

Influence of three carboxylic primers on bonding of an adhesive resin to titanium

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Purpose: The purpose of this study was to evaluate the influence of three primers on bonding to titanium of an adhesive luting agent.

Materials and Methods: The luting agent consisted of 4-methacryloyloxyethyl trimellitate anhydride (4-META), methyl methacrylate (MMA), and tri-*n*-butylborane (TBB) initiator. Forty pairs of disk specimens were prepared from 99.9% titanium metal, air-abraded with 50 μm grain size alumina, primed with one of the three carboxylic primers (Acryl Bond, MR Bond, and Primer B), and bonded with the 4-META/MMA-TBB resin along with an unprimed control. Shear bond strength was determined after 24 hours of immersion in 37°C water, and after 100,000 cycles of thermocycling at 4°C and 60°C.

Results: Bond strength was negatively affected by thermocycling and by the use of each of the three carboxylic primers. After 100,000 thermocycles, the average bond strengths were categorized statistically into three levels ($p < 0.05$): a higher group (unprimed, 37.0 MPa), medium groups (Acryl Bond, 24.4 MPa; and MR Bond, 25.5 MPa), and a lower group (Primer B, 17.8 MPa).

Conclusion: Each of the three carboxylic primers reduced the bonding between 4-META/MMA-TBB resin and titanium metal. (*Int Chin J Dent* 2002; 2: 116-120.)

Clinical Significance: There are some cases where primer should not be used. Clinicians need be informed of the longevity of resin-bonded titanium restorations.

Key words: bonding, carboxylic acid, thermocycling, titanium.

INTRODUCTION

Titanium is being used in the fabrication of resin-bonded fixed partial dentures,¹ resin composite veneered crowns,² and implant supported fixed restorations.³ Durable bonding between the resin and the titanium framework is required for these restorations to withstand the oral environment. Various functional monomers have recently been developed for use as primers or as adhesive luting agents.^{4,5}

Previous study has suggested that carboxylic monomers improve the durability of the bond between resin-based luting material and 99.9% pure titanium metal.^{6,7} This bonding durability is improved further when a phosphoric or a thiophosphoric primer is used, even when the luting agent contains carboxylic

monomers.^{8,9} However, it is still unclear whether or not the carboxylic primers assist bonding when the luting agent contains another functional monomer. The relationships between different types of functional monomers have not been clarified with regard to titanium bonding.

The purpose of this study was to evaluate the effect of primers containing a carboxylic monomer on bond strength between an adhesive luting agent containing 4-methacryloyloxyethyl trimellitate anhydride (4-META) and pure titanium metal, after thermocyclic stressing.

MATERIALS AND METHODS

The primers and the luting agent tested are summarized in Table 1. Two sizes of machine-milled disks (10 mm diameter x 2 mm thick, and 6 mm diameter x 2 mm thick) of 99.9% titanium metal (0.06% O, 0.0075% Fe, and 0.0075% C; Furuuchi Chemical Ind., Tokyo, Japan) were used.

Table 1. Primers and luting agent used.

Trade name	Manufacturer	Lot number	Component
<u>Primer</u>			
Acryl Bond	Shofu Inc., Kyoto, Japan	019213	4-AET in solvent
MR Bond	Tokuyama Soda Co., Ltd., Tokyo, Japan	002	MAC 10 in solvent
Primer B	Bisco Inc., Itasca IL, USA	129091	BPDM in solvent
<u>Luting agent</u>			
Super-Bond C&B	Sun Medical Co., Moriyama, Japan	00501	4-META, MMA, PMMA, TBB

4-AET: 4-acryloyloxyethyl trimellitate, MAC 10: 11-methacryloyloxyundecan-1,1-dicarboxylic acid, BPDM: adduct of 2-hydroxyethyl methacrylate and 3,4,4',5'-biphenyl tetracarboxylic anhydride, 4-META: 4-methacryloyloxyethyl trimellitate anhydride, MMA: methyl methacrylate, PMMA: poly(methyl methacrylate), TBB: tri-*n*-butylborane.

After each disk was ground using 600 grit silicon-carbide paper, the surfaces were sand-blasted with 50 μm alumina under 0.5 MPa pressure for 10 s (Pen-Blaster; Shofu Inc., Kyoto, Japan). A piece of 50- μm -thick masking tape with a 5 mm diameter circular hole was placed on the 10 mm diameter disk to determine the thickness of the adhesive resin and the adhesive area. One of the three primers was brushed onto the titanium specimens, the luting agent was applied, and the 10 mm and 6 mm diameter specimens were held together using finger pressure.

