the etching procedure were more efficient than those created by alumina blasting²⁸⁾. If an etchant can dissolve the ceramic surface, the undercut by etching is deeper and more retentive for bonding than that generated by alumina blasting.

Within the limitations of the current study, it can be concluded that etching with KHF_2 and NH_4HF_2 surpasses alumina blasting in the bond strength of a self-polymerizing acrylic resin bonded to zirconia. However, this study only evaluated the bonding ability of mechanical retention. Therefore, there is need to clarify the effect of mechanochemical combination of etching with KHF_2 and NH_4HF_2 and the primer with any functional monomer on bonding to zirconia.

ACKNOWLEDGMENTS

The present study was supported in part by a grant from the Dental Research Center Nihon University School of Dentistry (2016 and 2017).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest regarding this work.

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