Shear bond strength between autopolymerizing acrylic resin and Co-Cr alloy using different primers

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This study aimed to examine the shear bond strength between cobalt chromium alloy and autopolymerizing acrylic resin using experimental primers containing 5, 10, and 15 wt% of 4-methacryloxyethyl trimellitic anhydride or 1, 2, and 3 wt% of 3-methacryloxypropyl-trimethoxysilane comparison to 5 commercial primers (ML primers, Alloy primer, Metal/Zirconia primer, Monobond S, and Monobond plus). Sixty alloy specimens were sandblasted and treated with each primer before bonded with an acrylic resin. The control group was not primed. The shear bond strengths were tested and statistically compared. Specimens treated with commercial primers significantly increased the shear bond strength of acrylic resin to cobalt chromium alloy ($p < 0.05$). The highest shear bond strength was found in the Alloy primer group. Among experimental group, using 10 wt% of 4-methacryloxyethyl trimellitic anhydride or 2 wt% of 3-methacryloxypropyltrimethoxysilane enhanced highest shear bond strength. The experimental and commercial primers in this study all improved bonding of acrylic resin to cobalt chromium alloy.

Keywords: Primers, PMMA, Co-Cr alloy, Shear bond strength

INTRODUCTION

In prosthetic and restorative dentistry, high bond strength between material phases is necessary. The commonly used metal alloys for removable partial dentures (RPD) are cobalt-chromium alloy (Co-Cr alloy). An acrylic denture base is attached to the Co-Cr alloy by mechanical interlocking such as retention beads¹. The absence of chemical bonding between the poly(methyl methacrylate) (PMMA) denture base and the Co-Cr metal framework is a significant clinical problem in removable partial prosthodontics, leading to bond failure and microleakage. So optimizing shear bond strength between acrylic resin and the metal framework is essential for the success of the prosthesis. It was reported that a chemical etching method with Silicoater MD and Kevloc Systems improved retention between PMMA resin and alloys². These systems used to enhance chemical bonding include silanes as a coupling agent on a pyrolytically treated metal surface. However, these techniques are technique sensitive and require special devices. The silane most commonly applied in dental laboratories and chair-side is a monofunctional-3-methacryloxypropyltrimethoxysilane (3-MPS). The 3-MPS is known to promote the adhesion through chemical and physical coupling between metal-composites, ceramic-composites, and composites, particularly containing methacrylate groups.

The application of 4-methacryloxyethyl trimellitic

anhydride (4-META) has been promoted as a chemical bonding method for enhancing the bond strength between metal and acrylic resin³. Like carboxylate groups, its acid anhydride moiety should interact with tooth or metal substrates, and its methacrylate moiety can polymerize and copolymerize with monomeric composite resin. The previous studies reported that 4-META adhesive monomer adhered strongly to dental alloy and acrylic resin⁴⁻⁶.

Nowadays, various primers that are developed aim to bond to the metal surface⁷⁻¹⁰, but there is no report on the comparison of the bond strength among Co-Cr alloy and PMMA using different functional monomers such as 3-MPS, 4-META, MDP, and 6-MHPA. The amount of 4-META and 3-MPS in commercial products in the dental market varied, less than 10% of 4-META and 2.5% of 3-MPS^{11,12}. However, the optimum concentration of 4-META and the 3-MPS in bonding of acrylic resin to Co-Cr alloy is unclear.

Regardless of the improvement of bond strength between Co-Cr alloy and PMMA or for the repairing, satisfactory repair must have adequate strength. There are many available primers in dental market but there is no report on the comparison of the bond strength between Co-Cr alloy and PMMA using 3-MPS, 4-META, and these commercial primers.

So, the purpose of this study was to determine the shear bond strength of autopolymerized PMMA to Co-Cr alloy when treated with various primers, including experimental primers containing 5, 10, and 15 wt% of 4-META in acetone, 1, 2, 3 wt% of 3-MPS in acetone, ML

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primes, Alloy primer, Metal/Zirconia primer, Monobond S, and Monobond plus primer.

