

Comparative evaluation of metal priming agents applied for bonding of magnetic stainless steel with acrylic repair resin

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Abstract: The purpose of this study was to evaluate the effect of acidic priming agents on adhesive bonding to SUS XM27 stainless steel. Disk steel specimens were primed with one of the following materials; Acryl Bond, All-Bond 2 Primer B, Alloy Primer, Estenia Opaque Primer, Eye Sight Opaque Primer, Metal Primer II, M.L. Primer, MR Bond, and Super-Bond Liquid. The specimens were then bonded with an acrylic resin designed for denture repair (Repairsin), and bond strengths were determined. Unprimed specimen was used as control. The average bond strengths before thermocycling varied from 21.3 to 51.0 MPa, whereas post-thermocycling bond strengths ranged from 3.0 to 37.0 MPa. Of the nine priming agents, the Acryl Bond, All-Bond 2 Primer B, Estenia Opaque Primer, and MR Bond materials showed significantly higher bond strength after application of thermocycling. Within the limitation of the current experimental settings, it can be concluded that the use of the four acidic priming agents is recommended for bonding SUS XM27 stainless steel with Repairsin self-polymerizing repair material. (*J. Oral Sci.* 49, 277-281, 2007)

Keywords: bonding; magnetic attachment; primer; stainless steel.

Introduction

An increasing number of magnetic attachment systems

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have been introduced for retaining prostheses and removable dentures (1-12). Magnetic stainless steels with different chromium content are currently used for the cap, yoke, and keeper components (2,5). The keeper is either cast-bonded or adhesively bonded to the dowel posts, and then seated into the root canal as a root cap. The magnetic attachment is placed inside the denture base with auto-polymerizing resin.

The magnetic attachment and the denture base material should be strongly bonded to avoid detachment of the magnetic assembly from the denture base. Both mechanical and chemical methods are used for retaining magnetic attachments within the denture bases. The mechanical method involves simple carving of undercuts surrounding the attachments. The chemical method requires application of adhesive agents to the attachments. In the latter, adhesive bonding of magnetic attachment with polymer material is substantially the same situation as bonding of stainless steel with adhesive resin because the magnetic attachment is covered with steel.

Although there are various adhesive systems for bonding stainless steel and related dental alloys (13-19), limited information is available about various primers, especially related to the chemical ingredients and functional monomers. The purpose of this study was to evaluate the effect of acidic priming agents on the bond strength and durability of an acrylic repair resin bonded to stainless steel.

Materials and Methods

SUS XM27 (XM27) stainless steel (Hitachi Metals Ltd., Tokyo, Japan) applied for dental magnetic attachment systems was selected as the adherend material. Nine acidic priming agents were used; Acryl Bond (Shofu Inc., Kyoto, Japan), All-Bond 2 Primer B (Bisco Inc., Itasca, IL, USA), Alloy Primer (Kuraray Medical Inc., Tokyo, Japan), Estenia Opaque Primer (Kuraray Medical Inc.), Eye Sight Opaque Primer (Kanebo Corp., Tokyo, Japan), Metal Primer II (GC

Corp., Tokyo, Japan), M.L. Primer (Shofu Inc.), MR Bond (Tokuyama Dental Corp., Tokyo, Japan), and Super-Bond Liquid (Sun Medical Co., Ltd., Moriyama, Japan). All primers consisted of a single liquid and contained at least one adhesive functional monomer in the solvent. A self-polymerizing resin generally used for denture repair (Repairsin, GC Corp.) was selected as the luting material. Information about the materials used is summarized in Table 1.

A total of 160 steel disk pairs (10 and 8 mm in diameter and 2.5 mm in thickness) were prepared, ground with 1,500 grit silicon-carbide abrasive paper, and ultrasonically cleaned in acetone. The 160 pairs were divided into 10 sets (nine primers and an unprimed control) of 16 specimen pairs each. A piece of tape of 50- μ m thickness and a circular hole of 5-mm diameter, was attached to the 10-mm disk specimen surface to define the bonding area. Nine sets consisting of 16 pairs each were primed with one of the nine primers, whereas the remaining 16 pairs were left unprimed and considered as the controls. Each pair of 10-mm- and 8-mm-diameter specimens was bonded together with the Repairsin material using a brush-dip technique. A 5.0 N consistent load was applied to the specimens until the resin material had set.

