

Evaluation of single liquid primers with organic sulfur compound for bonding between indirect composite material and silver-palladium-copper-gold alloy

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The purpose of this study was to evaluate the effect of primers on bonding between a silver-palladium-copper-gold alloy and an indirect composite material. Cast disks were air-abraded with alumina, conditioned with one of five primers (Alloy Primer, Luna-Wing Primer, Metal Primer II, Metaltite, M.L. Primer), and bonded with a light-activated indirect composite. Shear bond strengths were determined after 20,000 times of thermocycling. The results showed that four of the primers, except the Luna-Wing Primer, were effective in enhancing the bond strength as compared with the unprimed control group. Of these four primers, Alloy Primer, Metal Primer II, and M.L. Primer exhibited significantly greater bond strengths. It can be concluded that the effectiveness of primers varies considerably according to the organic sulfur compounds added to the solvent, and that care must be taken in selecting priming agents for bonding the composite material and the silver-palladium-copper-gold alloy.

Keywords: Indirect composite, Primer, Silver-palladium-copper-gold alloy

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INTRODUCTION

Indirect composite materials have been used extensively in the fabrication of tooth-colored inlay and onlay restorations, as well as resin facing restorations. For composite resin veneered prostheses, it is necessary to establish a consistent and durable bond between the veneering material and the metal substructure¹.

Surface preparation combined with application of a priming agent is one of the simplest methods used for bonding between indirect composites and dental metal alloys²⁻⁵. Currently available metal priming agents can be categorized into three types according to the functional monomers employed: 1) organic acid including carboxylic acid and phosphate⁶⁻¹¹, 2) organic sulfur compound including thiol, thione, and disulfide¹²⁻¹⁴, and 3) both acidic and sulfur compounds^{6,7,10,12,13}. Metallic frameworks of the resin facing restorations are frequently fabricated with noble metal alloys. It is important for restorations that the facing material and alloy are bonded durably to ensure long-term success of prosthodontic treatment.

A triazine dithiol monomer, 6-(4-vinylbenzyl-*n*-propyl)amino-1,3,5-triazine-2,4-dithiol, or -2,4-dithione tautomer (VTD) was introduced for coating copper metal¹⁵. A thiouracil methacrylate was thereafter developed for priming noble metal alloys^{16,17}. Laboratory evaluation demonstrated that bonding ability to noble metals vary considerably according to the type of primer employed^{12,13}. Another primers based on organic sulfur compounds have been released. The functional monomers employed are 10-

methacryloyloxydecyl-6,8-dithiooctanoate (10-MDDT)¹⁸ and pentaerythritoltetrakis-3-mercaptopropionate (PETP)¹⁹. Although the efficiency of the sulfur based primers on bonding to noble metal alloys have been well recognized, little information is available about their comparative evaluation. Therefore, the purpose of the present study was to evaluate the effect of five priming agents on bonding between a light polymerized indirect composite and a silver-palladium based casting alloy.

MATERIALS AND METHODS

A silver-palladium-copper-gold alloy (Castwell M.C. 12, GC Corp., Tokyo, Japan) designed for inlay, onlay, and crown restorations as well as denture frameworks was selected as the adherend material. Five single-liquid primers were assessed. A microfilled light-activated indirect composite (New Meta Color Invis, Sun Medical Co. Ltd., Moriyama, Japan) was used as the veneering material. Information on the materials used in this experiment is summarized in Table 1.

A total of 120 disk-shaped specimens (10 mm in diameter and 2.5 mm in thickness) were cast from the alloy according to the manufacturer's specification. All disks were ground flat with a series of silicon-carbide abrasive papers (up to #600), followed by airborne-particle abrasion with 50-70 μ m alumina (Hi-Aluminas, Shofu Inc., Kyoto, Japan) for 5 s. The supply-side air-pressure was 0.3 MPa and the distance of the orifice from the metal surface was approximately 15 mm. The abraded surface was then air-blasted with compressed

air. The abraded disks were divided into six sets of 20 disks each. One set (20 disks) was left unprimed. The five primers were applied separately to the metal surfaces of five sets of 20 disks with a sponge pellet.