MATERIALS AND METHODS

Primer preparation

All primers used in this study are shown in Table 1. According to the pilot study, the concentration of 1%, 2% and 3% of 3-MPS and 5%, 10% and 15% of 4-META were selected to evaluate in this study. 3-MPS was dissolved in acetone to obtain 1%, 2% and 3% silane concentration by weight. The pH was adjusted to 4.5 with 1 M acetic acid. 4-META was prepared in acetone solvent at 5%, 10% and 15% concentration by weight. All prepared primers were allowed to stabilize for 24 h at room temperature. The commercial primers that used in this study were ML primer, Alloy primer, Metal/Zirconia primer, Monobond S, and Monobond plus. Non-primed samples served as the control.

Preparation of cast metal discs

Rectangular wax patterns (10.0×10.0×2.5 mm) were casted with Cobalt-Chrome PD alloys (BEGO, Wilhelm-Herbst-Strabe I, Bremen, Germany) according to the manufacturer's instructions. Each casting specimen was then embedded in an autopolymerized acrylic resin block ensuring that one surface of the alloy disc remained uncovered for bonding procedures. The casting surfaces were polished with emery paper No. 240 to 600 under water and sandblasted with 50 μ m grain-sized aluminum oxide for 10 s, using a grit blaster (Modular Blasting Line, Dentalform, Torino, Italy). The emission pressure was 0.48 MPa with the nozzle

positioned approximately 5 mm from the surface of the metal adherent. The grit-blasted cast disks were washed with steam and then immersed in distilled water for 10 min with an ultrasonic cleanser (Vibraclean 112 model 300, CA, USA). A piece of double-coated tape (50 μ m in thickness) with a circular hole of 5 mm in diameter was placed on the specimen to define the bonding area. The specimens were divided into 12 groups with 5 specimens per group according to the primer used. In the control groups, the sandblasted surfaces were bonded without using any primer. For the experimental groups, each primer was applied directly to the Co-Cr disc alloy with a brush and allowed to react for 30 min.

A silicone mold with a cylindrical hole of 5 mm in diameter and 5 mm in height was placed on the metal surface. An autopolymerizing acrylic resin (Ortho-Jet®, Lang Dental MFG.Co.,Inc., IL, USA, Lot No. 1380-4006) was mixed according to the manufacturers' instructions, until it reached a dough consistency and packed into the silicone mold. After complete curing, which took 30 min, the specimens were carefully removed from the silicone mold and immersed in water at 37°C for 24 h before shear bond strength testing.

Shear bond strength testing

The specimens were mounted in a universal testing machine (Instron model 5566, Instron Corporation, Buckinghamshire, UK) and the shear bond strength was evaluated at a crosshead speed of 0.5 mm/min¹³. The apparatus consisted of parallel guides, a tube holder, and a load cell of 1 KN. The apparatus ensured that the tube was perpendicular to the sample surface (Fig. 1). The blade started to shear 2 mm above the metal

Table 1 Materials used for this study

Primers	Functional monomers	Manufacturers
Experimental 3-MPS	γ -methacryloxypropyltrimethoxy silane (1, 2, 3 wt%) in acetone	Evonik Degussa, Marl, Germany (Lot No. 2390612802)
Experimental 4-META	4-methacryloxyethyl trimellitate anhydride (5, 10, 15 wt%) in acetone	Sun Medical Co.Ltd., Tokyo, Japan (Lot No. T1003)
ML primer	6-MHPA Phosphonate and thioctic acid in acetone	Shofu Inc., Kyoto, Japan (Lot No. 110835)
Alloy primer	VBATDT and 10-MDP in acetone	Kuraray Medical Co., Ltd., Osaka, Japan (Lot No. 00325A)
Metal/Zirconia primer	Phosphonic acid acrylate in tert-Butyl alcohol	Ivoclar Vivaden, Schaan, Liechtenstein (Lot No. K11988)
Monobond S	3-MPS in ethanol	Ivoclar Vivadent, Schaan, Liechtenstein (Lot No. K 06475)
Monobond plus	Silane methacrylate, phosphoric acid ester, sulphide methacrylate, ethanol	Ivoclar Vivadent, Schaan, Liechtenstein (Lot No. M24811)