After 30 minutes, the bonded specimens were stored in 37°C distilled water for 24 h. This state was defined as 0 thermocycle. Half of the specimens (eight specimens each in 10 priming conditions) were tested at this stage. The remaining half of the specimens (10 sets of eight specimens)

were subsequently thermocycled between 5°C and 55°C in a water bath for 20,000 cycles with a dwell time of 60 s per bath (Thermal Shock Tester TTS-1 LM, Thomas Kagaku Co., Ltd., Tokyo, Japan). Each specimen was seated in a shear test jig (ISO TS 11405) (20), and shear bond strength was determined with a mechanical testing device (Type 5567, Instron Corp., Canton, MA, USA) at a crosshead speed of 0.5 mm/min. The surfaces debonded after shear bond testing were observed through an optical microscope (8 \times ; SZX9, Olympus Corp., Tokyo, Japan).

For each group of eight replications, the mean shear bond strength, standard deviation, and median value were calculated. The results were primarily analyzed by Levene test for evaluation of equality of variance (SPSS 14.0.1J, SPSS Japan Inc., Tokyo, Japan). When the results of the Levene test did not show homoscedasticity in at least one category, Kruskal-Wallis test was performed separately for both pre- and post-thermocycling groups to evaluate the difference among variations of priming agents at $\alpha=0.05$. On the basis of the results of Kruskal-Wallis test, Steel-Dwass multiple comparison intervals (KyPlot 4.0, KyensLab Inc., Tokyo, Japan) were further applied to compare the difference among the 10 priming conditions for each of the 0- and 20,000-thermocycling conditions with the value of statistical significance set at $\alpha=0.05$. Difference between the bond strengths before and after thermocycling within an identical priming condition was analyzed with Mann-Whitney U test at $\alpha=0.05$.

Table 1 Materials assessed

Material/Trade name	Manufacturer	Lot number	Composition
Stainless steel			
SUS XM27	Hitachi Metals Ltd., Tokyo, Japan		Fe 72, Cr 26, Others 2, mass%
Priming agents			
Acryl Bond	Shofu Inc., Kyoto, Japan	050322	4-AETA, 2-HEMA, MMA
All-Bond 2 Primer B	Bisco Inc., Itasca, IL, USA	030009666	BPDM, Solvent
Alloy Primer	Kuraray Medical Inc., Tokyo, Japan	0214AA	MDP, VTD, Acetone
Estenia Opaque Primer	Kuraray Medical Inc.	0140AA	MDP, Solvent
Eye Sight Opaque Primer	Kanebo Corp., Tokyo, Japan	R37	MP, Solvent
Metal Primer II	GC Corp., Tokyo, Japan	0211051	MEPS, MMA
M.L. Primer	Shofu Inc.	040302	6-MHPA, 10-MDDT, Acetone
MR Bond	Tokuyama Dental Corp., Tokyo, Japan	01353	MAC-10, MMA, MMA-EMA co-polymer
Super-Bond Liquid	Sun Medical Co., Ltd., Moriyama, Japan	GG2	4-META, MMA
Self-polymerizing resin			
Repairsin	GC Corp.	0502018 0501182	Powder; Methacrylic acid ester co-polymer Liquid; Methacrylic acid ester

4-AETA, 4-acryloyloxyethyl trimellitate anhydride; 2-HEMA, 2-hydroxyethyl methacrylate; MMA, methyl methacrylate; BPDM, adduct of 2-hydroxyethyl methacrylate and 3,4,4',5'-biphenyl tetracarboxylic anhydride; MDP, 10-methacryloyloxydecyl dihydrogen phosphate; VTD, 6-(4-vinylbenzyl-*n*-propyl) amino-1,3,5-triazine-2,4-dithione -dithiol tautomer; MP, methacrylate-phosphate; MEPS, methacryloyloxyalkyl thiophosphate derivative; 6-MHPA, 6-methacryloyloxyhexyl phosphonoacetate; 10-MDDT, 10-methacryloyloxydecyl 6,8-dithiooctanoate; MAC-10, 11-methacryloyloxyundecan 1,1-dicarboxylic acid; EMA, ethyl methacrylate; 4-META, 4-methacryloyloxyethyl trimellitate anhydride.