A piece of double-coat tape with a circular hole 5 mm in diameter was positioned on the surface of each metal specimen to define the bonding area. A thin layer of an opaque resin (New Meta Color Infis Opaque Base, Sun Medical Co. Ltd.) was applied to the metal surface and exposed to light for 30 s in a polymerizing unit (Dentacolor XS, Heraeus Kulzer GmbH, Wehrheim, Germany). An additional opaque material (New Meta Color Infis Opaque Top, A3-O, Sun Medical Co. Ltd.) was applied twice on top of the primary opaque resin, each of which was exposed to light for 90 s. After light-exposure, a brass ring (6 mm inside diameter, 2 mm length, and 1 mm wall thickness) was placed surrounding the opaque resin. The ring was filled with a dentin shade of the indirect composite material (New Meta Color Infis Paste Body, A3-B, Sun Medical Co. Ltd.) and polymerized with the unit for 270 s. After 30 minutes of preparation, the specimens were immersed in water at 37°C for 24 hours, and this state was defined as thermocycling 0. The 20 disks were then divided into two groups of 10 specimens; half (six sets of 10 specimens) were tested for 24-hour shear bond

strength at 0 thermocycling. The remaining specimens were placed in a thermocycling apparatus (Thermal Cycler, Nissin Seiki Co. Ltd., Hiroshima, Japan) and cycled between 4°C and 60°C water with a 1-minute dwell time per bath for 20,000 cycles.

The specimens were positioned in steel molds, and seated in an ISO/TR 11405 shear testing jig. Shear bond strengths were determined by means of a mechanical testing device (AGS-5kNj, Shimadzu, Kyoto, Japan) at a crosshead speed of 0.5 mm/minute. The debonded surfaces were observed with an optical microscope (×8; S300II, Inoue Attachment Corp., Tokyo, Japan) and the failure modes were recorded as either an adhesive failure at the alloy-resin interface (A), a cohesive failure within the resin (C), or a combination of cohesive and adhesive failures (AC).

For each set of specimens, the mean shear bond strength, standard deviation (SD) of the 10 specimens, and rate of reduction (of 20,000 cycles value to 0 cycle) were calculated. The results were primarily analyzed by the Levene test for the evaluation of equality of variance. The values of each group were compared with two-way analysis of variance (ANOVA). The two factors were type of modification method and thermocycling status. *Post-hoc* Scheffé tests were performed with the value of statistical significance set at alpha = 0.05. In

Table 1 Casting alloy, primers, and composite materials assessed

Trade name	Composition (%)	Manufacturer	Lot No.
Casting alloy			
Castwell M.C. 12	Ag 46, Cu 20, Pd 20, Au 12, others (Zn, Ir, In) 2	GC Corp., Tokyo, Japan	0707171
Primers			
Alloy Primer	VTD and MDP in acetone	Kuraray Medical Inc., Tokyo, Japan	0244AA
Luna-Wing Primer	PETP in acetone	Yamamoto Precious Metal Co. Ltd., Osaka, Japan	1050617
Metal Primer II	MEPS in methyl methacrylate	GC Corp., Tokyo, Japan	701052
Metaltite	MTU-6 in ethanol	Tokuyama Dental Corp., Tokyo, Japan	2296
M.L. Primer	10-MDDT and 6-MHPA in acetone	Shofu Inc., Kyoto, Japan	120622
Composite veneering material			
New Meta Color Infis, Opaque Top/Paste Body	UDMA, TEGDMA, methacrylic polymer, aromatic amine, SiO ₂ , others	Sun Medical Co. Ltd., Moriyama, Japan	MR2
New Meta Color Infis, Opaque Top/Paste Body	UDMA, TEGDMA, aromatic amine, prepolymerized silica composite filler, others	Sun Medical Co. Ltd., Moriyama, Japan	MW11/ MX2

VTD = 6-(4-vinylbenzyl-*n*-propyl)amino-1,3,5-triazine-2,4-dithiol, or -2,4-dithione tautomer; MDP = 10-methacryloyloxydecyl dihydrogen phosphate; PETP = pentaerythritol tetrakis(3-mercaptopropionate); MEPS = methacryloyloxyalkyl thiophosphate derivative; MTU-6 = 6-methacryloyloxyhexyl 2-thiouracil-5-carboxylate; 10-MDDT = 10-methacryloyloxydecyl -6,8-dithiooctanoate; 6-MHPA = 6-methacryloyloxyhexyl phosphonoacetate; UDMA = dimethacryloyloxyethyl 2,2,4-(or 2,4,4-) trimethylhexamethylene diurethane; TEGDMA = triethyleneglycol dimethacrylate.

