Bonding performance of a thiohydantoin-methacrylate monomer on noble metal alloys

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This study assessed the effect of a primer containing 10-methacryloyloxydecyl-(2-thiohydantoin-4-yl)propionate (MDTHP) on the bonding of noble metal alloys to an acrylic resin. Three noble metal alloys were selected as adherends, and V-Primer containing 6-(4-vinylbenzyl-*n*-propyl)amino-1,3,5-triazine-2,4-dithione was used as a comparative control. The disk specimens of each noble metal alloy were wet-ground and divided into three conditions: specimens primed with MDTHP primer or V-Primer, and specimens without priming. An acrylic resin was bonded to each specimen, and the specimens were performed the shear bond test. The MDTHP primer showed higher shear bond strength than the V-Primer for all specimens. X-ray photoelectron spectroscopic analysis showed that MDTHP was adsorbed on the Au-Pt-Pd alloy surface even after acetone cleaning. MDTHP binds not only with Cu but also with Au and Ag, promoting the bond strength of noble metal alloys. The effectiveness of MDTHP on dental noble metal alloys was suggested.

Keywords: Adhesive, Bonding, Noble metal alloy, Thiohydantoin, Thione

INTRODUCTION

Noble metal alloys, such as those of gold-copper-silver, gold-platinum-palladium, and silver-palladium-copper-gold, are widely used to fabricate restorations and dental prostheses. The long-term prognosis of restorations and dental prostheses depends on the bond strength and durability between the dental alloy and luting agent used. Surface treatment with a primer composed of a sulfur-containing monomer promotes bond strength to noble metal alloys¹⁻⁶.

Several types of sulfur-containing functional monomers have been developed. The first report on sulfur-containing functional monomers for noble metal alloys was 6-(4-vinylbenzyl-*n*-propyl) amino-1,3,5-triazine-2,4-dithiol (VBATDT), which was used as a coating material for copper⁷. VBATDT has been studied for its bonding characteristics with noble metal alloys and is used in clinical practice⁸⁻¹⁰. The adsorption structure of VBATDT on a noble metal surface has also been analyzed^{11,12}. The analyses showed that VBATDT has a chemically stable thione structure during storage and changes from a thione to thiol structure on the noble metal alloy surface to promote bonding. Analyses using sulfur-containing functional monomers were performed. Imai *et al.* analyzed the noble metal alloy surface using electron spectroscopy for chemical analysis and

confirmed that sulfur-containing functional monomers were adsorbed on the noble metal alloy surface even after rinsing with acetone⁶.

In 2020, the synthesis of a novel sulfur-containing monomer, 10-methacryloyloxydecyl-(2-thiohydantoin-4-yl) propionate (MDTHP), was reported¹³. MDTHP is a monomer containing thiohydantoin, a five membered heterocyclic compound with a thione structure. The primer containing MDTHP reportedly promotes bond strength between noble metal elements and methyl methacrylate resin¹⁴. However, the effect of MDTHP on the bonding of noble metal alloys used in clinical practice has not yet been clarified. This study evaluated the effect of a primer containing MDTHP on the bond strength between noble metal alloys and a methyl methacrylate resin.

MATERIALS AND METHODS

Three casting alloys —a type IV gold alloy (Au-Cu-Ag; Casting Gold M.C. Type IV, GC, Tokyo, Japan), a gold alloy for metal-ceramic restoration (Au-Pt-Pd; DeguDent U, Degudent, Hanau, Germany), and a silver-palladium-copper-gold alloy (Ag-Pd-Cu-Au; Castwell M.C. 12% Gold, GC) were used as the adherend materials.

Two metal priming agents, V-Primer (VP; Sun Medical, Moriyama, Japan) and an MDTHP primer (MP), were assessed as bonding promoters. The VP contained VBATDT monomer. MP was synthesized according to a

Color figures can be viewed in the online issue, which is available at J-STAGE.