Table 2 Shear bond strength (MPa) to SUS XM27 steel of the Repairsin material with/without priming

Priming agent	0 thermocycle				20,000 thermocycles				M-W	Post-TC/pre-TC
	Mean	SD	Median	Category	Mean	SD	Median	Category		
Acryl Bond	49.9	1.5	49.4	a, b	37.0	3.6	36.5	d	Significant	74.1%
All-Bond 2 Primer B	51.0	0.8	51.3	a	35.3	3.7	34.2	d, e	Significant	69.2
Alloy Primer	48.8	1.6	49.2	a, b	28.4	3.0	26.6	e, f	Significant	58.2
Estenia Opaque Primer	49.4	1.3	49.6	a, b	32.1	4.1	30.7	d, e, f	Significant	65.0
Eye Sight Opaque Primer	49.2	1.1	49.5	a, b	19.1	2.6	19.3	g	Significant	38.8
Metal Primer II	48.1	1.3	48.0	b	24.8	4.0	24.6	f, g	Significant	51.6
M.L. Primer	48.8	1.4	48.3	a, b	20.1	1.5	20.1	g	Significant	41.2
MR Bond	50.3	2.3	49.4	a, b	26.7	6.8	26.2	d, e, f, g	Significant	53.1
Super-Bond Liquid	49.4	1.5	49.5	a, b	27.7	4.1	28.7	e, f, g	Significant	56.1
None (Control)	21.3	2.7	21.3	c	3.0	2.6	2.8	h	Significant	14.1

SD, Standard deviation. Category, Identical lower case letters indicate that they are not statistically different (Steel-Dwass test, $P > 0.05$). M-W, The term 'Significant' indicates that the difference between the pre- and post-thermocycling bond strengths is significant (Mann-Whitney U test, $P < 0.05$). TC, thermocycling.

Results

The results of the Kruskal-Wallis test showed that χ^2 values were 36.399 for the pre-thermocycling group and 61.906 for the post-thermocycling group. The P -values were less than 0.05 for both pre- and post-thermocycling bond strengths. Both the pre- and post-thermocycling results, therefore, were separately analyzed with the Steel-Dwass multiple comparisons. Table 2 summarizes the results of the shear bond testing. The mean bond strength before thermocycling varied from 21.3 to 51.0 MPa, whereas the post-thermocycling bond strength ranged from 3.0 to 37.0 MPa. Mann-Whitney U test run on the bond strengths revealed that there was a statistically significant reduction in bond strength after thermocycling for all conditions. The highest percentage value of post-thermocycling bond strength by pre-thermocycling bond strength was recorded for the Acryl Bond group (74.1%), while the lowest value was recorded for the control group (14.1%).

Among the nine primed groups, eight groups except for the Metal Primer II group showed the highest pre-thermocycling bond strength (category a). Additionally, bond strength of the eight groups, excepting the All-Bond 2 Primer B group, exhibited the second highest bond strength (category b). Pre-thermocycling bond strength of the All-Bond 2 Primer B group (category a) was statistically higher than that of the Metal Primer II group (category b). The unprimed group (control) resulted in the lowest bond strength before thermocycling (category c).

Bond strength after thermocycling was statistically categorized into five groups. Four groups primed with the Acryl Bond, All-Bond 2 Primer B, Estenia Opaque Primer, and MR Bond materials showed the highest bond strength after application of thermocycling (category d). Five

Table 3 Failure mode after the shear bond testing

Priming agent	0 thermocycle			20,000 thermocycles			
	Failure mode	A	AC	C	A	AC	C
Acryl Bond		6	2	0	8	0	0
All-Bond 2 Primer B		6	2	0	8	0	0
Alloy Primer		0	8	0	8	0	0
Estenia Opaque Primer		0	8	0	8	0	0
Eye Sight Opaque Primer		8	0	0	8	0	0
Metal Primer II		0	8	0	8	0	0
M.L. Primer		0	8	0	8	0	0
MR Bond		0	8	0	8	0	0
Super-Bond Liquid		4	4	0	8	0	0
None (Control)		8	0	0	8	0	0

A, Adhesive failure at the stainless steel interface;

C, Cohesive failure within the resin material;

AC, Combination of adhesive and cohesive failures.

groups, All-Bond 2 Primer B, Alloy Primer, Estenia Opaque Primer, MR Bond, and Super-Bond Liquid came second (category e), followed by the third group (category f, Alloy Primer, Estenia Opaque Primer, Metal Primer II, MR Bond, and Super-Bond Liquid), and then by the fourth group (category g, Eye Sight Opaque Primer, Metal Primer II, M.L. Primer, MR Bond, and Super-Bond Liquid). The unprimed group (control) again resulted in the lowest bond strength after thermocycling (category h).

