Effect of the type of acidic monomer on the bond durability of two-bottle type ceramic primer

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Running title: Effect of the type of acidic monomer on the bond durability of ceramic primer (71)

Abstract (195)

The ceramic primer, consisting of γ-methacryloxypropyl trimethoxysilane (γ-MPS) and 4-methacryloyloxyethyl trimellitate (4-MET) or 10-methacryloyloxydecyl dihydrogen phosphate (MDP), is a useful material to facilitate the bonding of resin cement to silica-based ceramic surfaces. However, it is well known that the bond stability of commercial ceramic primer existed at the resin-ceramic interface differs among products. To understand the ability of 4-MET or MDP to hydrolyze the methoxy group in γ-MPS, two-bottle type experimental ceramic primers that consist of γ-MPS solution and activator solution of 4-MET or MDP were designed. The effects of the type of acidic monomer on the contact angle and the ceramic bond durability of resin were investigated. The 4-MET and MDP not only promoted the chemisorption of γ-MPS on the ceramic surface, but also enhanced the ceramic bond strength of the resin. However, thermocycling decreased the ceramic bond strengths, reflecting the increased number of bonded specimens that had exhibited an interfacial failure of the resin. The 4-MET-activated ceramic primer provided a greater bond strength than the MDP-activated ceramic primer, although most of bonded specimen showed an interfacial failure of resin. The 4-MET-activated ceramic primer showed a different degradation behavior from the MDP-activated ceramic primer.

Key word: Ceramic primer; γ-methacryloxypropyl trimethoxysilane; Acidic monomer; Bond durability

Introduction

Numerous researchers have published that the ceramic primer is a useful material to facilitate the bonding of resin cement to silica-based ceramic surfaces (1-7). Generally, commercial ceramic primers consist of two bottles. One contains γ-methacryloxypropyl trimethoxysilane (γ-MPS) as a silane coupling agent, and other one contains 4-methacryloyloxyethyl trimellitate (4-MET) or 10-methacryloyloxydecyl dihydrogen phosphate (MDP) as an acid component. The acid component is necessary to induce the hydrolysis of the methoxy group in γ-MPS.

Li (5) and Aida et al. (7) have reported that the bond durability of commercial ceramic primers existed at the resin-ceramic interface differs among products. This was because Porcelain Liner M (4-MET-activated ceramic primer) showed higher ceramic bond strength of resin than Clearfil Mega Bond Porcelain Bonding kit (MDP-activated ceramic primer), even most of bonded specimens exhibited an interfacial failure of the resin during the thermocycling process.

In this study, to investigate why 4-MET-activated ceramic primer showed a higher ceramic bond durability than MDP-activated ceramic primer, two-bottle type ceramic primers were designed using γ-MPS and 4-MET or MDP. To clarify the ability of 4-MET and MDP to hydrolyze the methoxy group in γ-MPS and to enhance the ceramic bond strength of resin, two-bottle type acetic acid- or phosphoric acid-activating primers were also used. The effect of the type of acidic monomer on the adsorption behavior of γ-MPS on the ceramic surface was then examined by measuring the contact angles, before and after the silanated ceramic surface were wiped with tetrahydrofulan (THF). Furthermore, the effect of the

type of acidic monomer on the ceramic bond durability of the resin was examined. The null hypotheses were that (1) the ability of 4-MET or MDP to hydrolyze the methoxy group in γ-MPS is similar to that of acetic acid or phosphoric acid, and (2) the bond durability of 4-MET- or MDP-activated ceramic primer is the same as that of acetic acid- or phosphoric acid-activated ceramic primer, respectively.

Materials and Methods

Materials and chemical reagents used in this study are listed in Table 1.

Ceramic adherend

The ceramic plates were prepared by cross-sectioning the ceramic blocks for Computer-Aided Design/Computer-Aided Manufacturing (GN-I). The ceramic plates with a length of 6 mm, a width of 6 mm and a thickness of 2 mm were embedded in a self-curing resin (Pour Resin). The embedded ceramic plate surfaces were ground in sequence of 100-, 600-, and 1,000-grit silicon carbide papers under stream of water, and then used as adherends.

Designed experimental ceramic primer

In accordance to previous studies (5,8), two-bottle type experimental ceramic primers that consist of silane solution and activator solution were prepared by using of γ-MPS, 4-MET (purity= 97%), MDP (purity= 97%), acetic acid, and phosphoric acid. The components and compositions of a silane solution and activator solutions are summarized in Table 2. In brief, the silane solution was prepared after dissolving 50 mg of γ-MPS in 1 mL of ethanol. Next, 0.1 mol/L 4-MET- or MDP-activating solution was prepared using

50 vol% ethanol aqueous solution, respectively. Then, 0.005, 0.01 and 0.05 mol/L 4-MET- or

MDP-activating solutions were prepared by diluting 0.1 mol/L 4-MET- or MDP-activating solution with 50

vol% ethanol aqueous solution.

On the other hand, 0.005, 0.01 and 0.05 mol/L acetic acid (AA)- or phosphoric acid (PA)-activating

solutions were prepared, and each AA- and PA-activating solution was then prepared by diluting with

ethanol by 50/50 vol%, respectively (8).

Silanization of the ceramic surface by experimental ceramic primers

A single drop each of γ-MPS solution and activator solution was mixed for 30 s, and this mixture was

then applied to the ground ceramic surface using a sponge (Sun Medical Co. Ltd., Moriyama, Japan). The

silanized ceramic surface was left at room temperature for 3 min, and subsequently air-browed for 60 s.