Table 2 Shear bond testing results in MPa

Primer	0 thermocycle			20,000 thermocycles			S	Reduction
	Mean	SD	Category	Mean	SD	Category		
Unprimed (control)	6.6	1.0	a	0.5	0.2	e	S	92.4%
Alloy Primer	20.9	3.1	c	15.4	2.1	g	S	26.3%
Luna-Wing Primer	12.7	2.5	b	0.9	0.8	e	S	92.9%
Metal Primer II	18.4	2.3	c	12.9	1.6	f, g	S	29.9%
Metaltite	21.8	1.6	c	12.1	1.2	f	S	44.5%
M.L. Primer	25.8	2.3	d	15.2	2.6	g	S	41.1%

SD: Standard deviation; Category: Identical letters indicate that values are not statistically different ($p > 0.05$); S: Significant difference between pre- and post-thermocycling bond strengths ($p < 0.05$).

addition, to analyze the influence of the thermocycling, the results of the 0 and 20,000 cycles of an identical surface treatment were compared using Mann-Whitney's U tests with the value of statistical significance set at $\alpha = 0.05$ for each treatment. All analyses were carried out using SPSS 15.0 for Windows (SPSS Japan Inc., Tokyo, Japan).

RESULTS

The Levene test run on the shear bond strength for each treatment-thermocycling combination did not show homoscedasticity, and the two-way ANOVA results revealed that bond strength was significantly affected by primer ($F = 241.8$, $p < 0.001$), thermocycling ($F = 526.2$, $p < 0.001$), and by two-way interactions of primer and thermocycling ($F = 10.6$, $p < 0.001$).

The data were therefore analyzed by the *post-hoc* Scheffé tests and Mann-Whitney's U tests. The bond strength results are presented in Table 2. The strengths after thermocycling were significantly lower than those before thermocycling for all treatments. Regarding 0 thermocycling, the application of primers after air-abrasion was effective in enhancing bond strength as compared with air-abrasion only (unprimed condition). Bond strength generated with use of the M.L. Primer was the greatest (25.8 MPa, $p < 0.05$). After thermocycling, however, the strength of the Luna-Wing Primer group (0.9 MPa) was lower than that of other primed groups, and statistically identical to the unprimed group (0.5 MPa). Among the five primers, the effects of the Alloy Primer, Metal Primer II, and M.L. Primer were comparable after thermocycling (category g). Reduction (rate of reduction) in bond strength was the smallest for the Alloy Primer group (26.3%), whereas that for the Luna-Wing Primer group was the largest (92.9%).

For all specimens, debonding (0 MPa bond strength) was not observed before and after application of thermocycling. Failure modes after shear testing are summarized in Table 3. Combination of adhesive and cohesive failures (AC) was reduced for majority of groups by the application of thermocycling. All specimens of unprimed control and Luna-Wing Primer

Table 3 Failure modes after shear bond testing

Primer	0 thermocycle			20,000 thermocycles			
	Failure mode	A	AC	C	A	AC	C
Unprimed (control)		10	0	0	10	0	0
Alloy Primer		6	4	0	6	4	0
Luna-Wing Primer		10	0	0	10	0	0
Metal Primer II		9	1	0	10	0	0
Metaltite		8	2	0	9	1	0
M.L. Primer		3	7	0	6	4	0

A: Adhesive failure at the alloy-resin interface;

C: Cohesive failure within the resin;

AC: Combination of adhesive and cohesive failures.

groups showed adhesive failure (A) both before and after thermocycling.

DISCUSSION

A number of surface modification methods for dental casting alloys have been developed. Among them, application of a single liquid primer is widely accepted due to the simplicity of the procedure. Therefore, the present study evaluated the effectiveness of five primers on bond strength between an indirect composite and a silver-palladium-copper-gold alloy.