Observation of the debonded surfaces revealed that multiple specimens showed combination of adhesive and cohesive failures before thermocycling. However, all specimens exhibited adhesive failure between the metal surface and the resin material after 20,000 thermocycles (Table 3).

Discussion

This study examined the effects of nine acidic priming agents on adhesive bonding of XM27 stainless steel. This steel was selected as the substrate material because it is used as one of the parts of a magnetic attachment system (Hicorex, Hitachi Metals Ltd.), and the parts are usually bonded with an acrylic resin. A self-polymerizing acrylic resin (Repairsin) was selected as the luting material because this material is applied for repairing fractured denture bases as well as bonding metallic structures with denture base resin. Before application of priming agents, the substrate steel surfaces were ground with abrasive paper. In order to evaluate the single effect of chemical bonding characteristics of the primers, mechanical retention systems including air-borne particle abrasion (19) were not employed.

The pre-thermocycling bond strength of the primed groups varied from 48.1 MPa to 51.0 MPa. These values were greater than those of a previously reported research (17), in which a tri-*n*-butylborane (TBB) initiated resin was used as the luting agent. Unlike Repairsin material, the TBB-initiated resin contains approximately 8% TBB in the monomer liquid composition, and the unreacted TBB may play a role of a plasticizer in the hardened acrylic material. It is known that the more the amount of the plasticizer, the lower the strength of the polymerized material. As shown in Table 3, many of the debonded specimens exhibited adhesive-cohesive failure before application of thermal stress. It is therefore reasonable to consider that the difference in pre-thermocycling bond strength values between the previous report (17) and the current study is derived from factors related to the acidic primers and resin luting materials.

This study used a peroxide-amine redox-initiated acrylic resin as the luting agent. This material (Repairsin) is frequently used for placement of magnetic assemblies in the proper position of dentures. Post-thermocycling bond strength results demonstrated the effectiveness of Acryl Bond, All-Bond 2 Primer B, Estenia Opaque Primer, and MR Bond materials (category d), followed by the Alloy Primer and Super-Bond Liquid materials (category e). Of these, two materials (Estenia Opaque Primer and Alloy Primer) contain a hydrophobic phosphate monomer (MDP). The author speculates that the durable bond strength to XM27 steel is derived from interaction between the dihydrogen phosphate in the MDP and the passive chromium oxide film on the XM27 steel (21). Effectiveness of the MDP monomer in bonding stainless steel has already been reported (13,14,17,18). The results of the current study agree with those findings, although the composition of luting agents and adherends were not identical. In addition,

this study demonstrated the effectiveness of Acryl Bond, All-Bond 2 Primer B, MR Bond, and Super-Bond Liquid materials, all of which contain a hydrophobic carboxylic monomer. This result was different from a previous study (17). One possible explanation may be derived from the probable occurrence of a reversible reaction between the carboxylic monomers and amine reducing agents, i.e., formation and dissociation of an acid-base complex. If the reversible reaction activity was higher for the carboxylic acid-base complex than for the phosphoric acid-base complex, the inhibition effect on the propagation reaction of a peroxide-amine redox initiator system would be lower for the carboxylic compounds. This discussion, however, reflects the author's speculations for the difference in results between these studies.

Overall, the Acryl Bond, All-Bond 2 Primer B, Estenia Opaque Primer, and MR Bond materials exhibited statistically identical and superior bond strengths, within the limitation of the current experimental settings. Although there was remarkable reduction in bond strength after thermocycling, it can be concluded that the use of the four acidic priming agents is recommended for bonding XM27 stainless steel with Repairsin self-polymerizing repair material.

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