Measurement of the contact angle of a waterdrop to the silanized ceramic surfaces before and after being

wiped with THF

The contact angle measurements to the silanized ceramic surfaces were performed, before and after

the silanized ceramic surfaces were wiped with THF to remove γ-MPS species physisorbed on the ceramic

surface (9-13), using the MD100 Dropmaster Contact Angle Meter (Kyowa Electronic Instrument, Tokyo,

Japan). The number of specimens in each experimental group was 10, and the contact angle measurement

was done once in each specimen.

Preparation of the specimens for the adhesion test

An eighty-μm-thick double-faced tape with a circular hole of φ3.2 mm (Nichiban, Tokyo, Japan) was

placed on the silanized ceramic surface, and a 1-mm-thick silicone ring mold with a circular hole of ϕ3.2 mm was then mounted on the double-faced tape. The hole was then filled with Link Max (dual-curing-type resin cement). Immediately thereafter, visible light was irradiated to the resin cement using Curing Light XL 3000 (3M-ESPE, Grafenau, Germany) for 20 s, and the mold and tape were then removed. The bonded specimens were immersed in water at 37ºC for 1 day. The number of specimens prepared for each experimental group was 30.

Measurement of the shear bond strengths to the silanized ceramic surface, before and after thermocycling

After 1 day, thirty specimens were divided into two experimental groups: before and after thermocycling group. In the thermocycling group, fifteen bonded specimens were cycled between 5°C and 55°C in water baths for 10,000 cycles (14). The dwell time in each water bath was 60 s and the transfer time was 7 s. The shear ceramic bond strengths of the resin, before and after thermocycling, were measured using a universal testing machine (TG-5KN, Minebea, Nagano, Japan). The cross-head speed was 1.0 mm/min. The number of specimens in each experimental group was 15.

Determination of the type of fracture mode

To clarify the fracture type of bonded specimens, fifteen fractured ceramic surfaces and also respective resin cement surfaces obtained after the adhesion test were, in each experimental group, observed under a light microscope (Eclipse E800M, Nikon, Tokyo, Japan) at 10× magnification. In accordance to previous studies (5,7,8), each specimen was classified into one of three categories (Table 3).

Statistical analysis

Both data of shear bond strengths and contact angles obtained in each experimental group did not show the normal distribution. Therefore, the non-parametric statistical method was used for a statistical analysis.

The Kruskal-Wallis and Mann-Whitney U test adjusted with Bonferroni correction were applied to analyze the effects of the type of acid on 1) the contact angles before and after THF-wiping and 2) the bond strengths before and after thermocycling test. Further, the Mann-Whitney U test was applied to analyze 1) the effect of THF-wiping on the contact angle and 2) the effect of thermocycling on the shear bond strength before and after thermocycling in each experimental group.

All statistical analyses were performed using the statistical package IBM$^{\circledR}$ SPSS$^{\circledR}$ Statistics 21 (SPSS-IBM Inc., Chicago, IL, USA). The level of statistical significance in both cases was set at 0.05.

Results

Effect of the type of acid on the contact angle of a waterdrop to silnanized ceramic surfaces

Before THF-wiping (Table 4), the contact angle, in the MDP-activated ceramic primer, increased with increasing the acid concentration ($P < 0.05$). In contrast, in the 4-MET-activated ceramic primer, the contact angle tended to decrease with increasing the concentration of acid ($P < 0.05$). However, AA- and PA-activated ceramic primers showed a plateau value of the contact angles. The contact angles differed among the types of acid (Fig. 1). A significant difference was observed in the contact angles among the types of acid used in the activator solution ($P < 0.05$).

After THF-wiping (Table 5), the contact angle to the THF-wiped ceramic surface was dependent on the type of acid (Fig. 2). A significant difference was observed in the contact angles among the types of acid used ($P < 0.05$). However, the 4-MET-activated ceramic primer, in each acid concentration, shows a similar contact angle to the AA-activated ceramic primer. Similar to the 4-MET-activated ceramic primer, the MDP-activated ceramic primer, in each acid concentration, exhibited a similar contact angle to the PA-activated ceramic primer. There is no significant difference in the contact angles observed between the 4-MET and the acetic acid as well as between the MDP and the phosphoric acid.

THF-wiping led to a change in the contact angles in each acid used in the activator solution (Fig. 3). With the exception of MDP, a significant difference was observed in the contact angles in 4-MET, acetic acid and phosphoric acid, before and after THF-wiping, ($P < 0.05$).

Effect of the type of acid on the bond strength of resin to silanized ceramic surfaces

Before thermocycling (Table 6), the bond strengths to the silanized ceramic surface increased with increasing the acid concentration ($P < 0.05$). Reflecting an increase in the bond strength, the number of the bonded specimens that had exhibited a cohesive failure of the ceramic (Category 3) increased with increasing the acid concentration with the exception of the AA-activated ceramic primer (Table 7). The bond strength was strongly affected by the type of acid (Fig. 4). A significant difference was observed in the bond strengths between the 4-MET and the acetic acid, between the acetic acid and the MDP as well as between the acid acetic and the phosphoric acid ($P < 0.05$).