10-MDP, 10-methacryloxydecyl dihydrogenphosphate

6-MHPA, 6-methacryloxyhexyl-phosphonoacetate

VBATDT, 6-(4-vinylbenzyl-n-propyl)amine-1,3,5-triazine-2,-4-dithiol

on the sample. The force at which the bond failed was recorded, and then the bond strength was calculated in Megapascals (MPa).

The site of bond failure and the surface morphology of the debonded specimens were examined with a scanning electron microscope (SEM, Model JSM-5410 LV, JEOL LTD., Tokyo, Japan). Fracture surfaces were examined under optical microscope (Eclipse G400 POL;

Nikon, Tokyo, Japan) at $\times 20$ magnification. The mode of failure was classified as “adhesive” when the remaining material on the alloy surface was less than 25%, “cohesive” when it was more than 75%, and “combination” when it ranged between 25%–75%¹⁴.

Statistical analysis

The recorded shear bond strength values were analyzed. Means and standard deviation were computed and the interaction between primer and substrate were evaluated by one-way ANOVA. When a significant difference was noted, the multiple comparison test using Tukey HSD was used to determine the pair differences. The statistical differences were evaluated at a significance level of 0.05.

RESULTS

Table 2 summarizes the means and standard deviations (SD) of the shear bond strength between acrylic resins and Co-Cr alloy using 5, 10, 15 wt% of 4-META, 1, 2, and 3 wt% of 3-MPS, Alloy primer, ML primer, Metal/Zirconia primer, Monobond S, and Monobond Plus. The one-way ANOVA results are summarized in Table 3.

Fig. 1 Shear test apparatus (d=diameter).

Table 2 Mean shear bond strengths (MPa) and standard deviation (SD) of the control and all experimental groups

Group	Primer	Shear bond strengths
Group 1	Without primer	5.05±0.19 ^b
Group 2	5 wt% of 4-META	10.84±0.14 ^d
Group 3	10 wt% of 4-META	11.71±0.18 ^c
Group 4	15 wt% of 4-META	10.64±0.21 ^d
Group 5	1 wt% of 3-MPS	8.66±0.18 ^g
Group 6	2 wt% of 3-MPS	10.19±0.24 ^e
Group 7	3 wt% of 3-MPS	9.54±0.20 ^f
Group 8	ML primer	12.01±0.14 ^c
Group 9	Alloy primer	15.08±0.13 ^a
Group 10	Metal/Zirconia primer	10.04±0.15 ^e
Group 11	Monobond S	8.77±0.17 ^g
Group 12	Monobond Plus	13.87±0.24 ^b

Different superscript letters indicate significant difference at 95% confident.

Table 3 Summary of one-way ANOVA

Source of variation	Degree of freedom	Sum of Squares	Mean Square	F-value	P-value
Between Groups	11	367.32	33.39	975.80	0.00
Within Groups	48	1.64	0.03		
Total	59	368.96

Fig. 2 Optical microscope image illustrating adhesive failure.

The results indicated that using experimental and commercial primers significantly improved the shear bond strengths of acrylic resin to the sandblasted metal surface compared with the control group (non-primed group). No significant differences were detected between 10 wt% of 4-META (11.71 ± 0.18 MPa) and the ML primer group (12.01 ± 0.14 MPa). Shear bond strength values for alloys treated with 2 wt% of the 3-MPS group (10.19 ± 0.24 MPa) did not differ significantly from the Metal/Zirconia group (10.04 ± 0.15 MPa). With 1 wt% of 3-MPS the shear bond strength results did not differ statistically from the Monobond S group ($p > 0.05$). Figure 2 show representative optical microscope with $\times 20$ magnification images of the fracture surface. All specimens tested in this study showed adhesive failure. No cohesive failure within PMMA was found in this study.

