# Bond Strength to Primed Ti-6Al-7Nb Alloy of Two Acrylic Resin Adhesives

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This study aimed to evaluate the bonding behavior of two acrylic resin adhesives joined to titanium-aluminum-niobium (Ti-6Al-7Nb) alloy primed with two metal conditioners. Cast Ti-6Al-7Nb alloy disks were air-abraded with alumina and bonded with six combinations of two resin adhesives (Super-Bond C&B and Multi Bond) and three surface conditions (Alloy Primer, M.L. Primer, and unprimed control). Shear bond strengths were determined both before and after 20,000 thermal cycles. The tri-*n*-butylborane initiated Super-Bond C&B resin exhibited greater bond strength than the BPO-amine initiated Multi-Bond resin. Both the Alloy Primer with a hydrophobic phosphate and the M.L. Primer with a phosphonoacetate effectively improved the 24-hour bond strength of Multi-Bond resin as well as the post-thermocycling bond strength of Super-Bond C&B resin.

Key words: Bonding, Niobium, Titanium

# INTRODUCTION

The use of titanium and titanium alloys for cast restorations, denture frameworks, and milled prostheses has increased substantially. This trend is probably attributed to the development of laboratory techniques, mould materials, casting machines, and computer-aided designing/manufacturing (CAD/CAM) systems. While majority of titanium castings do function  $successfully^{1-3)}$ , several problems associated with the clinical application of titanium have been reported. One of which is insufficient mechanical strength of titanium in the fabrication of long-span fixed partial dentures (FPDs) and large removable denture frameworks. To overcome this weakness in mechanical properties, several titanium alloys were developed as a result. Among the titanium alloys reported for medical and dental use, the titaniumaluminum-niobium (Ti-6Al-7Nb) alloy currently seems to be the most suitable material for dental castings in view of its improved mechanical properties and corrosion resistance<sup>4</sup>).

It is necessary for Ti-6Al-7Nb castings to be strongly bonded to polymeric and composite materials to avoid detachment in the humid oral environment. Bonding between resin-based materials and titanium has been improved with the use of silane<sup>5)</sup> or titanate<sup>6)</sup> couplers, and carboxylic or phosphoric acid derivatives<sup>6-12)</sup>. Surface modification techniques were also reported to be effective for bonding titanium and Ti-6Al-4V alloy<sup>13-18)</sup>. According to recent studies<sup>19-22)</sup>, both a phosphate monomer and a surface modification technique effectively bonded Ti-6Al-7Nb alloy. Although priming agents containing different acidic functional monomers are available on the market, there is limited information about their adhesive performance to Ti-6Al-7Nb alloy when used with resinbased materials.

The purpose of the current study was to evaluate the effect of two metal conditioners on the bond strength and durability of two self-curable resin adhesives joined to cast Ti-6Al-7Nb alloy.

## MATERIALS AND METHODS

A titanium alloy – which consisted of titanium, 7.0 mass% niobium, and 6.0 mass% aluminum (Ti-6Al-7Nb, T-Alloy Tough, GC Corp., Tokyo, Japan) – was selected as the adherend material. Two single-liquid metal conditioners (Alloy Primer, Kuraray Medical Co., Ltd., Tokyo, Japan, AP; M.L. Primer, Shofu Inc., Kyoto, Japan, ML) were assessed as the priming agents. Both of which were single-liquid and contained an acidic functional monomer in the solvent. The former consisted of acetone solvent with a small amount of hydrophobic phosphate (MDP), whereas the latter comprised a phosphonoacetate (6-MHPA) and acetone solvent. Two self-curing resins were used as adhesive materials. The Super-Bond C&B resin (Sun Medical Co., Ltd., Moriyama, Japan, SB) was based on methyl methacrylate (MMA), initiated by tri-*n*-butylborane (TBB), and contained 4-methacryloyloxyethyl trimellitate anhydride (4-META) as the adhesive functional monomer. The Multi-Bond resin (Tokuyama Dental Corp., Tokyo, Japan, MB) was based on MMA, initiated by benzoyl peroxide (BPO)-amine redox systems, and contained 11-methacryloyloxyundecan-1,1-dicarboxylic acid (MAC-10). Information about the materials is summarized in Table 1.