Following storage at room temperature for 1 hour after bonding, the specimens were immersed in water at 37°C for 24 hours (thermocycle 0). The specimens were then immersed in 4°C and 60°C water alternately for 1 minute periods for 100,000 cycles using a thermocycling machine (Rika Kogyo, Hachioji, Japan).

Shear bond strength was determined by means of a universal testing device (AGS-10kNG; Shimadzu Corp., Kyoto, Japan) with a cross-head speed of 0.5 mm/minute, following dental materials guidance on the testing of adhesion to tooth structure (ISO/TR11405). The titanium surfaces of the debonded specimens were examined with an optical microscope (x 4, SMZ-10; Nikon Corp., Tokyo, Japan) to evaluate the conditions of failure.

The mean and standard deviation of the bond strength for the five specimens were calculated for each group. All data were analyzed by analysis of variance (ANOVA), and the mean values were compared using Duncan's new multiple range test, with $p < 0.05$ considered significant.

RESULTS

Two factor ANOVA demonstrated that bond strength was significantly influenced ($p < 0.05$) by thermocycling ($F = 81.5$), the type of primer used ($F = 21.3$), and thermocycling/primer interaction ($F = 9.7$). Mean bond strength, standard deviation, and the results of the Duncan's test are presented in Table 2.

Table 2. Shear bond strength results.

Group	Thermocycle 0			100,000 cycles		
	Bond strength (MPa)	Mean	SD	Category	Mean	SD
Unprimed	39.3	1.5	d	37.0	1.0	c d
Acryl Bond	32.8	5.5	c	24.4	2.9	b
MR Bond	35.1	3.5	c d	25.5	3.9	b
Primer B	36.3	4.2	c d	17.8	2.2	a

Identical letters indicate that the values are not statistically different ($n = 5$, $p > 0.05$). SD: Standard deviation calculated with degree of freedom.

Table 3. Type of bond failure.

Group	Failure mode	Thermocycle 0		100,000 cycles	
		AC	A	AC	A
Unprimed		5	0	4	1
Acryl Bond		5	0	2	3
MR Bond		5	0	0	5
Primer B		5	0	0	5

A: adhesive failure at resin-metal interface, AC: combined mode involving adhesive failure and cohesive failure within resin.

After 100,000 cycles, the bond strengths were categorized into three levels, a higher group (unprimed), medium groups (Acryl Bond and MR Bond), and a lower group (Primer B). The data of our previous study⁸ was used as the positive control (unprimed). Bond strength ranged from 17.8 to 39.3 MPa. The difference in bond strength between the unprimed group and the Acryl Bond group was significant, but no significant difference was found among the other groups at thermocycle 0. The bond strength of the unprimed group was maintained for up to 100,000 thermocycles. After thermocycling, the Acryl Bond group, the MR Bond group, and the Primer B group exhibited a significantly decreased bond strength.

As shown in Table 3, all of the specimen surfaces contained mixed adhesive and cohesive modes before thermocycling. One (unprimed), three (Acryl Bond) and five (MR Bond and Primer B) specimens exhibited substantial adhesive failure after 100,000 thermocycles.

DISCUSSION

This study investigated the role of carboxylic functional monomers and their propriety in titanium bond durability. The surface of pure titanium metal is coated with titanium oxide after sand-blasting, allowing aluminum oxide particles to become partially embedded.¹⁰ The functional monomers used consist of a carboxylic group with a methacryloyl or an acryloyl group. Carboxylic acid or the carboxylic acid anhydride group of 4-META is considered to interact with the metal oxides created on base metal alloys in the atmospheric environment.^{11,12}

The present findings suggest that bonding durability is affected by the primer that is applied to the titanium surface. A hypothetical explanation is that no competitive relationship exists between 4-META and the other carboxylic monomers. The carboxylic group of 4-META has a greater affinity with the titanium surface than MAC 10, BPDm, and 4-AET. If a less effective carboxylic monomer is used to cover the titanium surface, successful interaction between the 4-META and the original surface is less likely. The durability may be related to the primer solvent or to the TBB initiator existing at the resin-metal interface during the setting reaction.¹³ Further study is needed to confirm this hypothesis.

In contrast to these carboxylic primers, phosphoric and thiophosphoric primers significantly improve the durability of 4-META/MMA-TBB resin bonds.^{5,8} Therefore, when selecting a primer in combination with a luting agent, the type of functional monomer to be used should be considered.

CONCLUSION

When titanium metal is bonded with 4-META/MMA-TBB resin, the Acryl Bond, MR Bond, and Primer B carboxylic primers will not be needed.

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