Received Jun 24, 2021; Accepted Oct 27, 2021

doi:10.4012/dmj.2021-181 JOI JST.JSTAGE/dmj/2021-181

Table 1 Materials assessed in this study

Material/trade name	Abbr.	Manufacturer	Lot number	Composition
Adherend alloy				
Casting Gold M.C. Type IV	Au-Cu-Ag	GC	702151	Au 70, Cu 16, Ag 8, Pd 3, Pt 2, others 1 (mass%)
DeguDent U	Au-Pt-Pd	Degudent	B013339	Au 77.3, Pt 9.8, Pd 8.9, In 1.5, Ag 1.2, others 1.3 (mass%)
Castwell M.C.12% Gold	Ag-Pd-Cu-Au	GC	0912101, 0812161	Ag 46, Pd 20, Cu 20, Au 12, others 2 (mass%)
Primer				
V-Primer	VP	Sun Medical	RE1	VBATDT, acetone
MDTHP Primer	MP			0.1 mol% MDTHP, acetone
Luting material				
Methyl methacrylate		Tokyo Chemical Industry	YMVAAOL	MMA 99.8%
Super-Bond C&B Opaque Ivory Powder	MMA	Sun Medical	SS1, SG1	PMMA, TiO ₂
Super-Bond C&B Catalyst V		Sun Medical	SS51	TBB, TBB-O, hydrocarbon

VBATDT, 6-(4-vinylbenzyl-*n*-propyl)amino-1,3,5-triazine-2,4-dithione; MDTHP, 10-methacryloyloxydecyl-(2-thiohydantoin-4-yl)propionate; MMA, methyl methacrylate; PMMA, polymethyl methacrylate; TBB, tri-*n*-butylborane; TBB-O, partially oxidized tri-*n*-butylborane.

previously described method¹³). Both primers were of a single liquid type and contained one adhesive monomer in the acetone.

As a luting material, an acrylic resin consisting methyl methacrylate, polymethyl methacrylate, and tri-*n*-butylborane was used. The materials used have been summarized in Table 1.

Shear bond strength

A total of 33 disk specimens were prepared for each Au-Pt-Pd and Ag-Pd-Cu-Au alloy, and 22 specimens were prepared for the Au-Cu-Ag alloy. The specimens (10 mm in diameter and 3 mm in thickness) of each alloy were prepared using dental casting technique according to the manufacturer's instructions. All specimens were wet ground with 1500-grit abrasive paper (Wetordry Tri-M-ite Sheet, 3M, St. Paul, MN, USA) and cleaned with acetone (Tokyo Chemical Industry, Tokyo, Japan) using an ultrasonic bath (SUC-110, Shofu, Kyoto, Japan).

The alloy specimens were evenly assigned ($n=11$) to one of the following three treatment conditions: 1) unprimed control (UP), 2) primed with VP, and 3) primed with MP. The shear bond strength of UP for the Au-Cu-Ag alloy was quoted by Hiraba *et al.*¹²). Each of two primers was applied to the specimen surfaces and air-dried. The bonding area were determined using a masking tape with circular hole 5 mm in diameter. The luting material was filled into the rings (thickness of 1 mm, height of 2 mm, and inner diameter of 6 mm) fixed to the specimens. After half an hour, the specimens were

stored at 37°C in distilled water for 24 h. Each specimen was seated in a testing jig (ISO TR 11405). Shear bond strengths were determined by means of a universal testing machine (Type 5567, Instron, Canton, MA, USA) at 0.5 mm/min crosshead speed.

Failure mode analysis

After the shear bond test, the debonded alloy surfaces were observed using a stereo microscope (Stemi DV4, Carl Zeiss, Jena, Germany). Image analysis was performed by means of image analysis application (LM eye, Lasertec, Yokohama, Japan), and the cohesive failure ratio was calculated using the following formula: cohesive failure ratio (%) = cohesive failure area (mm²) × 100 / bonded area (mm²).