DISCUSSION

This study attempts to compare the effect of various primers on the shear bond strength between Co-Cr alloy and autopolymerizing acrylic resin. It is known that the bonding mechanism between acrylic resin and metal alloy substrate is a combination of chemical and micro-mechanical bonding or either methods. In this study, all Co-Cr alloys were sandblasted with $50 \mu\text{m}$ Al_2O_3 particles to create surface roughness. Sandblasting with Al_2O_3 particles removes contaminated layers and creates a roughened surface which provides mechanical interlocking for the acrylic resin as well as providing a great surface area for the bond. It has been reported that the sandblasting process makes the-alloy-water

contact angle smaller and wettability greater¹⁵. According to Yoshida *et al.*¹⁶, metal sandblasting with Al_2O_3 particles could form a passive film made of Ni, Cr, and Co oxides. Ohno *et al.*¹⁷ defined the passive film of hydrated chromium oxyhydroxide and generalized this film by the formula: $\text{Cr}_x(\text{OH})_{3.2} \cdot n\text{H}_2\text{O}$, which is capable of forming on stainless steel and alloys containing Ni, Co, and Cr. Several chemical methods capable of enhancing the bonding of veneer resin to cast alloys have been reported including an adhesive heat-cured opaque resin, a Silicoater system, a silane coupling agent and adhesive metal primer, a self-curing 4-META/MMA-TBB opaque resin, a light-cured 4-MET opaque resin, and other commercial adhesive bonding promoters. The functional monomers residing in each primer have an affinity with the layer of chromium oxide surfaces. Therefore, the mechanical and chemical factors for bonding are indispensable in creating a stable bond between the acrylic resin and the surface of metal alloy. In this study, the alloy specimens in the control group were blasted without priming and the results showed lower shear bond strength than those of primed groups. The non-primed specimens yielded 5.05 ± 0.19 MPa which is comparable to the relatively limiting low bond value of 5 MPa specified in ISO 10477¹³. This bond strength value, however, is lower than the resin-metal bond strength of 10 MPa suggested by Matsumura *et al.*, as a minimum clinically relevant value¹⁸.

The result of our study also suggested that the experimental primers, both 4-META and 3-MPS, increase the bond of acrylic resin to the Co-Cr alloy surface. The bond strength of these primer are equivalent to some commercial primers (Table 2), although the strength was not the highest compared to all commercial primers in this study. Previous studies reported the successful adhesion of denture base resin to cast metal alloys by using 4-META^{19,20}. The chromium content in the Co-Cr alloy produces an oxide layer at room temperature which can enhance chemical bonding with 4-META²¹. According to Urapepon *et al.*²², they reported that 4-META has an ability to bond metal oxide on Ag-Sn filler particle to polymeric matrix in a metal-resin composite. Moreover, this study also reported in depth that different oxide form (SnO and SnO_2) produced different adhesion ability of 4-META. The SnO oxide form exhibited better adhesion to 4-META and Ag-Sn particle than SnO_2 . Similarly, the present study illustrates the improvement in shear bond strengths between a Co-Cr alloy and auto-polymerizing acrylic resin when using a 5, 10, and 15 wt% 4-META primer. However, the use of 10 wt% 4-META offers the highest shear bond strength. It is possible that at 10 wt% of 4-META, optimal amount of carboxylic group to react with Co-Cr oxide layer are obtained. This may suggest that 10 wt% of 4-META in acetone is the optimum content for bonding resin to Co-Cr alloy.