The test results showed that application of the Luna-Wing Primer was ineffective, especially after thermocycling (Table 2). The Luna-Wing Primer contains PETP as a thiol compound (Table 1). However, PETP does not include a radically polymerizable group (Fig. 1). The adhesive functional monomer must include both adhesive functional and polymerizable groups; otherwise, the functional monomer cannot achieve adhesion²⁰. Although there are four mercapto groups in PETP, a polymerizable double bond is not available in

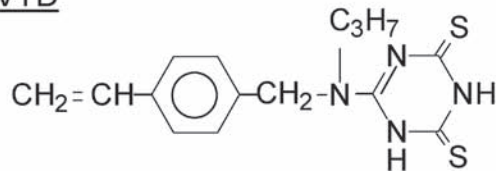
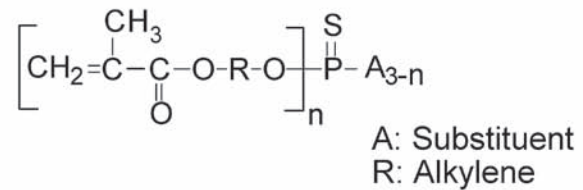
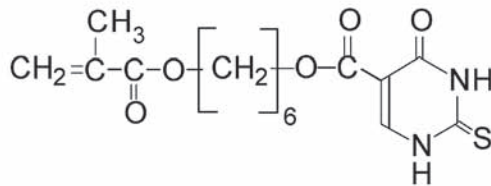
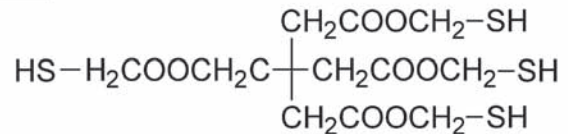
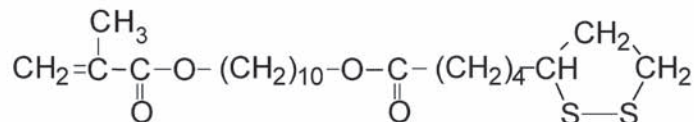
VTDMEPSMTU-6PETP10-MDDT

Fig. 1 Structural formulae of organic sulfur compounds.

the structure. Specifically, PEPT interacts with the noble metals, whereas it is not co-polymerizable with any of the monomers in the bonding agents and resin-based adhesives¹⁹. The authors speculate that the ineffectiveness of the Luna-Wing Primer is derived from the lack of polymerizable double bonds in the PEPT compound. Failure mode analysis (Table 3) supports this hypothesis. Combination of adhesive and cohesive failures (AC) was reduced for majority of groups by the application of thermocycling. The results were similar with the tendency for the bond strength to decrease by thermocycling. However, all specimens of Luna-Wing Primer group showed adhesive failure (A) as well as unprimed control group in before thermocycling.

The effectiveness of the sulfur based functional monomers, except for PETP, in bonding noble metals has been reported¹²⁻¹⁴. VTD thiol-thione tautomer was developed originally as a coating agent for copper¹⁵. According to the published literature, VTD chemisorbed via sulfur atoms on gold, silver, and copper^{21,22}. Furthermore, VTD can be copolymerized through a vinyl group with another monomers to form co-polymer at the adhesive interface^{21,22}. Although negative results have been reported regarding the chemical bond between thiol and metallic elements^{23,24}, the mechanism for bonding with metals, if any, of the sulfur-based monomers, MEPS (Metal Primer II), MTU-6 (Metalite) and 10-MDDT (M.L. Primer), might be identical or very similar to that of VTD. In addition, the primers used in

this study is single liquid and composed of adhesive functional monomer and volatile solvent without initiator. The authors therefore consider that bonding ability of the primers is primarily dependent on type of functional monomer.

Within the limitations of this study, the effectiveness of four primers in bonding a composite to a silver-palladium-copper-gold alloy was confirmed. The four compounds added to the primer were organic sulfur compounds with polymerizable double bonds. The present findings demonstrate that clinicians and dental laboratory technicians should be aware that selection of an appropriate priming agent. Specifically, they should consider that a functional monomer is indispensable for achieving a durable bond between composite materials and casting alloys.

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