Scanning electron microscope (SEM) observation

The debonded alloy surfaces were sputtered with gold and observed using an FE-SEM (ERA-8800FE, Elionix, Tokyo, Japan) with an accelerating voltage of 10 kV.

X-ray photoelectron spectroscopic analysis

The primed and unprimed surfaces of the Au-Pt-Pd alloy specimens were analyzed by X-ray photoelectron spectroscopy (XPS; JPS-9010MC, JEOL, Tokyo, Japan). A magnesium anode was used for the measurements with a tube power of 100 W. All spectra were excited using a Mg *Kα* line (1,253.6 eV). The vacuum in the chamber during the measurements was in the range of 2.5–4.5 × 10^{−7} Pa. The detection angle of the photoelectrons

was 90° from the surface of the alloy.

The three disk specimens of the Au-Pt-Pd alloy were wet-ground with a 2000-grit abrasive paper and were polished with felt (TexMet 1500, Buehler, Lake Bluff, IL, USA) and diamond suspension (9, 6, 3, and 1 µm, MetaDi, Buehler). They were cleaned with acetone in the ultrasonic bath. The specimen surfaces were treated under the following three conditions: 1) unprimed, 2) primed with MP, and 3) primed with VP. After priming, all specimens were cleaned with acetone in the ultrasonic bath at 24–31 kHz for 30 s.

Wide scan spectra (0–1,100 eV) were detected by analyzing the specimen surfaces at a pass energy of 50 eV. Narrow scan spectra were performed to confirm the presence of certain elements at a pass energy of 20 eV. Qualitative analysis of the spectra was performed using the software (Casa XPS ver. 2.3.13 Dev 34, Casa Software, Teignmouth, UK).

Statistical analysis

The results of the shear bond test were analyzed using

statistical application (GraphPad Prism 9.1.2 software, GraphPad Software, La Jolla, CA, USA). At first, the results were analyzed using the D'Agostino and Pearson omnibus test. When the results of the test did not show a normal distribution, the Kruskal-Wallis test and Dunn's multiple comparison test were performed as nonparametric tests; when the results showed a normal distribution, Dunnett's T3 multiple comparison test was performed. An $\alpha=0.05$ level of the significance was selected for all tests.

RESULTS

Shear bond strength

The results of the normality tests for Ag-Pd-Cu-Au (MP group) did not show a normal distribution. Ag-Pd-Cu-Au was therefore analyzed using the nonparametric tests. The Au-Cu-Ag and Au-Pt-Pd showed a normal distribution and were analyzed using Dunnett's T3 multiple comparisons test.

Table 2 presents the results of shear bond strength.

Table 2 Shear bond strength between gold alloy and MMA-TBB resin in MPa

Alloy	Primer	Mean (SD)	Median	IQR	Category
Au-Cu-Ag	UP*	1.6 (0.5)	1.8	1.0	a
	VP	29.7 (1.5)	29.7	2.0	b
	MP	32.3 (1.1)	32.6	1.7	c
Au-Pt-Pd	UP	1.9 (0.5)	2.0	0.8	a
	VP	20.7 (3.7)	21.0	6.8	b
	MP	26.2 (3.3)	27.0	5.0	c
Ag-Pd-Cu-Au	UP	1.7 (0.9)	2.1	1.6	a
	VP	29.2 (1.5)	29.9	2.1	b
	MP	32.7 (0.7)	32.5	0.4	c

$n=11$; SD, standard deviation; IQR, interquartile range; Different categories indicate that the values are significantly different in the statistical analysis performed for each alloy. Data of each of the Au-Cu-Ag and Au-Pt-Pd alloys was analyzed by Dunnett's T3 multiple comparisons, and Ag-Pd-Cu-Au was analyzed by Dunn's multiple comparisons. *The value of UP for the Au-Cu-Ag alloy was quoted from Hiraba *et al.*, 2017¹².