A total of 96 disk specimens, 10 mm in diameter by 2.5 mm thick, were cast from the Ti-6Al-7Nb alloy using a magnesia-based investment material (Selevest CB, Selec, Osaka, Japan) and a centrifugal casting apparatus (Ticast Super R, Selec). All disks were sanded with 600-grit silicon carbide abrasive paper followed by air abrasion (Micro Blaster MB102, Comco Inc., Burbank, IL, USA) with 50 to 70- $\mu$ m grain-sized alumina (Hi-Aluminas, Shofu Inc.) for 15 seconds. Air pressure was 0.3 MPa, and distance between orifice and metal surface was approximately 20 mm.

The disks were divided into 12 sets of eight specimens according to the combination of three surface adhesive preparations, two resins, and two thermocycling conditions. The three surface preparations were: (1) unprimed control; (2) priming with the AP material; and (3) priming with the ML material. For the control specimens, they were left unprimed after air abrasion with alumina. For the two primed groups, the AP and ML materials were separately applied to the air-abraded metal surfaces with a sponge pellet, and then air-dried.

After surface preparation, a piece of doublecoated tape with a circular hole 5 mm in diameter was positioned on each metal specimen to define the bond area. A brass ring (6 mm inside diameter, 2 mm height, and 1 mm wall thickness) was placed so as to surround the opening. The ring was filled with either SB resin or MB resin using the brush-dip technique.

Thirty minutes after preparation, the specimens were immersed in  $37^{\circ}$ C water for 24 hours, and this state was defined as 0 thermocycle. Half of the specimens (six sets of eight specimens) were tested for 24-hour shear bond strength at 0 thermocycle. The remaining six sets of eight specimens were placed in a thermocycling apparatus (Thermocycling Machine, Rika-Kogyo, Hachioji, Japan) and cycled in water between 4°C and 60°C with a one-minute dwell time per bath for 20,000 cycles. Each specimen was embedded in an acrylic resin mould and seated in a shear testing jig. Shear bond strengths were then determined with a mechanical testing machine (AGS-10kNG, Shimadzu Corp., Kyoto, Japan) at a crosshead speed of 0.5 mm/minute.

The average bond strength and standard deviation (SD) of eight specimens were calculated for each condition. The results were primarily analyzed by Levene test for evaluation of equality of variance. Either Dunnett's T3 test or a combination of Kruskal-Wallis and Mann-Whitney U tests was performed with the value of statistical significance set at p=0.05. Bond strength results of the Unprimed-SB and AP-SB combinations have already been reported in a previous study<sup>21)</sup>, and were therefore quoted from literature.

After shear bond testing, the debonded surfaces were observed through an optical microscope (8x; SZX9, Olympus Corp., Tokyo, Japan). The failure modes were classified into the following three categories - A: adhesive failure at resin-metal interface; C:

Table 1 Materials assessed

Material	Abbreviation		Lot number	Composition
Titanium alloy				
T-Alloy Tough	Ti-6Al-7Nb		270781	86.5 Ti, 7 Nb, 6 Al, mass%
Primer				
Alloy Primer	AP		0007AC	MDP, VTD, Acetone
M.L. Primer	ML		040302	6-MHPA, 10-MDDT, Acetone
Adhesive resin				
Super-Bond C&B	SB	Catalyst	GE23	Tri- <i>n</i> -butylborane (TBB)
		Monomer liquid	EF1	4-META, MMA
		Clear powder		PMMA
Multi-Bond	MB	Monomer liquid	303	MAC-10, MMA, Multi-functional monomer, Amine
		Powder	504	PMMA, BPO

