Original

Trace of organic sulfur compounds detected from debonded interface between transparent acrylic resin and gold alloy

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Abstract: The purpose of the current study was to evaluate the bonding performance of two single-liquid primers, which contained 6-(4-vinylbenzyl-*n*-propyl) amino-1,3,5-triazine-2,4-dithione (VTD) or 6-methacryloyloxyhexyl 2-thiouracil 5-carboxylate (MTU-6), used for bonding between metals and an acrylic resin. A gold alloy and high-purity titanium were used as adherend materials, and a transparent acrylic resin initiated with tri-*n*-butylborane derivative was selected as the luting material. Both adherends were treated with one of the primers and bonded with the luting material, after which shear bond strength was determined. Fourier transform infrared spectroscopy was used to analyze debonded resin specimens. Shear bond strength to gold alloy was significantly greater than that to titanium for both the VTD and MTU-6 primers. A trace of thiol structure, probably derived from VTD and MTU-6, was detected on resin surfaces debonded from gold alloy. These results indicate that the two organic sulfur compounds, which are stable in an atmospheric environment, are tautomerized into a thiol structure, thus allowing adsorption onto noble metals. In addition, the adsorbed thiol compounds contribute to chemical bonding between the acrylic

resin and noble metal alloy, as polymerizable adhesive functional monomers.

Keywords: adhesive; bonding; gold alloy; thiol; thione.

Introduction

Organic sulfur compounds interact directly with copper, gold, silver, and other noble metals and have therefore been used for bonding noble metal alloys. Mori and Nakamura (1) reported coating copper plates with the sulfur compound 6-(4-vinylbenzyl-*n*-propyl) amino-1,3,5-triazine-2,4-dithiol (VTD). A VTD acetone solution has since been used to prime dental noble metal alloys (Kojima et al., J J Dent Mater 6, 702-707, 1987), (2-8). Using infrared reflection absorption spectroscopy and surface-enhanced Raman scattering (SERS) spectroscopy, Suzuki et al. studied the structure of VTD adsorption to noble metals (9,10). Ohno et al. described the structure of VTD on a Ag-Pd alloy analyzed with X-ray photoelectron spectroscopy (11). These reports revealed that mercapto groups in VTD promote bonding to noble metals. Sulfide formation on alloy surfaces was confirmed by X-ray photoelectron spectroscopy under ultra-high vacuum conditions but not by environmental techniques such as infrared spectroscopy (12).

Another functional monomer, 6-methacryloyloxyhexyl 2-thiouracil 5-carboxylate (MTU-6), was synthesized later (13). The bonding characteristics of MTU-6 are better than those of VTD (3,8,14,15). However, few studies have examined the characteristics of MTU-6 bonding to dental metal alloys. This study compared the

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Table 1 Materials assessed

Material/Trade name	Manufacturer	Lot	Composition (mass %)
Metal, Alloy			
Casting Gold M.C. Type IV	GC Corp., Tokyo, Japan	0702151	70 Au, 8 Ag, 16 Cu, 2 Pt, 3 Pd
High-purity titanium	Nilaco Corp., Tokyo, Japan	452651	99.9 Ti
Primer			
V-Primer	Sun Medical Co., Ltd., Moriyama, Japan	FX1	VTD, Acetone
Metaltite	Tokuyama Dental Corp., Tokyo, Japan	032	MTU-6, Ethanol
Luting material			
Super-Bond C&B Catalyst V	Sun Medical Co., Ltd.	LE12F	TBB, TBB-O, Hydrocarbon
Super-Bond C&B Clear Powder	Sun Medical Co., Ltd.	LS1	PolyMMA
Methyl methacrylate	Tokyo Chemical Industry Co., Ltd., Tokyo, Japan	ZJ3WJII	99.8 MMA
Reagent			
VTD	Sun Medical Co., Ltd.	KS1	
Acetone	Tokyo Chemical Industry Co., Ltd.	TU7MJ	

VTD, 6-(4-vinylbenzyl-*n*-propyl)amino-1,3,5-triazine-2,4-dithione; MTU-6, 6-methacryloyloxyhexyl 2-thiouracil-5-carboxylate; TBB, tri-*n*-butylborane; TBB-O, partially oxidized tri-*n*-butylborane; MMA, methyl methacrylate.