Table 3 Cohesive failure ratio analysis

Alloy	Primer	Mean (SD)	Median (%)	IQR
Au-Cu-Ag	UP*	38% (4.8)	36	8
	VP	73% (9.8)	73	9
	MP	86% (6.7)	86	6
Au-Pt-Pd	UP	26% (2.6)	26	4
	VP	65% (18.4)	68	31
	MP	94% (5.0)	97	8
Ag-Pd-Cu-Au	UP	29% (2.9)	29	5
	VP	76% (18.6)	81	22
	MP	83% (12.7)	90	23

$n=11$; Cohesive failure ratio was analyzed using optical micrograph and computer application. cohesive failure ratio (%)=cohesive failure area (mm²)×100/bonded area (mm²)

*The value of UP for the Au-Cu-Ag alloy was quoted from Hiraba *et al.*, 2017¹².

The shear bond strengths were categorized into three groups for each alloy (categories a–c). In each alloy, the median bond strengths of MP ranged from 27.0 MPa to 32.6 MPa, showing the highest bond strengths (category c). The median bond strengths of UP ranged from 1.8 MPa to 2.1 MPa, showing the lowest bond strengths (category a). MP exhibited a higher bond strength than VP for all alloys. These results suggest that MP is effective in promoting bond strength between noble metal alloys and acrylic resin.

Failure mode analysis

Table 3 presents the results of the failure mode analysis. The median cohesive failure ratio varied from a minimum of 26% to a maximum of 97% and showed higher values for MP in each alloy, as well as the bond strength.

SEM observation

Figure 1 shows the scanning electron images of the debonded surfaces. Figures 1a, c, and e show the surfaces of each alloy specimen primed with VP, and Figs. 1b, d, and f show the surfaces of each alloy specimen primed with MP. Remnants of the debonded resin were observed on the surfaces of all the primed specimens (Figs. 1a–f).

XPS analysis

Fig. 1 SEM images of the debonded alloy surfaces, (a) Au-Cu-Ag alloy primed with VP, (b) Au-Cu-Ag alloy primed with MP, (c) Au-Pt-Pd alloy primed with VP, (d) Au-Pt-Pd alloy primed with MP, (e) Ag-Pd-Cu-Au alloy primed with VP, and (f) Ag-Pd-Cu-Au alloy primed with MP (original magnification $\times 1,000$).

Figure 2 shows the wide scan spectra of the Au-Pt-Pd surface treated under three conditions: 1) unprimed, 2) primed with MP, and 3) primed with VP. The narrow scan spectra of C 1s, N 1s, S 2p, Au 4f_{5/2}, Au 4f_{7/2}, Ag 3d_{3/2} and Ag 3d_{5/2} on the Au-Pt-Pd surface were also analyzed under the same conditions (Figs. 3–5). The peaks of N 1s and S 2p were detected on all specimen

Fig. 2 XPS wide scan spectra of polished Au-Pt-Pd alloy surfaces, (a) unprimed, (b) primed with MP, and (c) primed with VP.

Fig. 3 XPS narrow scan spectra of the C 1s (a), N 1s (b), S 2p (c), Au 4f_{5/2} and Au 4f_{7/2} (d), and Ag 3d_{3/2} and Ag 3d_{5/2} (e) regions of the polished and unprimed Au-Pt-Pd specimen.

Fig. 4 XPS narrow scan spectra of the C 1s (a), N 1s (b), S 2p (c), Au 4f_{5/2} and Au 4f_{7/2} (d), and Ag 3d_{3/2} and Ag 3d_{5/2} (e) regions of the Au-Pt-Pd specimen primed with MP.

Fig. 5 XPS narrow scan spectra of the C 1s (a), N 1s (b), S 2p (c), Au 4f_{5/2} and Au 4f_{7/2} (d), and Ag 3d_{3/2} and Ag 3d_{5/2} (e) regions of the Au-Pt-Pd specimen primed with VP.