MDP, 10-methacryloyloxydecyl dihydrogen phosphate; VTD, 6-(4-vinylbenzyl-*n*-propyl)amino 1,3,5-triazine-2,4-dithione; 6-MHPA, 6-methacryloyloxyhexyl phosphonoacetate; 10-MDDT, 10-methacryloyloxydecyl-6,6-dithiooctanoate; 4-META, 4methacryloyloxyethyl trimellitate anhydride; MMA, methyl methacrylate; PMMA, poly(methyl methacrylate); MAC-10, 11methacryloyloxyundecan 1,1-dicarboxylic acid; BPO, benzoyl peroxide. cohesive failure within resin material; and CA: combination of cohesive and adhesive failures.

## RESULTS

Levene test run on the shear test results did not show equality of variance for several groups. Therefore, bond strengths were further analyzed by Dunnett's T3 test. Shear bond strength results are summarized in Table 2. For SB resin, the 24-hour bond strength without thermocycling ranged from 38.1 to 39.8 MPa - and they were not statistically different from each other (category A). For MB resin, pre-thermocycling bond strength varied from 13.6 to 23.4 MPa. Although no significant differences were found between the two primed groups (category C), the control group showed a lower bond strength than the other two primed groups (category B).

Post-thermocycling bond strength of SB resin ranged from 6.0 to 21.8 MPa. No significant differences were found between the two primed groups (category E), whereas the control group showed a statistically lower bond strength than that of the two primed groups (category D). For MB resin, application of Dunnett's T3 test to the postthermocycling bond strengths divided the bond strengths into two categories: unprimed and ML (category F), and ML and AP (category G).

For each identical priming-thermocycling combination, the SB resin consistently exhibited greater bond strength than the MB resin (p<0.05). However, Kruskal-Wallis and Mann-Whitney U tests revealed that reduction in bond strength after application of thermocycling was remarkable for all primerresin combinations (p<0.05). Rate of bond strength reduction was 45.2-84.3% for SB resin, and 89.6-90.6% for MB resin.

After shear bond testing, all specimens demonstrated combination of cohesive and adhesive (CA) failures. Moreover for MB resin, a brownish discoloration after thermocycling was visibly noted.

## DISCUSSION

The purpose of this study was to evaluate the differences in bonding characteristics between a phosphate and phosphonate monomer, and between a TBBinitiated and BPO-amine initiated adhesive resin. when used to bond Ti-6Al-7Nb alloy. As shown in Table 2, the 24-hour bond strength of SB resin was not affected by priming (category A). The results suggested that the bond strength of SB resin joined to Ti-6Al-7Nb alloy was neither improved nor reduced through the use of primers within 24 hours, and that the difference in bonding characteristics among MHPA, MDP, and 4-META functional monomers was unclear within a short period. Comparison between categories B and C in Table 2 suggested that both MDP in the Alloy Primer and MHPA in the M.L. Primer enhanced MB resin's bonding to the titanium alloy. Indeed, similar results for MDP were obtained using different combinations of primers and resin materials<sup>19,21)</sup>.

The results of 24-hour bond strength (categories A, B and C) exhibited superiority of the SB resin over the MB resin. One of the possibilities of difference in bonding characteristics of the two resins is difference in type of initiation system. Due to the chemical structure of Super-Bond Catalyst, i.e., partially oxidized TBB  $(TBBO)^{23}$ , the initiator was not likely to be attacked by acidic compound both before and after the mixing of powder and liquid components. This speculation was based on the fact that butyloxy-radical or butoxybutylborooxyeither radical was formed prior to the polymerization of vinyl monomers<sup>24)</sup>. The BPO-amine redox initiated resin, on the contrary, might form a salt if an acidic monomer such as MAC-10 were added to the liquid component. The authors speculated that the formation of an undesirable salt negatively affected the proper bonding behavior between the resin and alloy.