In practice, 3-MPS is the most routinely used in the clinic¹². The rationale for this study was that the selected 3-MPS coupling agent was thought to react with the hydroxyl groups on the Co-Cr alloy surface. Therefore, it becomes a crosslinking structure composed

by intermolecular bonding of the methoxy group with autopolymerizing acrylic resin. The commercial silane primer, 3-MPS, is diluted in a binary solvent, *i.e.*, a water/ethanol or water/methanol solution²³. The study of a 3-MPS primer in hexane was also reported by Kurata and Yamazaki²⁴. Matinlinna *et al.*²⁵, studied the effect of 2-propanol solvent and acetone-water to 3-MPS and vinylsilane for bonding of composite resin to titanium metal. In their study, 3-MPS and vinylsilane in acetone-water appeared as a slightly milky solution. However, in our study, the 3-MPS was prepared in acetone and the solution was clear.

There are 2 available forms of silane coupling agents on the market, one bottle in a pre-hydrolyzed form or in a form where hydrolysis occurs by mixing silane and acid (thus, two bottles)^{26,27}. The function of acid is to hydrolyze the silane ester group ($-\text{Si}-\text{O}-\text{CH}_3$) to silanol ($-\text{Si}-\text{OH}$). The optimum time for adsorption from a silane solution is after hydrolysis and before oligomerization, since the silane coupling agents are most effective when adsorbed as monomers. At pH 4–5, the rate of condensation between silanol groups of monomeric silane molecules to larger oligomers is minimal, and the stability of silane solutions is highest at a pH of about 4²⁸. In this study, the acetic acid is used for the pH adjustment to 4.5 according to previous study²⁸. The result showed that priming sandblasted Co-Cr alloy with 1, 2, 3 wt% of 3-MPS could increase the shear bond strength and at 2 wt% of 3-MPS showed the highest shear bond strength. When the results of the group using 2wt% of 3-MPS were compared to that of Monobond S, which also used 3-MPS as an active agent, the use of 2 wt% of 3-MPS provided higher bond strength. However, there was no statistical significant difference in 1 wt% of 3-MPS and Monobond S. While the concentration of 3-MPS in Monobond S is unknown, this may imply that the concentration of 3-MPS in Monobond S might be less than 2%.

In this study, compared with commercial primers, the Alloy primer revealed the highest shear bond strengths (15.08 ± 0.13 MPa), followed by the Monobond plus group (13.87 ± 0.24 MPa). There is no statistical significant difference in 10 wt% of 4-META (11.71 ± 0.18 MPa) and the ML primer group (12.01 ± 0.14 MPa). Alloy primer comprises VBATDT (6-(4-vinylbenzyl-n-propyl) amino-1,3,5-triazine-2,4-dithione) and 10-MDP (10-methacryloxydecyl dihydrogen phosphate) in acetone solvent. VBATDT reacts with noble metal alloys. The MDP monomer consists of 3 different functioning components; methacryloyl, decyl and dihydrogen phosphate groups. The dihydrogen phosphate group in MDP presents great chemical bonding to metal oxides of chrome formed in the surface of the Co-Cr alloy²⁹. There are published works reporting the superior effectiveness of MDP to 4-META^{7,29}. The result in this study was similar to the previous studies, indicating the superior effectiveness of the MDP monomer over the carboxylic 4-META monomer. This is probably because of the interaction between the di-hydrogen phosphoric group in MDP and the passive oxide layers formed on the alloy surface. It has been reported that the MDP exceeded

the 4-META monomer in bonding ability to the base metal alloy³⁰.

