

## Effects of Primers Containing Thiouracil and Phosphate Monomers on Bonding of Resin to Ag-Pd-Au Alloy

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The purpose of the present study was to evaluate the effects of four experimental primers on bond strength between a self-curing luting agent and silver-palladium-gold alloy. The experimental primers were in mixed solutions of a thiouracil primer (Metaltite) and a phosphate primer (Epicord, PM, PE, or PP), which were designated as Metaltite/Epicord, Metaltite/PM, Metaltite/PE, and Metaltite/PP respectively. Three primers (Metal Primer II, V-Primer, and Alloy Primer) were also prepared as controls. Alumina-blasted metal alloys were bonded with acrylic rods. After 5,000 thermocycles, the maximum shear bond strength was obtained with Metaltite/PE ( $27.8 \pm 2.4$  MPa) and Metaltite/Epicord ( $27.6 \pm 5.9$  MPa), followed by Metaltite/PP, Alloy Primer, Metaltite, Metaltite/PM, Metal Primer II, V-Primer, and Epicord. PE, PM, and PP showed the lowest bond strength. Results of this study revealed that the combined use of a thiouracil monomer and a phosphate monomer improved adhesive bonding. In this light, clinicians should pay attention to the types of functional monomers dissolved in a primer when fabricating resin-bonded prostheses.

Keywords: Metal alloy, Adhesive bonding, Surface treatment

### INTRODUCTION

Silver-palladium-gold (Ag-Pd-Au) alloy is one of the most popular dental metal alloys in the fabrication of inlays, crowns, veneered crowns, and resin-bonded fixed partial dentures. While strong and durable bonding between the metal framework and luting agent is indispensable for the resin-bonded fixed partial denture, clinicians occasionally encounter detachment failures<sup>1-3</sup>. Compared to the conventional fixed partial denture, the use of resin-bonded fixed partial dentures yields the advantage of minimal intervention<sup>4,5</sup>. Therefore, there is an impetus to improve resin bonding to Ag-Pd-Au alloy in order to decrease tooth tissue loss with tooth preparation.

On promoting adhesive bonding as well as surface modification of substrate materials, the type of functional monomer contained in a resin cement or primer plays an influential role. Although the use of some phosphate or carboxylic monomers has been shown to improve the bond strength of resins to base metal alloys, these monomers were not as effective for noble metal alloys<sup>6-8</sup>. To bond noble metal alloys, additional surface modification treatments such as tin plating<sup>9</sup>, high temperature oxidation<sup>10</sup>, gallium-tin alloy technique<sup>11</sup>, and silica coating<sup>12</sup> were devised.

On bonding to noble metal alloys, methacrylate monomers which contain sulfur in the molecules were synthesized<sup>13-18</sup> and used clinically as primers<sup>19-21</sup>. Sulfur-containing monomers which dissolved in commercially available primers were tautomers of 6-[N-(4-vinylbenzyl)propylamino]-1,3,5-triazine-2,4-dithiol and 6-[N-(4-vinylbenzyl)propyl-

amino]-1,3,5-triazine-2,4-dithione (VBATDT)<sup>22</sup>, thiophosphoric acid derivative (MEPS)<sup>23</sup>, 6-methacryloxyhexyl 2-thiouracil-5-carboxylate (MTU-6)<sup>24</sup>, and 10-methacryloxydecyl-6,8-dithiooctanate (10-MDDT). Priming techniques required neither special equipment nor complicated manipulations. However, these monomers were not always effective in promoting adhesion to base metal alloys<sup>25,26</sup>.

In recent years, two commercially available dual-function primers are in widespread use. These primers employed sulfur-containing monomers together with a phosphate monomer. One primer (Alloy Primer, Kuraray Medical Co. Ltd., Tokyo, Japan)<sup>27</sup> contained VBATDT and 10-methacryloxydecyl dihydrogen phosphate (MDP), and another primer (Metal Link, Shofu Inc., Kyoto, Japan) contained 10-MDDT and 6-methacryloxyhexyl phosphonoacetate (6-MHPA)<sup>28</sup>. Although these dual-function primers were effective for both noble and base metal alloys<sup>29-31</sup>, limited information is available regarding primers with other combinations of sulfur-containing monomers and phosphate monomers<sup>32</sup>.

The purpose of the present study, therefore, was to investigate the effects of modifying a thiouracil primer with phosphate monomers on bond strength between a self-curing luting resin and Ag-Pd-Au alloy and on the bonding durability of these primers against thermocycling stress.