After thermocycling (Table 8), with the exception of the PA-activated ceramic primer, the bond strengths leveled off at 9.1-11.7 MPa for the 4-MET-activated ceramic primer, at 6.6-8.6 MPa for MDP-activated ceramic primer, at 0 MPa for the AA-activated ceramic primer. Most of bonded specimens showed an interfacial failure of the resin (Table 7). The bond strength after thermalcycling depended on the type of acid (Fig. 5). A statistical difference was observed in the bond strengths between the 4-MET and the acetic acid, between the 4-MET and the MDP, between the acetic acid and MDP as well as between the acetic acid and the phosphoric acid ($P < 0.05$), but not between the MDP and the phosphoric acid.

Thermocycling decreased the bond strength in each experimental primer (Fig. 6). A significant difference in the bond strengths obtained before and after thermocycling was observed in each acid used.

Discussion

In this study, to speculate the ability of 4-MET or MDP to hydrolyze the methoxy group in γ-MPS, the contact angle measurements were performed after the silanized ceramic surface was wiped with THF. This is due to the contact angle being very sensitive to the amount of γ-MPS that chemisorbed on the ceramic surface until γ-MPS formed the saturated adsorption (Sakanashi K et al. J J Dent Mater 3: 284-294, 1984; Nishiyama N. J J Dent Mater 5, 519-528, 1986).

The contact angle measurements to the THF-wiped ceramic surface showed the ability of 4-MET or MDP to hydrolyze the methoxy group in γ-MPS was the same as the ability of acetic or phosphoric acid, respectively (Fig. 2). This was due to the chemisorption of γ-MPS on the ceramic surface being limited by the production of the molecular species of hydrolyzed γ-MPS: $R-Si-(OCH_3)_2(OH)$, $R-Si-(OCH_3)(OH)_2$, and $R-Si-(OH)_3$ (9,13,15). The observed greater contact angles of MDP- and PA-activated ceramic primers than 4-MET- and AA-activated ceramic primers was probably due to MDP and phosphoric acid providing greater amounts of protonated protons than 4-MET and acetic acid. This was because the hydrolysis rate of the methoxy group in γ-MPS is strongly affected by the proton concentration in the activator solution (8,13).

However, 4-MET- or MDP-activated ceramic primer, before THF-wiping, showed a different effect on the contact angle from AA- or PA-activated ceramic primer (Fig. 1), respectively. The observed lower contact angles of 4-MET- or MDP-activated ceramic primer than AA- or PA-activated ceramic primer were due to the carboxyl group in 4-MET and the phosphate group in MDP increasing the hydrophilicity of the

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γ-MPS multilayer created on the ceramic surface. This was because these acidic monomers were included within the γ-MPS multilayer.

On the other hand, 4-MET-activated ceramic primer, before thermocycling, showed a higher bond strength than AA-activated ceramic primer (Fig. 4). This may be due to 4-MET enhancing the bonding ability of the resin to the ceramic surface more effectively than acetic acid, since 4-MET can copolymerize with not only the γ-MPS species adsorbed onto the ceramic surface, but also the base monomer used in the resin cement. However, there was no difference in the bond strengths between MDP- and PA-activated ceramic primers, although MDP is also able to copolymerize with the γ-MPS species and the base monomer, in contrast to phosphoric acid.

Thermocycling decreased the bond strength in each experimental primer, reflecting the increased number of bonded specimens that had exhibited an interfacial failure. This may be due to water that had permeated into the adhesive interface between the resin and the ceramic during the thermocycling process decreasing a cohesive force of the γ-MPS multilayer existed at the resin-ceramic interface.

Previously, our group reported that the ceramic bond durability of the resin through the γ-MPS multilayer strongly depended on the type of the acid used as an activator, and increased with increasing the degree of dissociation of acid: acetic, phosphoric and hydrochloric acid (8). This was due to the hydrolysis rate of three methoxy groups in γ-MPS strongly depended upon the proton concentration in the activator solution and the production of the completely hydrolyzed γ-MPS species, $R-Si-(OH)_3$ allowed for a creation of the γ-MPS multilayer with a higher cohesive force through a formation of the hydrogen-bonded

interaction of themselves (Nishiyama N. J J Dent Mater 5, 519-528, 1986).

However, the result that the 4-MET-activated ceramic primer showed a different degradation behavior from the AA-activated ceramic primer disagreed with the previous study (8), although the ability of 4-MET to hydrolyze the methoxy group is the same as the AA (Fig. 3). This may be due to the formation of a hydrogen-bonded interaction between the carboxyl group in the polymerized 4-MET and the silanol group of the hydrolyzed γ-MPS species adsorbed on the ceramic surface and/or the silanol group existed on the ceramic surface. In contrast, the MDP-activated ceramic primer showed a similar degradation behavior in the bond strength to the PA-activated ceramic primer. This was due to the hydrogen-bonded interaction that the phosphate group in the polymerized MDP had formed being unstable more than that of the carboxyl group in the polymerized 4-MET, since the degree of dissociation of the phosphate group in MDP is greater than that of the carboxyl group in 4-MET.

It was concluded that the 4-MET-acitivated ceramic primer, after thermocycling, exhibited noticeably high bond strength than the MDP-activated ceramic primer. However, 4-MET-activated ceramic primer will be unable to have a high clinical reliance, since most of bonded specimens showed an interfacial failure during the thermocycling process. This is because 4-MET is unable to completely hydrolyze three methoxy groups in γ-MPS.

Acknowledgement

Conflict of interest

The author declares conflicts of interest and is solely responsible for the content and writing of this report.

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Figure legends

Figure 1   The effect of the type of acid on the contact angle to the silanized ceramic surface, before

THF-wiping.