For the ML primer, it consists of 10-methacryloyloxydecyl-6,6-dithiooctanoate (MDDT) and an ester phosphate group of 6-methacryloxyhexylphosphonoacetate (6-MHPA) in an acetone solvent. The ML primer is effective for bonding to noble metal and base metal alloy. It showed ability to enhance shear bond strength between Co-Cr alloy and auto-polymerizing acrylic resin. In this study, the initial shear bond strength (24 h) between Co-Cr alloy and auto-polymerizing acrylic resin in the ML primer group was lower than the Alloy primer group. This might be due to the fact that the longer hydrocarbon connecting segment in the MDP yields more hydrophobicity and flexibility than the 6-MHPA. However, there is no report the difference in bonding characteristics between a phosphate monomer (MDP) and phosphonate monomer (6-MHPA) when used to bond Co-Cr alloy and auto-polymerizing acrylic resin. Koizumi *et al.*³¹, reported that there is no difference between MDP and 6-MHPA primer on the shear bond strength of titanium alloy to Super-Bond C&B resin.

Metal/Zirconia primer consists of phosphonic acid acrylate. The manufacturer claimed that it is suitable for oxide ceramic and all type of metal alloy. In this study, the result showed that the efficiency of Metal/Zirconia primer in enhancing shear bond strength (24 h) between Co-Cr alloy and auto-polymerizing acrylic resin was inferior to Alloy primer, Monobond Plus, ML primer, and 10 wt% of 4-META. Alloy primer and Monobond Plus contain methacrylic phosphoric acid monomer, ML primer contains methacrylic phosphonic acid monomer, and Metal/Zirconia primer contains acrylic phosphonic acid monomer. For 4-META, it is comprised of carboxylic acid group. The different structure of adhesion monomers could have different effect on the bond strength.

Recently, Monobond Plus has been introduced to the dental market. The manufacturer claimed that it is a universal primer for all types of restorative materials. Monobond Plus contains 3-MPS, phosphoric acid methacrylate and sulphide methacrylate in an alcohol solution but the chemical structure of functional monomers were not reported. Attia *et al.*³² reported that the Monobond plus was very efficient for bonding resin to zirconia. However, there are no earlier reports regarding the use of Monobond Plus for bonding Co-Cr alloy to acrylic resin.

Alloy primer, ML primer, and Monobond Plus contain a phosphoric acid derivative which can react with metal oxides and create the bonding. This might a possible explanation for their high bond strength.

Monobond-S, which was used in the present study, is a single-component silanizing agent designed to promote the adhesion of ceramic materials to luting composites. Its component is the mixture of ethanol, water, and 3-MPS. The results showed that the shear bond strength in the Monobond S (8.77 ± 0.17 MPa) group was lower than the 2 wt% of 3-MPS primer (10.19 ± 0.24 MPa). Nevertheless, it must be kept in mind that 3-MPS silane is not intended in general as a metal conditioner

but it can enhance the shear bond strength between composite resin and porcelain³³. All specimens showed adhesive failure in the metal-resin interface because of the bonding between primer and metal did not overcome the cohesive resistance of PMMA resin.

Finally, the long-term minimum bonding force value that the resin-metal interface has to withstand in order to have a good clinical performance is still unknown. According to the requirements of ISO 10477, the minimum acceptable bond strength value is 5 MPa¹³. In this study, the results observed in 10 wt% of 4-META, 2 wt% of 3-MPS, the ML primer, the Alloy primer, the Monobond plus, and the Metal/Zirconia primer improved the initial shear bond strength (24 h) between Co-Cr alloy and auto-polymerizing acrylic resin.

CONCLUSION

Within the limitations of this study, the following conclusions were drawn:

1. γ -methacryloxypropyltrimethoxysilane (3-MPS) in acetone and 4-methacryloxyethyl trimellitate anhydride (4-META) were effective to bond autopolymerizing acrylic resin to Co-Cr alloy, and 2 wt% of 3-MPS and 10 wt% of 4-META were the most effective concentrations for bonding.
2. Commercial primers such as ML primer, Alloy primer, Monobond Plus, and Metal/Zirconia primer would probably be clinically acceptable for the improvement in shear bond strength between Co-Cr alloy and auto-polymerizing acrylic resin.

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