Post-thermocycling bond strength of the SB resin (categories D and E) demonstrated the difference in bond strength between the primed groups and the unprimed control group. Since the specimens in categories D and E were thermocycled in water for

Primer	Resin	0 Thermocycle			20,000 Thermocycles						
		Median	Mean	Category	SD	Median	Mean	Category	SD	S	Reduction (%)
Unprimed	Super-Bond C&B	38.5	38.1*	А	2.3	6.3	6.0*	D	3.3	S	84.3
Alloy Primer	Super-Bond C&B	39.6	39.8*	А	2.0	21.2	$21.8^{*}$	Е	2.7	$\mathbf{S}$	45.2
M.L. Primer	Super-Bond C&B	39.3	39.6	А	2.5	19.6	19.6	Е	1.7	$\mathbf{S}$	50.5
Unprimed	Multi-Bond	13.5	13.6	В	1.6	1.0	1.3	F	0.7	S	90.4
Alloy Primer	Multi-Bond	22.0	23.4	С	6.6	2.2	2.2	G	0.4	S	90.6
M.L. Primer	Multi-Bond	16.5	16.4	С	2.3	1.6	1.7	F, G	0.5	S	89.6

Table 2 Median, mean, and standard deviation of shear bond strength in MPa

S, Significant difference between pre- and post-thermocycling bond strengths (p<0.05); SD, Standard deviation.

\* Quoted from Yanagida *et al.*  $(2003)^{21}$ . Identical category letters indicate that values are not statistically different (p>0.05).

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approximately four weeks, difference in bonding durability among the functional monomers was apparent. Specifically, MDP was superior to 4-META in terms of bonding characteristics. The results agreed with other reports concerning bonding to titanium and titanium alloys<sup>9,18,19,21</sup>). It was additionally confirmed that difference between the MDP primer and 6-MHPA primer is not apparent, hence both the AL and ML primers can be used for priming the titanium alloy when the luting agent is the SB resin. This result was in contrast with the other study<sup>25)</sup>, in which steel alloys and metal-to-metal bonded specimens were employed. It is notable, however, that the primers containing MDP maintain the best ranking in bond strength when used to titanium and other base metal alloys  $^{9,18,19,21,25)}$ .

The AP and ML primers contained both acidic and organic sulfur compounds. The former is substantially effective for bonding base metal elements and the latter for noble metals. A synergistic effect of an acidic and sulfur compound (MEPS, Metal Primer II, GC Corp.) has been confirmed for bonding Ti-6Al-7Nb alloy<sup>26)</sup>. This information is useful for clinicians, because different types of alloy are frequently bonded in the clinic.

Concerning the post-thermocycling bond strength results of MB resin (categories F and G), they exhibited the poor bonding characteristics of MB resin rather than the effect of the two primers. As revealed from statistical analysis, SB resin showed greater bond strength than MB resin in all the six conditions in this study. The results indicated that the use of SB resin combined with either AP or ML material was suitable for bonding the titanium alloy within the limitations of the current experiment.

Thermal cycling significantly reduced the bond strength of all groups. Clinicians should therefore keep in mind that there is a limitation to the bonding durability of unfilled acrylic resins, especially when used in bulky material structures (such as provisional splinting of anterior dentition) and repairing of denture base materials.

Color stability is one of the prerequisites for resin-based materials. The MB resin exhibited considerable discoloration after undergoing thermocycling in water. Difference in color stability between SB resin and MB resin has already been reported<sup>27)</sup>. Formation of a salt between an amine reducing agent and an aromatic compound or a carboxylic monomer (MAC-10) may negatively affect the color stability of resin material, especially in the post-polymerization condition. Although color of the polymerized resin is not detectable through the metallic adherend, it is beneficial for clinicians to use a resin material with long-term color stability for applications in visible areas and anterior dentition.

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