### MATERIALS AND METHODS

Table 1 lists the metal alloy, primers, and luting agent used in this study. Figure 1 shows the chemical structures of seven functional monomers<sup>22-24,27</sup>.

Table 1 Adherend material, primers, and luting agent evaluated in the present study

Name	Component (%)	Manufacturer	Lot No.
<b>Adherend material</b>			
Castwell M.C. 12	Ag=46, Pd=20, Cu=20, Au=12, others=2	GC Corp., Tokyo, Japan	
<b>Primer</b>			
Metaltite	MTU-6, Alcohol	Tokuyama Dental Corp. Tokyo, Japan	0212
Epicord	Opaque Primer: MDP, Solvent, Others	Kuraray Medical Co. Ltd., Osaka, Japan	00143B
PM	Phosmer PM 5%	Uni-Chemical Co. Ltd., Osaka, Japan	170702
	MMA 95%	Wako Pure Chemical Ind. Ltd., Osaka, Japan	KSJ4437
PE	Phosmer PE 5%	Uni-Chemical Co. Ltd., Osaka, Japan	80312
	MMA 95%	Wako Pure Chemical Ind. Ltd., Osaka, Japan	KSJ4437
PP	Phosmer PP 5%	Uni-Chemical Co. Ltd., Osaka, Japan	170618
	MMA 95%	Wako Pure Chemical Ind. Ltd., Osaka, Japan	KSJ4437
Metaltite/Epicord	Metaltite 50%, Epicord 50%		
Metaltite/PM	Metaltite 50%, PM 50%		
Metaltite/PE	Metaltite 50%, PE 50%		
Metaltite/PP	Metaltite 50%, PP 50%		
V-Primer	VBATDT, Acetone	Sun Medical Co. Ltd., Moriyma, Japan	MT1
Alloy Primer	MDP, VBATDT, Acetone	Kuraray Medical Co. Ltd., Osaka, Japan	00123A
Metal Primer II	MEPS, MMA	GC Corp., Tokyo, Japan	0511111
<b>Luting agent</b>			
MMA-TBB resin	MMA	Wako Pure Chemical Ind. Ltd., Osaka, Japan	KSJ4437
	Polymerization initiator: tri- <i>n</i> -butylborane	Sun Medical Co. Ltd., Moriyma, Japan	LW62
	Polymer powder: poly(methyl methacrylate)	Sun Medical Co. Ltd., Moriyma, Japan	KS1

MTU-6, 6-methacryloxyhexyl 2-thiouracil-5-carboxylate; MDP, 10-methacryloxydecyl dihydrogen phosphate; PM, acidphosphoxyethyl methacrylate; MMA, methyl methacrylate; PE, acidphosphoxypolyoxyethylene glycol methacrylate; PP, acidphosphoxypolyoxypropylene glycol methacrylate; VBATDT, tautomer of 6-[N-(4-vinylbenzyl)propylamino]-1,3,5-triazine-2,4-dithiol and 6-[N-(4-vinylbenzyl)propylamino]-1,3,5-triazine-2,4-dithione; MEPS, thiophosphoric acid derivative.

The primers used were four sulfur-containing primers (Metaltite, V-Primer, Alloy Primer, and Metal Primer II), four phosphate primers without sulfur component (Epicord, PM, PE, and PP), and four primers composed of Metaltite with a phosphate monomer (Metaltite/Epicord, Metaltite/PM, Metaltite/PE, and Metaltite/PP). The self-curing luting agent (MMA-TBB resin) was composed of methyl methacrylate, poly(methyl methacrylate), and tri-*n*-butylborane.

#### Shear bond test

A total of 144 disk-shaped acrylic patterns, 10 mm in diameter and 2.5 mm in thickness, were embedded in a cristobalite investment material (Cristoquick II, GC Corp., Tokyo, Japan), and then cast using Ag-Pd-Au alloy with a centrifugal casting apparatus (CM-30, J. Morita Tokyo Manufacturing Corp., Saitama, Japan). All metal disks were ground with a series of silicon carbide papers (320- and 600-grit) and subsequently air-abraded (Jet Blast III, Morita Corp.,

Tokyo, Japan) with 50- $\mu$ m alumina (Hi-Aluminas, Shofu Inc., Kyoto, Japan) for five seconds. An air pressure of 0.4 MPa was applied, and the nozzle was positioned approximately 10 mm from the specimen surface. A 50- $\mu$ m-thick piece of masking tape with a circular hole of 5 mm diameter was positioned on the surface of each specimen to delineate the bonding area. Primer of 1  $\mu$ L was applied to the specimen with a micropipette (Eppendorf AG, Hamburg, Germany). The primers (Metaltite/Epicord, Metaltite/PM, Metaltite/PE, and Metaltite/PP) were immediately used after mixing. An acrylic rod (8 mm in diameter and 5 mm in height) was bonded to the specimen with a self-curing luting agent using the brush-on technique.