Table 4 Peaks of bonding energies (eV) obtained from the Au-Pt-Pd specimens primed with VP

Element	Peak energy (eV)	Peak assignment (Compound)	References values (eV)
C 1s	285.654	(CH ₂) _n	285.10 ¹⁸⁾
Au 4f _{7/2}	84.367	Au(0)	83.3 ¹⁷⁾
Au 4f _{7/2}	85.095	Au-S	84.6 ¹⁷⁾
Au 4f _{5/2}	87.991	Au(0)	86.9 ¹⁷⁾
Au 4f _{5/2}	88.343	Au-S	88.2 ¹⁷⁾
Ag 3d _{5/2}	368.200	Ag(0)	367.9 ²⁰⁾
Ag 3d _{5/2}	369.382	Ag-S	368.6 ²⁰⁾
Ag 3d _{3/2}	374.316	Ag(0)	373.8 ²⁰⁾
Ag 3d _{3/2}	375.700	Ag-S	374.7 ²⁰⁾
S 2p	162.432	S-Au, S-Ag	162.13 ¹⁶⁾ , 161.67 ¹⁹⁾
S 2p	163.212	S-H	163.35 ¹⁶⁾

surfaces except the unprimed specimen. The peaks attributed to the Au-S¹⁵⁻¹⁷⁾ bond were observed at 84.578 eV (Fig. 4d) and 85.095 eV (Fig. 5d) in the spectra of Au 4f_{7/2}, and at 88.023 eV (Fig. 4d) and 88.343 eV (Fig. 5d) in the spectra of Au 4f_{5/2}. The peaks attributed to the Ag-S¹⁸⁻²⁰⁾ bond were observed at 369.020 eV (Fig. 4e) and 369.382 eV (Fig. 5e) in the spectra of Ag 3d_{5/2}, and at 374.454 eV (Fig. 4e) and 375.700 eV (Fig. 5e) in the spectra of Ag 3d_{3/2}. The peaks obtained from the Au-Pt-Pd specimens primed with VP are also presented in

Table 4.

DISCUSSION

The effect of primers containing MDTHP on the bonding of noble metal alloys was assessed. Kodaira *et al.* reported on a study using MDTHP and VBATDT for elemental noble metal alloys. MDTHP showed high bond strength with elemental noble metal alloys, especially copper¹⁴⁾. However, the effects on noble metal alloys

have not yet been clarified. Therefore, three dental noble metal alloys with different compositions were selected as adherends, and the shear bond strengths of each alloy were compared.

The organic sulfur compound showed higher shear bond strength to noble metal alloys than UP, as previously reported. In addition, the shear bond strength of MP was significantly higher than that of VP in each alloy. MP showed high shear bond strength to the Au-Cu-Ag and Ag-Pd-Cu-Au alloys, which are noble metal alloys containing copper. MP was also effective for the Au-Pt-Pd alloy, which scarcely contained copper. The cohesive failure ratio was calculated by image analysis of the specimen debonded surface after the shear bond strength tests, and the MP showed a high value for each alloy. The cohesive failure ratio and the shear bond strength values showed similar trends. As a result of the SEM observation of the debonded surface, resin remnants were observed on all surface-treated specimen surfaces (Fig. 1). The observed SEM images were similar to those previously reported for organic sulfur compounds²¹⁾.