The contact angle is an averaged value of all experimental groups in each acid group.

The numbers show the median values of the contact angle in each experimental group. The

upper and lower bars show the maximum and minimum vales of the contact angle in each

experimental group. The asterisk shows a statistical difference ($P < 0.05$).

Figure 2   The effect of the type of acid on the contact angle to the silanized ceramic surface after

THF-wiped.

The contact angle is an averaged value of all experimental groups in each acid group.

The numbers show the median values of the contact angle in each experimental group. The

upper and lower bars show the maximum and minimum vales of the contact angle in each

experimental group. The asterisk shows a statistical difference ($P < 0.05$).

Figure 3   The effect of THF wiping on the contact angle to the silanized ceramic surface.

The contact angle is an averaged value of all experimental groups in each acid group.

White squares: before THF-wiping; gray squares: after THF-wiping. The upper and lower

bars show the maximum and minimum vales of the contact angle in each experimental group.

The asterisk shows a statistical difference ($P < 0.05$).

Figure 4   The effect of the type of acid on the bond strength to the silanized ceramic surface, before

thermocycling.

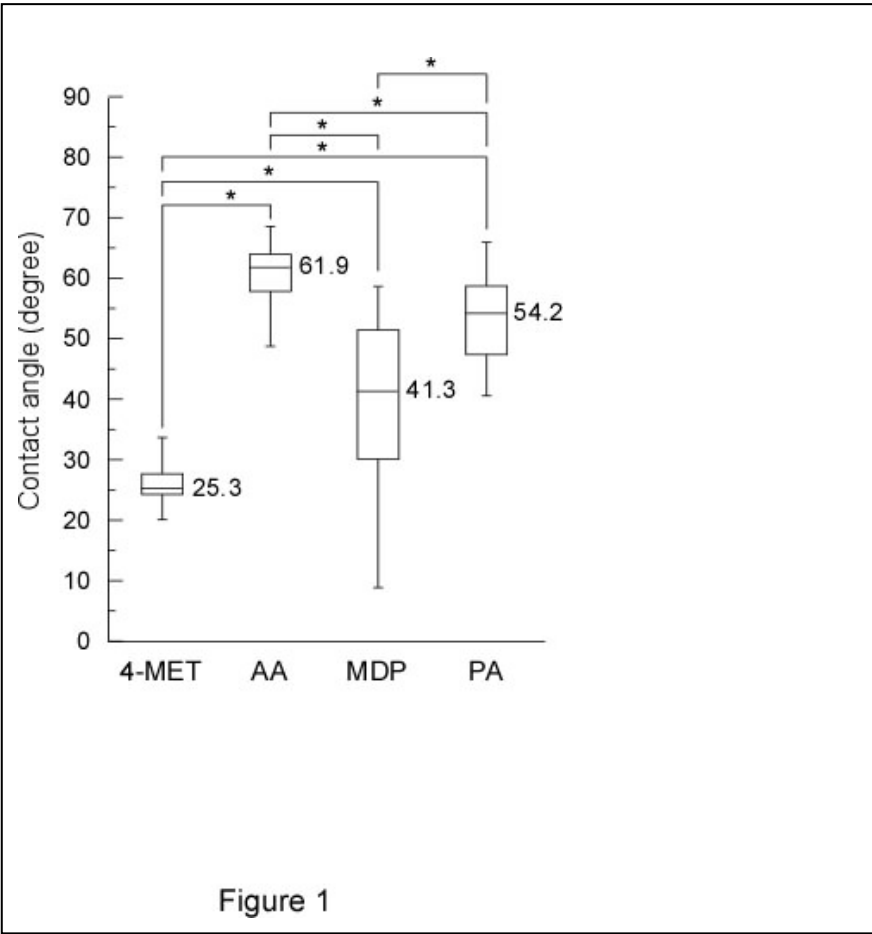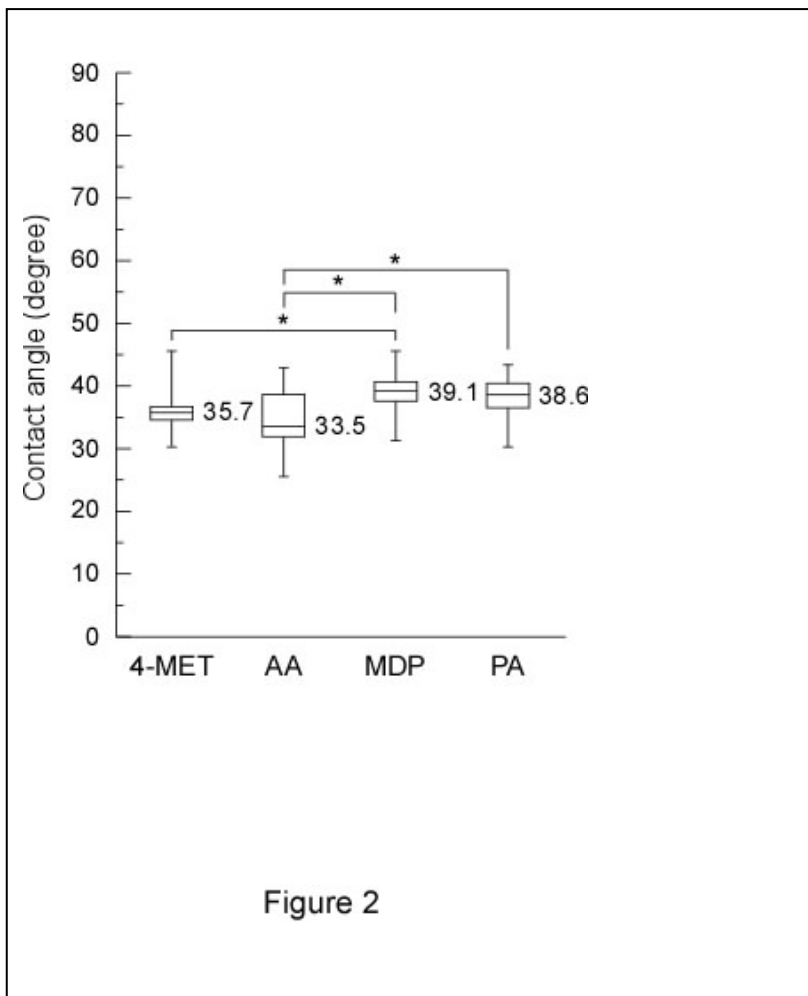The bond strength is an averaged value of all experimental groups in each acid group. The numbers show the median values of the bond strength in each experimental group. The upper and lower bars show the maximum and minimum vales of the bond strength in each experimental group. The asterisk shows a statistical difference (P< 0.05).