The bonded specimens were stored in room temperature for 60 minutes and then immersed in water at 37°C for 24 hours. Half of the specimens (12 sets of six specimens) were tested for 24-hour shear bond strength, whereby this state was defined as 0 thermocycles. The other specimens were thermocycled

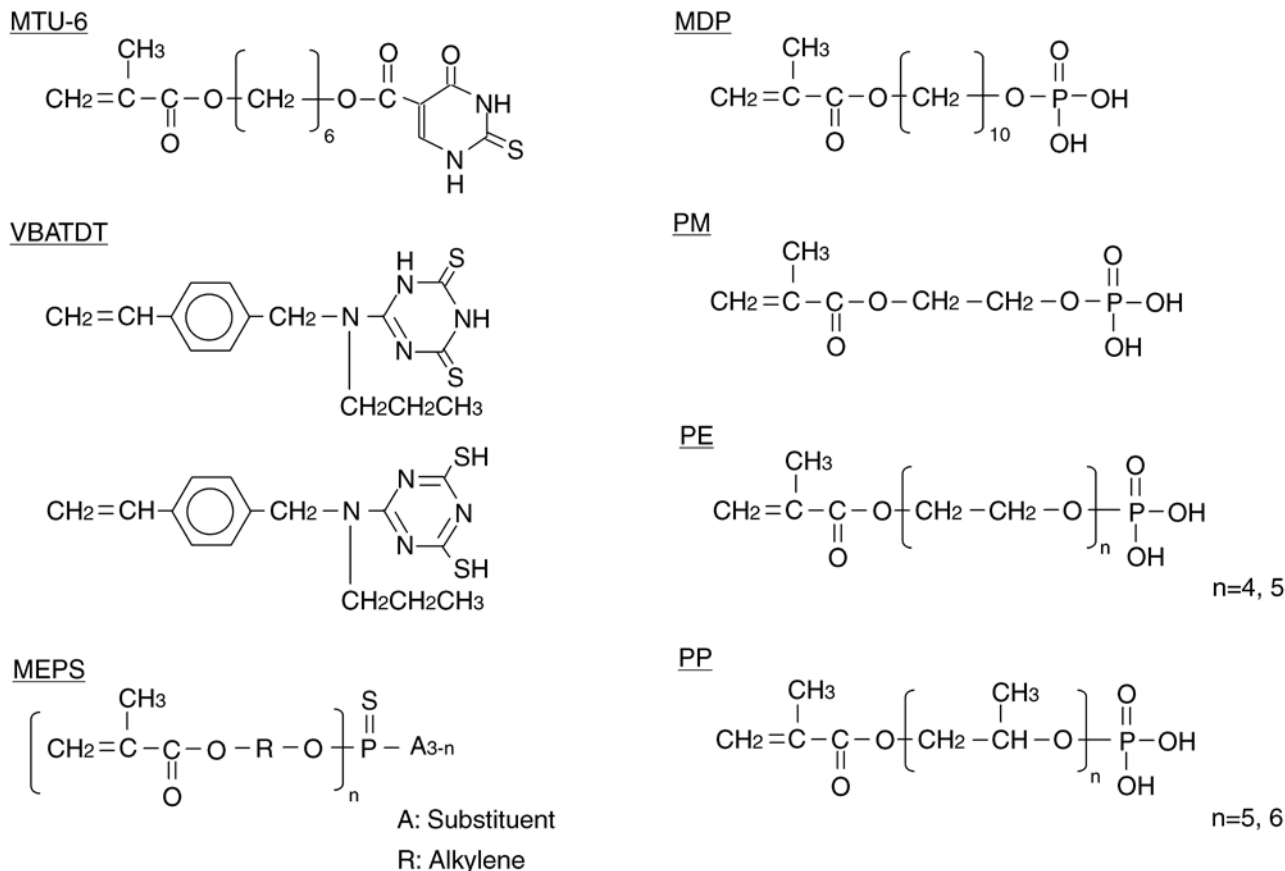


Fig. 1 Chemical structures of three sulfur-containing monomers and four phosphate monomers evaluated in this study<sup>22-24,27</sup>.