Surface analysis by XPS was performed to confirm the adsorption state of MDTHP on the surfaces of the Au-Pt-Pd alloy. MDTHP has a thiohydantoin structure, which is a five membered heterocyclic compound with a thione group, and can be tautomerized in the same way as VBATDT¹⁴⁾. The peaks of sulfur and nitrogen, which are elements derived from MDTHP, were detected on the surface of the Au-Pt-Pd alloy even after acetone cleaning for 30 s using an ultrasonic bath after the MP treatment (Figs. 4b and c). This suggests that MDTHP is strongly adsorbed on Au-Pt-Pd alloy surfaces. Kodaira *et al.* analyzed the copper surface by XPS using MDTHP¹⁴⁾. The peaks of sulfur and nitrogen were detected on the copper surface, indicating that MDTHP adsorbed on the copper surface promoted bonding¹⁴⁾. However, MP showed a high bond strength to the Au-Pt-Pd alloy, which scarcely contained copper. XPS analysis was performed on the Au-Pt-Pd alloy to clarify which elements other than copper are bound to MDTHP. Suzuki *et al.* reported the chemisorption of VBATDT on Au and Ag substrates using Raman scattering techniques²²⁾. XPS analysis of the bonding of Au and Ag in noble metal alloys with organic sulfur compounds has not been performed. Therefore, XPS analysis was performed using VBATDT. Because alloys scarcely containing copper were used, the specimens could be observed without considering the effect of copper. With XPS analysis, a peak attributable to the intermediate chain¹⁸⁾ of VBATDT was observed in the narrow scan spectrum of C 1s, and peaks attributable to Au-S¹⁵⁻¹⁷⁾ and Ag-S¹⁸⁻²⁰⁾ bonds were detected in the narrow scan spectra of Au 4f_{7/2}, Au 4f_{5/2}, Ag 3d_{5/2}, Ag 3d_{3/2}, and S 2p (Table 4 and Fig. 5). The narrow scan spectra of Au 4f_{7/2}, Au 4f_{5/2}, Ag 3d_{5/2}, and Ag 3d_{3/2} showed chemical shifts coincident with previous reports^{17,20)} (Table 4 and Fig. 5). Similar peaks and chemical shifts to those of VBATDT were observed for MDTHP (Figs. 4, 5 and Table 4). MDTHP is assumed to promote the bond strength in copper-free noble metal alloys by adsorbing on Au or Ag instead of Cu.

Bonding performance of organic sulfur compounds to noble metal elements has been reported previously^{14,23)}. Kodaira *et al.* reported that MDTHP showed high bond strength to Cu, Au, and Ag¹⁴⁾. It showed high bond strength with Au-Cu-Ag and Ag-Pd-Cu-Au alloys and inferior bond strength with the Au-Pt-Pd alloy. From the results, it was speculated that in comparison with Au-S and Ag-S bonds, the Cu-S bond may be more related to the bond strength of the noble alloys.

Another organic sulfur compound is 6-methacryloyloxyhexyl 2-thiouracil-5-carboxylate (MTU-6). The primer containing MTU-6 is Metaltite (Tokuyama Dental, Tokyo, Japan). Hiraba *et al.* reported the Metaltite primer copolymerized with the TBB-initiated methacrylic resin and improved bonding to the Au-Cu-Ag alloy^{12,21)}. The Metaltite primer was not assessed as a comparison in this study. The Metaltite primer contains ethanol as a solvent, therefore, VP and MP, which contain acetone as a solvent, were used for comparison in this study. In future, other organic sulfur compounds used in clinical practice will also be included for comparison.

In conclusion, the primer containing MDTHP showed superior bond strength between noble metal alloys and an acrylic resin compared to the primer containing VBATDT. The effect of MDTHP on the bond durability of noble metal alloys will be the subject of further study. The adsorption of MDTHP on the noble metal alloy surface was confirmed even after cleaning with acetone. MDTHP binds not only with Cu but also with Au and Ag, promoting the bond strength of noble metal alloys. These results suggest that MDTHP is effective for use with dental noble metal alloys.

ACKNOWLEDGMENTS

This study was supported in part by a grant (2021) from the Dental Research Center, Nihon University School of Dentistry. The authors thank Dr. Peng Chen of Tokyo Medical and Dental University for assistance with the X-ray photoelectron spectroscopic analysis.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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