Figure 5   The effect of the type of acid on the bond strength to the silanized ceramic surface, after thermocycling.

The bond strength is an averaged value of all experimental groups in each acid group. The numbers show the median values of the bond strength in each experimental group. The upper and lower bars show the maximum and minimum vales of the bond strength in each experimental group. The asterisk shows a statistical difference (P< 0.05).

Figure 6   The effect of thermocycling on the bond strength to the silanized ceramic surface.

The bond strength is an averaged value of all experimental groups in each acid group. White squares: before thermocycling; gray squares: after thermocycling. The upper and lower bars show the maximum and minimum vales of the bond strength in each experimental group. The asterisk shows a statistical difference (P< 0.05).
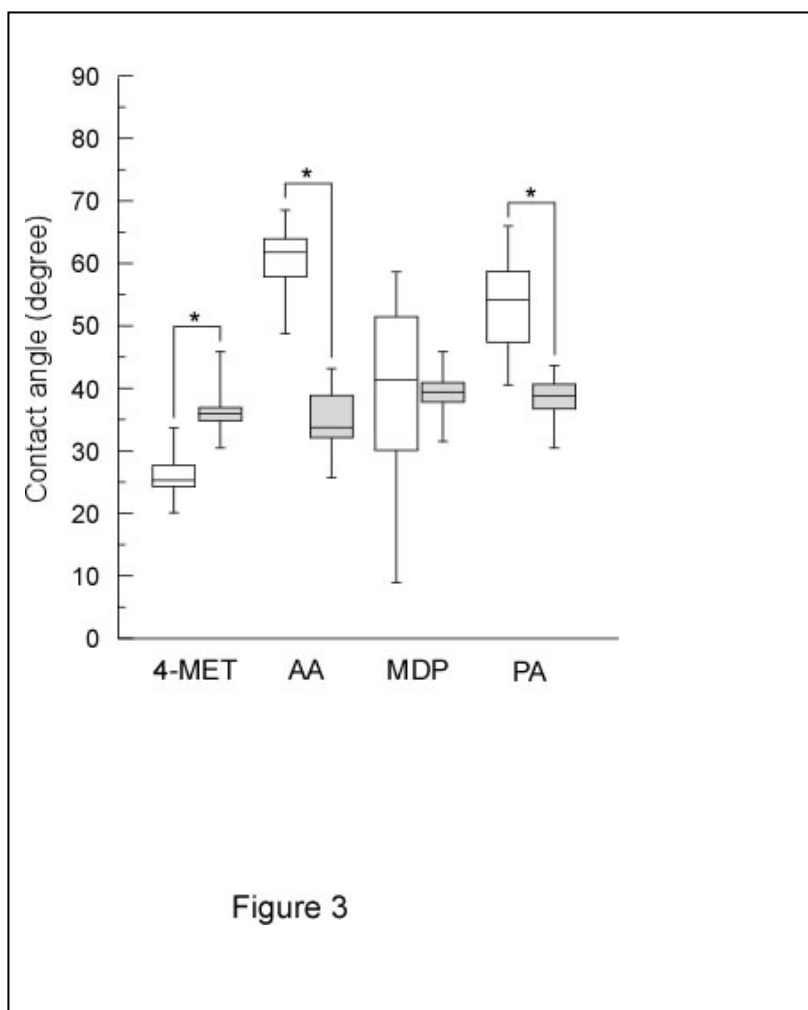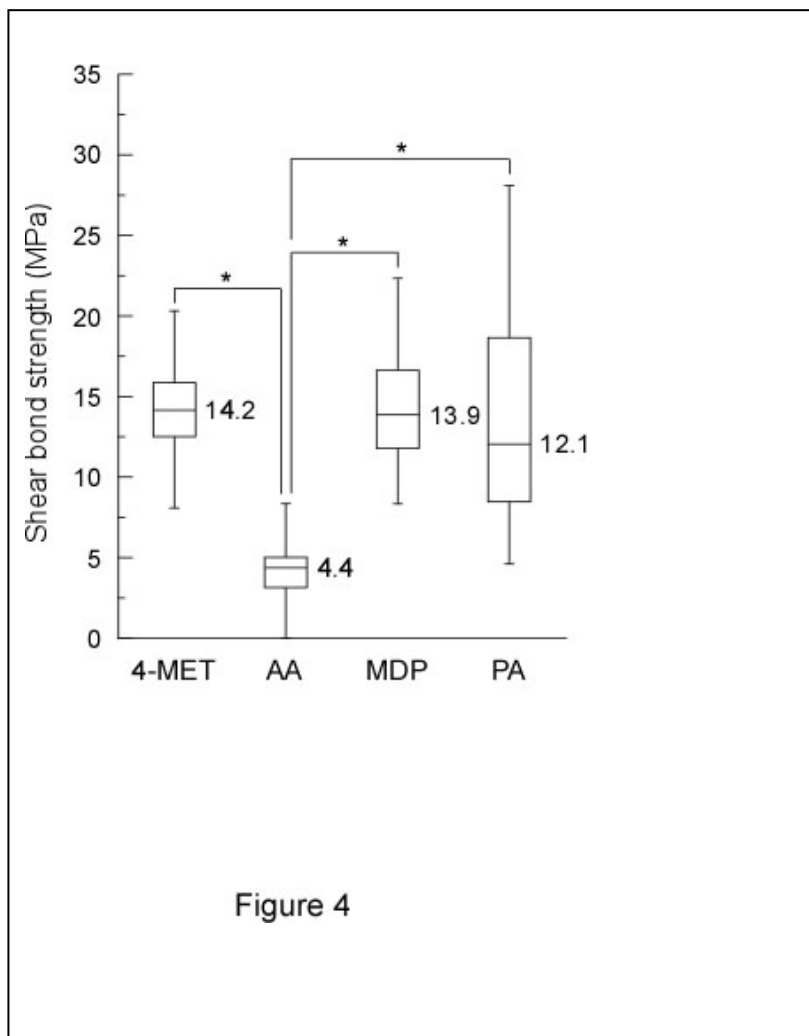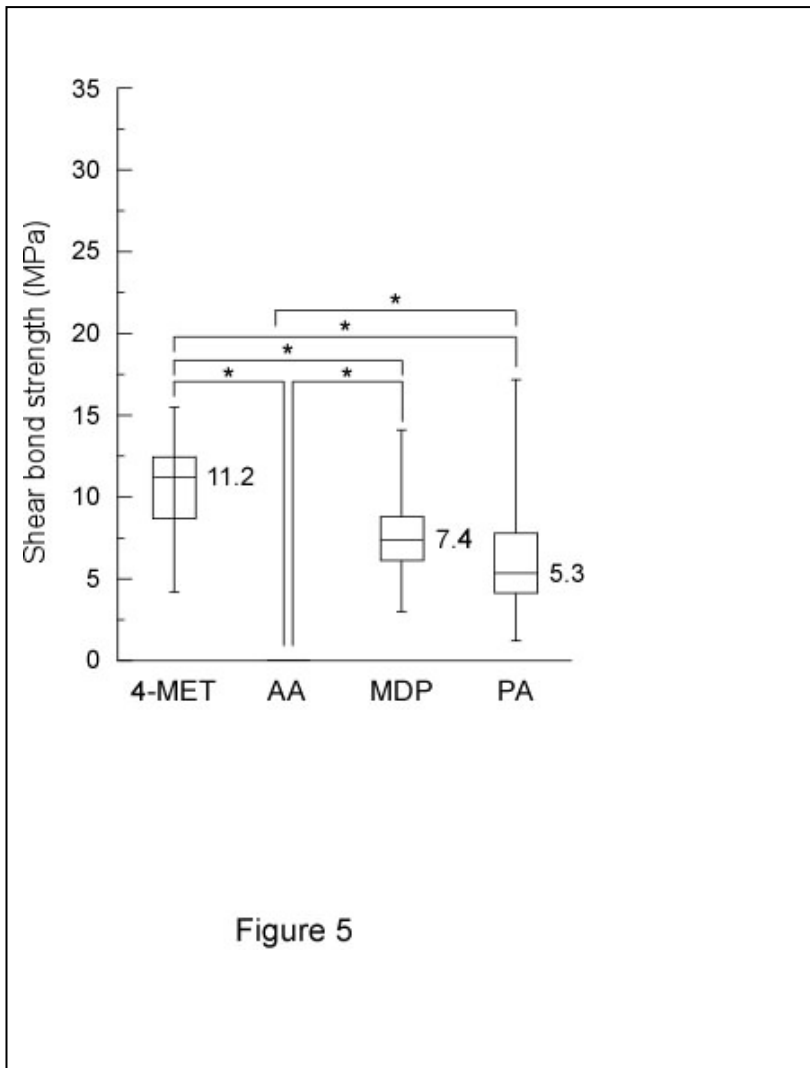
Figure 1