Fig. 1 Structural formulae of MTU-6 and VTD, *Suzuki et al. (9).

priming effects of VTD and MTU-6 on bonding between metals and an acrylic resin. In addition, adhesive monomers remaining on a debonded metal-resin interface were analyzed.

Materials and Methods

Materials

The materials used are described in Table 1. A gold alloy (Casting Gold M.C. Type IV, GC Corp., Tokyo, Japan) and high-purity titanium (Nilaco Corp., Tokyo, Japan) were used as adherend materials. Two single-liquid materials (V-Primer, Sun Medical Co., Ltd., Moriyama, Japan; Metaltite, Tokuyama Dental Corp., Tokyo, Japan) were used for priming adherend materials. V-Primer contains VTD in acetone; Metaltite contains MTU-6 in ethanol (Fig. 1).

A transparent acrylic resin was selected as the luting material. The resin material consists of tri-*n*-butylborane (TBB) derivative initiator (Super-Bond C&B Catalyst V, Sun Medical Co., Ltd.), methyl methacrylate (MMA) monomer liquid (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), and poly(methyl methacrylate)

(PolyMMA) powder (Super-Bond C&B Clear Powder, Sun Medical Co., Ltd.). In addition to the adhesive systems, VTD monomer and acetone solvent were used as the reagents for spectral analysis.

Shear bond strength testing

Disk-shaped specimens of gold alloy (10 mm in diameter and 3 mm in thickness) were cast by using conventional lost-wax technique. The gold alloy specimens were placed for 5 min in an electronic furnace at 700°C and then quenched in cold water. The specimens were heated again to 200°C after being placed in an electronic furnace preheated to 450°C for 7 min. Disk-shaped titanium specimens (10 mm in diameter and 3 mm in thickness) were cut from rods supplied by the manufacturer. All disk-shaped specimens were wet-ground with 2,000-grit silicon carbide abrasive paper (WetorDry Sheet, 3M Corp., St. Paul, MN, USA) and polished with felt (TexMet 1500, Buehler, Lake Bluff, IL, USA) and a monocrystalline diamond suspension (3-μm and 1-μm, MetaDi, Buehler). The specimens were later ultrasonically cleaned with acetone and air-dried.

Fig. 2 Procedure for bond strength testing and spectral analysis.

V-Primer or Metaltite was applied to the adherend surface, air-dried, and rinsed for 7 s with acetone. A steel ring (SUS303, inner diameter of 6 mm, height of 2 mm, and wall thickness of 1 mm) was positioned on each disk specimen, to define the bond area. The acrylic resin was filled into the ring with brush-dip technique. Specimens were placed under pressure (0.7 MPa) for 10 min in an air-compressing device (Press technic, Yoshida Dental MFG Co., Ltd., Tokyo, Japan) and then immersed in 37°C distilled water for 24 h. Eleven specimens were prepared for each adherend.

The specimens were fixed in a steel mold and placed in a testing jig to determine shear bond strength with a mechanical testing device (Type 5567, Instron, Canton, MA, USA) at a crosshead speed of 0.5 mm/min. Thus, the polymerized resin block for spectral analysis was obtained along with shear bond strength determination (Fig. 2).

After testing, the debonded surfaces were observed with an optical microscope (SZX9, Olympus, Tokyo, Japan). Failure mode was classified as follows: A, adhesive failure at the acrylic resin-alloy interface; C, cohesive failure within the acrylic resin; and CA, combined adhesive/cohesive failure.

Statistical analysis

Shear bond strength was analyzed by using descriptive statistics (mean and standard deviation) and the statistical software package GraphPad Prism 6 (GraphPad Software Inc., La Jolla, CA, USA). The results were primarily analyzed with the D'Agostino and Pearson omnibus test, to evaluate distribution. The Bartlett test was then used for testing equality of variance. After checking normality and equality of variance, mean shear bond strength values were analyzed by two-way analysis of variance (ANOVA), to determine the effect of the primer and metal alloy as factors. When the two-way ANOVA test indicated interaction, parametric *t*-tests were used for pairwise comparison between gold alloy and titanium, and between the two primers. The significance level was set at $\alpha = 0.05$.

Infrared absorption spectroscopic analysis

Transmission spectra were obtained by means of a Fourier transform infrared absorption spectrophotometer (FTIR 480 plus, Jasco Corp., Tokyo, Japan). All IR spectra were obtained from a total of 100 scans over the 4,000–400 cm^{-1} range, at a resolution of 2 cm^{-1} .