for 5,000 cycles between water held at 4°C and 60°C, with a dwelling time of one minute, by means of a thermocycling apparatus (Rika Kogyo, Tokyo, Japan). Shear bond strength was determined on a universal testing machine (AGS-10kNG, Shimadzu, Kyoto, Japan) at a crosshead speed of 0.5 mm/minute.

The means and standard deviations of six specimens for each group were calculated. Data were analyzed by two-way analysis of variance (ANOVA). The mean values were compared by *post hoc* Fisher's Protected LSD test ( $\alpha=0.05$ ) following one-way ANOVA. The debonded surfaces of all specimens were observed through an optical microscope (SMZ-10, Nikon Corp., Tokyo, Japan) at a magnification of  $\times 20$ .

#### X-ray photoelectron spectroscopy (XPS)

An additional Ag-Pd-Au alloy sample was alumina-blasted as described above. XPS analysis was carried out with a spectrometer (JPS-9000MC, JEOL Ltd., Tokyo, Japan) equipped with magnesium X-ray source of  $\phi 6$  mm operating at 10kV and 15mA. The take-off angle between sample surface and the electron optical axis of the spectrometer was controlled at 45°.

## RESULTS

#### Shear bond test

Table 2 shows the means and standard deviations of shear bond strength before and after thermocycling for 5,000 cycles. Two-way ANOVA results suggested that bond strength was affected by both thermocycling and primer, as well as by their interaction (Table 3). At 0 thermocycles, mean bond strength ranged from 13.2 MPa (PM) to 37.6 MPa (Metaltite/Epicord). Six groups (Metaltite, Epicord, Metaltite/Epicord, Metaltite/PE, Alloy Primer, and Metal Primer II) showed the highest bond strengths with no significant differences. The bond strengths of PE, Metaltite/PM, Metaltite/PP, and V-Primer were intermediate. All the specimens were observed to suffer a mixed mode of adhesive failure at the metal-luting agent interface and cohesive failure within the luting agent.

After 5,000 thermocycles, the bond strengths ranged from 0.6 to 27.8 MPa. In each group, the thermocycling test revealed decreased bond strength. The group primed with Epicord, PM, PE, or PP showed the lowest bond strengths with differences among them but not statistically significant. The

Table 2 Shear bond strengths between a self-curing luting agent and alumina-blasted silver-palladium-gold alloy

Group	0 Thermocycles Mean (SD) (MPa)	5,000 Thermocycles Mean (SD) (MPa)
Metaltite	35.6 (5.3) <sup>mn</sup>	17.6 (6.6) <sup>def</sup>
Epicord	34.1 (4.7) <sup>klmn</sup>	7.5 (3.1) <sup>b</sup>
PM	13.2 (4.0) <sup>cd</sup>	0.6 (0.2) <sup>a</sup>
PE	28.6 (5.1) <sup>ij</sup>	2.2 (1.6) <sup>a</sup>
PP	18.7 (2.5) <sup>efg</sup>	0.7 (0.3) <sup>a</sup>
Metaltite/Epicord	37.6 (2.9) <sup>n</sup>	27.6 (5.9) <sup>hi</sup>
Metaltite/PM	30.6 (6.5) <sup>ijkl</sup>	16.0 (6.5) <sup>de</sup>
Metaltite/PE	36.1 (3.1) <sup>mn</sup>	27.8 (2.4) <sup>hi</sup>
Metaltite/PP	32.5 (5.0) <sup>klm</sup>	23.2 (3.4) <sup>sh</sup>
V-Primer	29.5 (4.5) <sup>ijk</sup>	10.2 (4.8) <sup>bc</sup>
Alloy Primer	36.0 (3.3) <sup>mn</sup>	21.8 (1.5) <sup>fg</sup>
Metal Primer II	34.6 (2.1) <sup>lmn</sup>	14.8 (3.5) <sup>cde</sup>

Bond strength values assigned the same letters indicate no statistically significant difference ( $p \geq 0.05$ ).