Half column: 7 cm

Figure 2

Half column: 7 cm
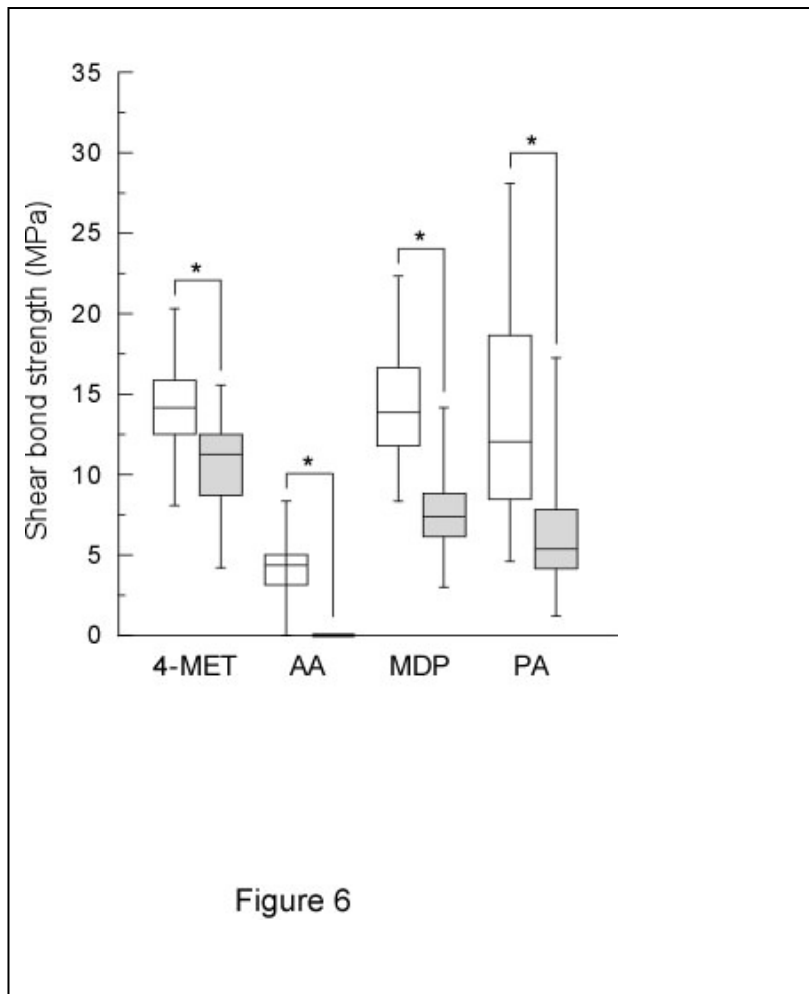
Figure 3

Half column: 7 cm

Figure 4

Half column: 7 cm

Figure 5

Half column: 7 cm

Figure 6

Half column: 7 cm

Table 1   Materials used in this study, and their abbreviations, manufactures, lot numbers and countries

Name	Abbreviation	Manufacture	Lot Number	City, Country
Materials				
Ceramic plate (GN-1)	-	GC Corporation	1102231	Tokyo, Japan
Pour resin				
Powder	-	Shofu	051220	Tokyo, Japan
Liquid	-	Shofu	09090	Tokyo, Japan
Link Max	-	GC Corporation	1402041	Tokyo, Japan
Chemicals				
γ-methacryloylpropyl trimethoxysilane	γ-MPS	Shin-Etsu Chemical Corporation	810345	Tokyo, Japan
4-methacryloyloxyethyl trimellitate	4-MET	Wako Pure Chemical Industries	DSQ9716	Tokyo, Japan
10-methacryloyloxydecyl dihydrogen phosphate	MDP	Wako Pure Chemical Industries	KPR9339	Tokyo, Japan
0.1 mol/L Acetic acid	AA	Wako Pure Chemical Industries	STE3154	Tokyo, Japan
0.5 mol/L Phosphoric acid	PA	Kanto chemical Corporation	3021U0125	Tokyo, Japan
Ethanol	-	Wako Pure Chemical Industries	EBR2882	Tokyo, Japan
Tetrahydrofuran	THF	Wako Pure Chemical Industries	WEJ0125	Tokyo, Japan

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Table 2 Components and composition of silane solution and activator solutions

Silane solution	Concentration of γ-MPS
γ-MPS	50 mg of γ-MPS in 1.000 g of ethanol
Activator solution	Concentration of acid
4-MET-activating solution	0.005, 0.01, 0.05, 0.1 mol/L
MDP-activating solution	0.005, 0.01, 0.05, 0.1 mol/L
AA-activating solution	0.005, 0.01, 0.05, 0.1 mol/L
PA-activating solution	0.005, 0.01, 0.05, 0.1 mol/L

Half column: 7 cm

Table 3   Clarification of the type of fracture mode (Category: [1/2/3]) of the bonded specimens

Category	Fracture mode
1	an interfacial failure of the resin from the silanated ceramic interface
2	a mixed failure consisting of an interfacial failure and a cohesive failure of the ceramic
3	a cohesive failure of the ceramic

Half column: 7 cm

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Table 4　　The contact angles of a waterdrop to the silanized ceramic surfaces, before THF-wiping, by varying the type of acid used and its concentration, 4-MET, MDP, acetic acid and phosphoric acid.

Concentration of acid (mol/L)	4-MET			MDP			Acetic acid			Phosphoric acid		
	Median	IQR	SD	Median	IQR	SD	Median	IQR	SD	Median	IQR	SD
0.005	26.2	25.0-28.6	3.5	$26.0^{a,b}$	21.2-30.6	8.5	62.8	55.4-63.7	7.3	55.6	43.6-57.9	8.2
0.01	27.6^{a}	27.0-29.4	2.7	$30.6^{c,d}$	29.4-31.0	2.8	62.1	56.8-65.0	5.7	51.2	45.1-52.5	4.2
0.05	24.5	24.2-25.8	2.3	$51.5^{a,c}$	50.2-53.8	3.1	60.7	59.5-63.2	3.6	58.0	43.7-59.9	8.5
0.1	24.0^{a}	22.6-24.5	2.4	$50.6^{b,d}$	47.0-55.5	5.3	61.2	58.5-63.6	4.3	56.5	53.6-59.2	4.5

For each vertical column, the median values of the contact angle: superscript characters with same letters (a–d) indicate a statistically significant difference ($p < 0.05$).
SD: Standard deviation

Whole page

Table 5　The contact angles of a waterdrop to the silanized ceramic surfaces, after THF-wiping, by varying the type of acid used and its concentration, 4-MET, MDP, acetic acid and phosphoric acid.