IR spectra for VTD and MTU-6 were measured by using the potassium bromide (KBr) tablet method.

Table 2 Results of shear bond strength testing (two-way ANOVA)

Source of variation	% of total variance	<i>P</i> value			
Interaction	0.06463	0.0482			
Primer	0.05212	0.0747			
Metal alloy	99.29000	<i>P</i> < 0.0001			
ANOVA table	Sum of squares	<i>df</i>	Mean square	F (DFn, DFd)	<i>P</i> value
Interaction	5.602	1	5.602	F (1, 40) = 4.152	<i>P</i> = 0.0482
Primer	4.518	1	4.518	F (1, 40) = 3.349	<i>P</i> = 0.0747
Metal alloy	8,604.000	1	8,604.000	F (1, 40) = 6,377	<i>P</i> < 0.001
Residual	53.970	40	1.349		

df, degree of freedom.

Table 3 Shear bond strengths (MPa), results of statistical analysis, and failure modes after shear-bond testing

Primer	Gold alloy			Titanium			Gold alloy and titanium
	Mean (SD)	A	CA	Mean (SD)	A	CA	
VTD	27.8 (1.5) ^a	0	11	0.6 (0.2) ^b	11	0	<i>P</i> < 0.0001
MTU-6	29.2 (1.6) ^a	0	11	0.5 (0.3) ^b	11	0	<i>P</i> < 0.0001

n = 11; SD, Standard deviation. Identical superscript letters indicate that the difference between the two priming conditions is not significant (*P* > 0.05). A, adhesive failure at acrylic resin-metal interface; CA, combined adhesive/cohesive failure.

MTU-6 was procured by vaporization of the Metaltite solvent. The VTD tablet was prepared by mixing 100 mg KBr and 0.5 mg VTD, and the MTU-6 tablet was prepared by mixing 100 mg KBr and 0.4 mg MTU-6. The IR spectra of MMA were determined with the liquid-film method, and spectra of polymerized acrylic resin were obtained from debonded specimens (Fig. 2). The results were compared with those of previous reports (1,10,12,16) and with reference compounds (17).

Results

Shear bond strength

The D'Agostino and Pearson omnibus test showed that the results of shear bond strength testing were normally distributed. Additionally, the validity of equal variance assumptions of bond strength values was confirmed by the Bartlett test (*P* > 0.05). Parametric statistical procedures were thus selected. Two-way ANOVA revealed a significant interaction between the metal alloy factors (*P* < 0.001; Table 2). Hence, *t*-tests were used for pairwise comparison between gold alloy and titanium, and to analyze differences between the two priming conditions (Table 3).

The results of the shear bond strength tests are summarized in Table 3. Shear bond strength was significantly higher for gold alloy treated with VTD primer (27.8 MPa) than for titanium (0.6 MPa). In addition, shear bond strength was significantly higher for gold alloy treated with MTU-6 primer (29.2 MPa) than for titanium (0.5 MPa). The difference in bond strength between the two priming conditions was not significant for either adherend material (*P* > 0.05). The results of failure mode

analysis are shown in Table 3. No specimen exhibited cohesive failure under any experimental condition. Combined adhesive/cohesive failure was detected in the gold alloy groups, and adhesive failure was detected in the titanium groups.

Figure 3A shows a typical polished gold alloy surface before testing. Figure 3B shows a debonded gold alloy surface treated with VTD primer before bonding. This surface shows combined adhesive/cohesive failure. Figure 3C shows a debonded surface exhibiting partial cohesive failure within the resin material.

Infrared absorption spectra

Figure 4A shows the IR spectra of the VTD monomer. The spectra exhibited peaks indicating a thione structure. Specifically, peaks were seen at 1,535, 1,281, 1,191, 1,145, and 462 cm⁻¹, which are derived from C=S stretching (Table 4). In addition, N-H stretching at 3,411 and 3,111 cm⁻¹ were observed (Table 4). These peaks indicate that VTD has a thione structure. Figure 4B shows the IR spectra of the MMA monomer, and Fig. 4C shows the IR spectra of the polymerized acrylic resin.