Table 3 Analysis of variance results for shear bond strength

Source of variation	d.f.	Sum of squares	Mean square	F-value	P-value
Thermocycling	1	9715.9	9715.9	570.8	0.0001
Primer	11	9013.4	819.4	48.1	0.0001
Thermocycling/ Primer	11	1217.9	110.7	6.5	0.0001
Residual	120	2042.5	17.0		

group primed with Metaltite/Epicord or Metaltite/PE exhibited the highest bond strengths, followed by Metaltite/PP and Alloy Primer. Although the bond strengths of Metaltite/Epicord and Metaltite/PE were significantly higher than that of Metaltite, no significant difference was observed between Metaltite/PM and Metaltite. The bond strength of Alloy Primer was significantly higher than those of Epicord and V-Primer. No significant differences in bond strength were observed between Metaltite and Alloy Primer, between V-Primer and Metal Primer II, and between Epicord and V-Primer. With the exception of those applying PM, PE, and PP, all groups were observed to suffer partial cohesive failure within the luting agent. In contrast, groups applying PM and PP demonstrated complete adhesive failure.

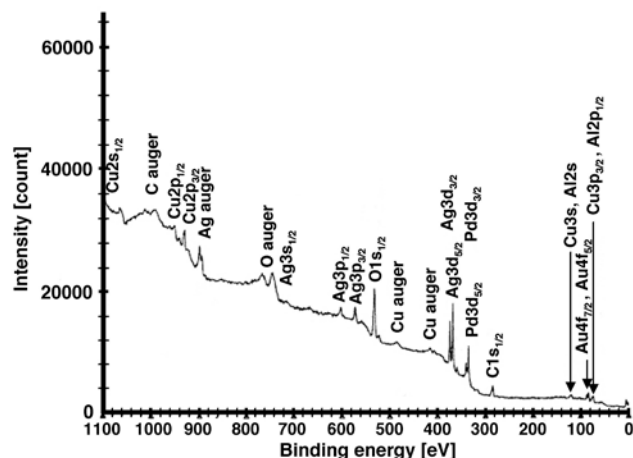


Fig 2 X-ray photoelectron spectroscopy spectra obtained.

### XPS

XPS analysis showed the presence of Ag, Pd, copper (Cu), Au, aluminum (Al), oxygen (O), and carbon (C) on the alumina-blasted Ag-Pd-Au alloy (Fig. 2). The detection depth was about 0.5–3 nm. The spectrum peaks detected were Ag3s<sub>1/2</sub>, Ag3p<sub>1/2</sub>, Ag3p<sub>3/2</sub>, Ag3d<sub>5/2</sub>, Ag3d<sub>3/2</sub>, Pd3d<sub>5/2</sub>, Pd3d<sub>3/2</sub>, Cu2p<sub>3/2</sub>, Cu2p<sub>1/2</sub>, Cu3s, Cu3p<sub>3/2</sub>, Au4f<sub>7/2</sub>, Au4f<sub>5/2</sub>, Al2p<sub>1/2</sub>, Al2s, O1s<sub>1/2</sub>, and C1s<sub>1/2</sub>. The peaks Cu3p<sub>3/2</sub> (74 eV) and Cu3s (120 eV) overlapped with Al2p<sub>1/2</sub> (74 eV) and Al2s (118 eV), respectively. Upon comparing the obtained energy peaks of Pd3d<sub>5/2</sub> (335.2 eV) and Au4f<sub>7/2</sub> (84.0 eV) to the reported chemical shifts<sup>33</sup>, it appeared that Pd and Au were close to the metal state (Pd: 334.8 eV, Au: 84.0 eV) rather than the metal oxide state (PdO: 336.3 eV, PdO<sub>2</sub>: 337.9 eV, Au<sub>2</sub>O<sub>3</sub>: 85.9 eV). With regard to Ag or Cu, it was impossible to distinguish the metal state from the metal oxide state, because their chemical shifts were within a narrow range<sup>33</sup>.

### DISCUSSION

Adhesive bonding to noble metal alloys was improved by the use of sulfur-containing functional monomers<sup>13-24</sup>. In the present study, an innovative advance in bonding resin to Ag-Pd-Au alloy was achieved by modifying a thiouracil primer with a phosphate monomer.