Concentration of acid (mol/L)	4-MET			MDP			Acetic acid			Phosphoric acid		
	Median	IQR	SD	Median	IQR	SD	Median	IQR	SD	Median	IQR	SD
0.005	$34.2^{a,b}$	33.0-35.0	1.8	38.5	37.0-39.8	3.3	32.1	29.4-36.3	4.6	36.4^{a}	31.7-39.2	4.2
0.01	35.8	35.1-35.9	0.9	38.5	36.5-40.4	2.5	33.8	33.1-35.8	3.5	36.6	34.3-38.7	3.0
0.05	35.9^{a}	35.5-36.1	1.6	39.5	38.4-40.2	2.9	35.9	31.8-39.1	4.1	38.5	37.0-39.7	1.9
0.1	38.4^{b}	37.3-39.1	3.6	41.2	38.8-42.6	2.9	36.7	33.0-40.5	4.5	40.2^{a}	39.2-41.3	1.7

For each vertical column, the median values of the contact angle: superscript characters with same letters (a–d) indicate a statistically significant difference ($p < 0.05$).

SD: Standard deviation

Whole page

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Table 6   The bond strengths of resin to the silanized ceramic surfaces, before thermocycling, by varying the type of acid used and its concentration, 4-MET, MDP, acetic acid and phosphoric acid.

Concentration of acid (mol/L)	4-MET			MDP			Acetic acid			Phosphoric acid		
	Median	IQR	SD	Median	IQR	SD	Median	IQR	SD	Median	IQR	SD
0.005	$12.5^{a,b}$	13.8-16.1	1.8	$10.1^{a,b,c}$	8.9-12.2	1.8	$2.6^{a,b}$	2.1-2.6	1.5	$6.7^{a,b}$	6.1-8.1	1.6
0.01	13.7	12.5-14.7	1.8	12.4^{a}	11.8-17.1	3.4	3.7^{c}	3.1-4.3	0.8	11.1^{c}	9.3-12.1	2.4
0.05	17.2^{a}	13.8-18.7	3.3	15.5^{b}	14.4-17.1	2.4	4.8^{a}	4.4-5.5	0.8	14.7^{b}	12.1-19.2	4.4
0.1	14.9^{b}	13.8-16.1	2.3	17.1^{c}	14.8-18.5	2.9	$5.6^{b,c}$	4.6-7.3	1.5	$21.6^{b,c}$	18.8-25.1	4.5

For each vertical column, the median values of the bond strength: superscript characters with same letters (a–d) indicate a statistically significant difference ($p<0.05$).

SD: Standard deviation

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Table 7   Type of fracture mode (Category: [1/2/3]) of the bonded specimens, before and after thermocycling, by varying the type of acid used and its concentration.

Concentration of acid (mol/L)	4-MET		Acetic acid		MDP		Phosphoric acid	
	Before	After	Before	After	Before	After	Before	After
0.005	[4/3/8]	[12/1/2]	[15/0/0]	[15/0/0]	[6/2/7]	[14/0/1]	[14/1/0]	[15/0/0]
0.01	[2/1/12]	[10/2/3]	[15/0/0]	[15/0/0]	[0/2/13]	[11/3/1]	[8/6/1]	[15/0/0]
0.05	[0/0/15]	[11/1/3]	[15/0/0]	[15/0/0]	[0/0/15]	[13/0/2]	[6/3/6]	[13/2/0]
0.1	[0/0/15]	[11/1/3]	[15/0/0]	[15/0/0]	[0/0/15]	[11/1/3]	[0/1/14]	[10/4/1]

Fracture type [1, 2, 3]: Category 1: interfacial failure at the resin-ceramic interface; Category 2: mixed failure consisting of interfacial failure and cohesive failure of the ceramic, and Category 3: cohesive failure of the ceramic.

The sample size for each experimental group was 15.

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Table 8   The bond strengths of resin to the silanized ceramic surfaces, after thermocycling, by varying the type of acid used and its concentration, 4-MET, MDP, acetic acid and phosphoric acid.

Concentration of acid (mol/L)	4-MET			MDP			Acetic acid			Phosphoric acid		
	Median	IQR	SD	Median	IQR	SD	Median	IQR	SD	Median	IQR	SD
0.005	10.5	6.9-11.6	2.9	6.7	5.2-8.3	2.1	0	0	-	$2.6^{a,b}$	2.1-4.1	1.3
0.01	11.8	10.2-13.1	2.2	7.8	6.4-10.6	2.8	0	0	-	$5.0^{c,d}$	4.3-5.5	1.0
0.05	11.4	9.0-13.8	2.6	7.3	5.7-7.8	2.3	0	0	-	$7.4^{a,d}$	6.5-7.4	2.3
0.1	11.1	9.1-12.1	2.3	7.6	6.4-8.6	2.1	0	0	-	$9.1^{b,c}$	5.8-11.9	4.3

For each vertical column, the median values of the bond strength: superscript characters with same letters (a–d) indicate a statistically significant difference ($p<0.05$).

SD: Standard deviation

Whole page