Figures 4D and 4E show the IR spectra of the debonded resin block. Although the 1,558 cm⁻¹ peak derived from the triazine dithiol structure (10) was not detected in the VTD monomer, it was present in acrylic resin specimens debonded from gold alloy. The trace peak at 656 cm⁻¹ is probably derived from C-S stretching of VTD (Table 4). The absorption based on vinyl groups at 988 and 904 cm⁻¹ disappeared from the polymerized resin specimen. Detection of 1,558 and 656 cm⁻¹ peaks at the debonded resin surface indicate that VTD was adsorbed on gold

Table 4 Band assignments for the IR spectra of VTD and organic compounds

Assignment	Wavenumber (cm ⁻¹)	
	VTD monomer	Acrylic resin debonded from gold alloy
1,4-Benzene	γ CH	822
Aromatic structure	ν (C=C)	1,487
Triazine dithiol*	ν (C=C)	1,558
Amino group**	$>NH$	ν (N-H)
Amino group	$>NH$	ν (N-H)
Amino group	$>NH$	δ (N-H)
Amino group	$-C=N(+H)-$	ν (C=N)
Thioketone***	$-C=S$	ν (C=S)
Thiouredide**	$-NH-C(=S)-$	ν (C=S)
Thiouredide**	$-NH-C(=S)-$	ν (C=S)
Thioureido group	$N-CS-N$	ν (C=S)
Thioureido group	$N-CS-N$	ν (C=S)
Thiol	$-C-SH$	ν (C-S)
Methyl group, Methylene group**	$-CH_3, -CH_2-$	ν (C-H)
Methyl group, Methylene group**	$-CH_3, -CH_2-$	ν (C-H)
Vinyl group****	$CH_2=CH-$	γ (C-H)
Vinyl group****	$CH_2=CH-$	γ (C-H)

*Suzuki et al. (10), **Kojima et al., J J Dent Mater 6, 702, 1987, ***Shtenberg et al. (16), ****Mori and Nakamura (1).

Fig. 3 Gold alloy specimens and debonded resin. (A) Polished gold alloy, (B) debonded surface of gold alloy treated with VTD primer before bonding, and (C) acrylic resin surface debonded from VTD-primed gold alloy. The white arrows indicate the direction of shearing. Digital photographic system: (A and B) original magnification $\times 8$, (C) original magnification $\times 10$.

Fig. 4 IR spectra of (A) VTD, (B) MMA, (C) the polymerized acrylic resin block, (D) acrylic resin debonded from gold alloy primed with V-Primer, and (E) acrylic resin debonded from titanium primed with V-Primer.

alloy and showed that VTD on the acrylic resin block from gold alloy has a thiol or thione-thiol structure.

Figure 5A shows the IR spectra of the MTU-6 monomer. Peaks at 1,331, 1,157, and 1,077 cm⁻¹, due to C=S stretching, can be observed (Table 5). The peak of the C=O stretching of carbonyl group was at 1,718 cm⁻¹ (Table 5). Additionally, peaks from N-H stretching and bending were observed at 3,440, 3,148, and 1,652 cm⁻¹ (Table 5). These IR spectra indicate that MTU-6 has a thione structure.

Figures 5B and 5C show the IR spectra of acrylic resin debonded from gold alloy and titanium. Peaks probably derived from MTU-6 were observed with the resin specimen debonded from gold alloy (Fig. 5B). The peaks at 1,558, 1,506, 1,456, 794, and 597 cm⁻¹ are thus substantially identical with those of MTU-6 (Fig. 5A).

Table 5 Band assignments for the IR spectra of MTU-6 and organic compounds

Assignment			Wavenumber (cm ⁻¹)	
			MTU-6	Acrylic resin debonded from gold alloy
Pyrimidine*****	v (C=C)		1,558	1,558
Aromatic structure	v (C=C)		1,506	1,506
Aromatic structure*	v (C-N)		1,455	1,456
Pyrimidine*****	γ CH		791	794
Aromatic structure*	δ (CNC)		597	597
Amino group	>NH	v (N-H)	3,440	
Amino group*, **, ***	>NH	v (N-H)	3,148	
Amino group	>NH	δ (N-H)	1,652	1,652
Amino group	- C=N(+H) -	v (C=N)		1,683
Thiouredide	- NH-C(=S) -	v (C=S)	1,331	
Thiouredide**	- NH-C(=S) -	v (C=S)	1,157	
Thiouredide*	- NH-C(=S) -	v (C=S)	1,077	
Carbonyl group*, ****	>C=O	v (C=O)	1,718	1,716
Methyl group**, ****	- CH ₃ , - CH ₂ -	v (C-H)	2,934	