Generally, metal elements are classified into two categories: noble metals (Au, Pd, or Ag) and base metals (Cu or Al). In contrast to noble metals, base metals are characterized by an oxide layer, which is created on the metal surface in an atmospheric environment<sup>34</sup>. In addition to the oxide layer, XPS analysis results suggested that the metal states of Pd and Au also existed on the substrate material. It was tempting to speculate that the Al detected originated from the alumina powder used in the air

abrasion procedure.

The relationship between primer type and bond strength manifested after thermocycling. Thermal stress is mainly derived from the difference between the thermal expansion coefficients of the substrate materials used<sup>35</sup>. It was reported that the coefficients of thermal expansion of MMA-TBB resin ( $89.9 \times 10^{-6}/^{\circ}\text{C}$ ) and acrylic resin ( $77.5 \times 10^{-6}/^{\circ}\text{C}$ ) were considerably greater than that of Ag-Pd-Au alloy ( $18.3 \times 10^{-6}/^{\circ}\text{C}$ ) or a resin composite material ( $37.1 \times 10^{-6}/^{\circ}\text{C}$ )<sup>36</sup>. A number of factors such as thermal and mechanical stresses, hydrolysis of resin, water diffusion into the bonded interface, and corrosion of substrate materials can affect bonding durability in the oral environment<sup>37,38</sup>. Therefore, the thermocycling test performed in the present study should be regarded as a screening tool to evaluate and compare the different bonding systems. Without clinical evaluation, it is impossible to predict the potential service period or when a restoration would fail.

To evaluate the effect of functional monomers dissolved in primers, MMA-TBB resin luting agent that contained no functional monomers was used in the present experiment. As shown in Table 2, no phosphate primers exhibited durable bonding. When compared to the phosphate primers, the bond strengths of three sulfur-containing primers (Metaltite, Alloy Primer, and Metal Primer II) were high. The greater bond strength after thermocycling was achieved with mixed solutions (Metaltite/Epicord and Metaltite/PE), in which the mean bond strength was above 27 MPa. The differences among MDP, PM, PE, and PP suggested that adhesive bonding depended upon the chemical structure linking the phosphate group with the methacrylate group, designated as the intermediate group (Fig. 1). The molecular weight (Mw) of MDP (Mw: 306) was close to that of PE (Mw: 360). PM (Mw: 210) with its shorter intermediate group was relatively hydrophilic, while PP (Mw: 460) with its longer intermediate group was hydrophobic. These findings suggested that an optimum length of the intermediate group would contribute favorably to adhesive bonding.

By means of surface-enhanced Raman scattering and infrared reflection spectroscopy, investigation findings on the bonding mechanism between Alloy Primer and pure metal substrates were as follows<sup>26</sup>. VBATDT is chemisorbed *via* sulfur atom on Au, Ag, and Cu. The adsorbed monomer is copolymerized through C=C double bonds with the other monomers to form a polymer network. This bonding mechanism may be applied to other sulfur-containing monomers including MTU-6.

Comparisons between Metaltite and V-Primer and between Metaltite/Epicord and Alloy Primer suggested that MTU-6 was superior to VBATDT

as an adhesion promoting monomer for Ag-Pd-Au alloy. Both functional monomers possessed the thione group (=S) in their molecules. Therefore, adhesive force should be influenced by the other chemical structures apart from the thione group.

The authors separated the two bottles (Metaltite and Epicord, PM, PE, or PP) immediately before priming due to shelf life concerns for the mixtures of MTU-6, phosphate monomer, and MMA. Since every primer solvent used was volatile, the concentration of the functional monomer existing on the primed substrate materials should be higher than that of the original primer liquid.

Within the limitations of the present experiment, the results obtained suggested that the addition of Epicord, PE, or PP to Metaltite improved the bond strength of resin to Ag-Pd-Au alloy, but the addition of PM was ineffective. The thermocycling test resulted in decreased bond strength in each primer group. After 5,000 thermocycles, maximum bond strengths were obtained with Metaltite/Epicord and Metaltite/PE, followed by Metaltite/PP, Alloy Primer, Metaltite, Metaltite/PM, Metal Primer II, V-Primer, and Epicord.

In conclusion, the types of functional monomers dissolved in a primer clearly influenced the adhesive bonding of resin to Ag-Pd-Au alloy. Combined use of a thiouracil monomer and a phosphate monomer significantly improved the bond strength. In light of the results obtained in this study, clinicians should hence pay attention to the types of functional monomers present when selecting an appropriate primer to fabricate resin-bonded prostheses with Ag-Pd-Au alloy.

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