*Shtenberg et al. (16), ** Kojima et al., J J Dent Mater 6, 702, 1987, ***Suzuki et al. (9), ****Silikas et al. (12), *****Akyuz and Akyuz (17)

These peaks were detected from C=C, C-N, and C-H groups of MTU-6. Similarly, a peak representing C=O stretching of the carbonyl group was seen at 1,716 cm⁻¹ (Table 5). A peak caused by N-H bending at 1,652 cm⁻¹ was observed, whereas peaks caused by N-H stretching in MTU-6 (3,440 and 3,148 cm⁻¹) were not seen. A new peak, at 1,683 cm⁻¹, was found and was caused by C=N stretching of MTU-6. These results suggest that MTU-6 in a resin block debonded from gold alloy has a thiol structure.

No trace of functional monomers was detected in resin specimens debonded from titanium.

Discussion

This study used spectral analysis to examine functional monomers remaining on debonded acrylic resin surfaces. To prevent contamination by foreign substances, such as brush fibers in the acrylic resin, each primer was dropped on the adhesive surface. Unreacted monomers remaining on the metal surface may affect the appearance of the IR spectrum for observation of the bonding mechanism, because excess VTD induces a chain transfer reaction with the resin monomer. Excess monomers were therefore removed by rinsing specimens with acetone. The acetone washing time was based on that described in a previous study, which found that VTD spectra depended on acetone washing time (10). For MTU-6, the effectiveness of acetone washing was confirmed in a previous study, which reported that MTU-6 was strongly adsorbed onto an Ag-Pd-Cu-Au alloy surface, even after repeated acetone cleaning (8).

Suzuki et al. used SERS spectroscopy to analyze the

Fig. 5 IR spectra of (A) MTU-6, (B) acrylic resin debonded from gold alloy primed with Metaltite, and (C) acrylic resin debonded from titanium primed with Metaltite.

structure of VTD adsorbed to a colloidal gold surface (9). The results suggested that structural changes occurred within the VTD monomer upon adsorption to gold and transformed the C=S bonds. The molecule appears to undergo thione-thiol tautomerization during adsorption. Using SERS spectroscopy and infrared reflection absorption spectroscopy, the same group later observed the same structural changes in VTD after adsorption to silver and copper (10). The previously reported triazine dithiol peak of VTD (1,560 cm⁻¹) (10) was also found (1,558 cm⁻¹) in the present study (Table 4), which suggests that the structure of the VTD monomer is thiol or thione-thiol at the bonded interface between gold alloy and acrylic resin. No peak was detected at 462 cm⁻¹, which represents the thioketone of VTD (16), perhaps because the transmission method of analysis yields considerable noise below 500 cm⁻¹ when measuring acrylic resin.

The results for MTU-6 also showed a reduction in thione structure from the debonded acrylic resin block.

Specifically, peaks including the C=S bonds of thiourea-dides (1,331, 1,157, and 1,077 cm^{-1}) (16) in the MTU-6 monomer were not clearly detected in the spectra of the debonded resin (Table 5). The peak at about 2,600 cm^{-1} , attributable to S-H bonds, was not observed in MTU-6 or the debonded resin. Sulfur was involved in bonding to gold alloy, as indicated by attenuation of the C=S bond peaks and the absence of the S-H bond peaks in the resin block. The decrease in peaks attributable to N-H stretching (3,440 and 3,148 cm^{-1}) denotes a change in the amino group. The change in peaks attributable to N-H stretching suggests a thiol structure forms after bonding to gold alloy. Spectral analyses indicate that MTU-6 likely has a thione structure. The structure tautomerizes to thiol during the priming process and contributes to the bonding of gold alloy and acrylic resin.

This study used titanium as the experimental control adherend. Bonding between titanium and acrylic resin was insufficient after application of the two thione primers. In addition, trace organic sulfur compounds were not detected in debonded resin specimens, because thione compounds do not adsorb onto titanium and are ineffective for bonding titanium.

In conclusion, VTD and MTU-6 were effective for enhancing bonding between gold alloy and tri-*n*-butylborane-initiated acrylic resin but were ineffective for bonding titanium. Infrared absorption spectroscopic analysis detected trace VTD, and MTU-6 remained on acrylic resin specimens debonded from gold alloy. VTD and MTU-6 in debonded resin had a thiol structure rather than a thione structure.

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Conflict of interest

None declared.

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