Bond Strength of Resin Cements to Co-Cr and Ni-Cr Metal Alloys Using Adhesive Primers

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Abstract

Purpose: The aim of this study was to evaluate the effectiveness of adhesive primers (APs) applied to Co-Cr and Ni-Cr metal alloys on the bond strength of resin cements to alloys.
Materials and Methods: Eight cementing systems were evaluated, consisting of four resin cements (Bistite II DC, LinkMax, Panavia F 2.0, RelyX Unicem) with or without their respective APs (Metaltite, Metal Primer II, Alloy Primer, Ceramic Primer). The two types of dental alloys (Co-Cr, Ni-Cr) were cast in plate specimens ($10 \times 5 \times 1$ mm^3) from resin patterns. After casting, the plates were sandblasted with aluminum oxide (100 μm) and randomly divided into eight groups ($n = 6$). Each surface to be bonded was treated with one of eight cementing systems. Three resin cement cylinders (0.5 mm high, 0.75 mm diameter) were built on each bonded metal alloy surface, using a Tygon tubing mold. After water storage for 24 hours, specimens were subjected to micro-shear testing. Data were statistically analyzed by two-way ANOVA and Tukey's studentized range test.
Results: The application of Metal Primer II resulted in a significantly higher bond strength for LinkMax resin cement when applied in both metal alloys. In general, the cementing systems had higher bond strengths in Co-Cr alloy than in Ni-Cr.
Conclusions: The use of AP between alloy metal surfaces and resin cements did not increase the bond strength for most cementing systems evaluated.

Although there is a tendency to use esthetic restorative and prosthetic materials such as direct or indirect resin composite inlays, adhesive metal-free bonded bridges (partial dentures), and all-ceramic restorations, dental casting alloys are still used in a variety of dental applications. The alloys have been used in clinical procedures involving metal crowns, ceramometal restorations, full veneer crowns, implant prosthodontics, and cast metal dowel-and-cores.[1-5]

Conventionally, base metal alloys are cemented with glass ionomers, resin-modified glass ionomers, or zinc phosphate. On the other hand, resin luting materials were developed to cement esthetic materials, such as all-ceramics and indirect composites. Due to their improved physical characteristics, lower solubility, and better wear resistance and marginal closure than conventional luting cements, resin cements are also indicated to cement base metal alloys;[3,6-8] however, a durable bond of resin cements to metal alloys without any surface treatment has not been achieved because the luting materials have a low chemical affinity with metal alloys.[9-12]

In an attempt to improve the bonding of composites to alloys, electrolytic etching, chemical etchants, adhesive primer (AP) application, and silica coating methods and techniques for surface treatment of base metal alloys have been proposed.[8-10,13-22] Alloy primers contain monomers capable of chemically bonding to noble cast dental alloys; however, for non-precious alloys, the adhesion reactions are little known, and clinical indications remain controversial.[17-20]

The purpose of this study was to evaluate the effects of APs on shear bond strength of dual-cured resin cementing systems to Co-Cr and Ni-Cr cast dental alloys. The null hypothesis tested was that bond strength is not influenced by the AP application regardless the type of dual-cured resin cement used.

Materials and methods

Metal alloy specimen preparation

Two non-precious metal alloys were used: Co-Cr and Ni-Cr (Table 1). Forty-eight plates (10-mm length, 5-mm width, 1-mm thick) were cast for each alloy. The resin patterns (GC Corp., Tokyo, Japan) were invested under vacuum with investment (Heat Shock, Polidental, Cotia, Brazil), and after burnout at 850°C (EDG 3000, EDG Equip., Sao Carlos, Brazil), the specimens were centrifugally cast (Powercast 1700, EDG Equip.) in each alloy at the following temperatures: Co-Cr: 1240 to 1350°C; Ni-Cr: 1250 to 1310°C. After casting, the alloy plates were sandblasted with aluminum oxide (100 μm) for 10 seconds at an emission pressure of 0.5 MPa with the nozzle 5 mm from the metal surface. The plates (Fig 1A) from each metal alloy were randomly divided into eight groups (n = 6).

Bonding procedures

Materials used in the bonding procedures are described in Table 1. Four resin cements, Bistite II DC, LinkMax, Panavia F 2.0, and RelyX Unicem, and their respective APs, Metaltite, Metal Primer II, Alloy Primer, and Ceramic Primer were evaluated. APs and resin cements were applied and handled according to manufacturers' instructions. All light-curing procedures were performed with the XL 3000 curing unit (3M ESPE), under standard irradiation mode and 650 mW/cm^2. The output of the light was monitored throughout the course of the experiment, using a radiometer (Optilux Radiometer, Demetron Research, Danbury, CT).

The methodology developed by Shimada et al[23] was used to prepare specimens for the micro-shear test. The groups were divided for specimen preparation through random sorting of specimens. Three cylindrical translucent molds (Tygon tubing, TYG-030, Saint-Gobain Performance Plastic, Maime Lakes, FL) were positioned over the primed or non-primed metal surface of each alloy plate (Fig 1B), and freshly mixed dual-cure resin cements were inserted into the molds (Fig 1C), using a composite spatula (Duflex # 3, SS White, Juiz de Fora, Brazil). The resin cement cylinders were irradiated from the top for 40 seconds on each side.

Specimens were stored in distilled water at 37°C for 24 hours.[8,9] The tube molds were removed to expose the resin cement cylinders (0.75-mm diameter, 0.5-mm height) bonded to the metal surface. Three bonded resin cement cylinders were obtained for each metal alloy plate (Fig 1D). Prior to testing,

Table 1 Compositions of metal alloys, resin cements, and adhesive primers

Material (manufacturer)	Type	Composition (batch number)
Durabond Universal (Odonto Comercial Import. Ltda., Sao Paulo, Brazil)	Metal alloy	Nickel, chromium, molybdenum, niobium, silicon, iron (TAB000053)
d.SIGN 30 (Ivoclar Vivadent, Amherst, NY)	Metal alloy	Cobalt, chromium, gallium, niobium, silicon, molybdenum, iron, boron, aluminum, lithium (J17379)
Bistite II DC (Tokuyama Dental Corp., Tokyo, Japan)	Resin cement	Base: Neopentyldimethacrylate, silica-zirconia, activators Catalyst: MAC-10, Neopentyldimethacrylate, silica-zirconia, initiators (A70128)
LinkMax (GC Corp., Tokyo, Japan)	Resin cement	Fluoro-alumino silicate glass, urethane dimethacrylate, HEMA, silica (341A)
Panavia F 2.0 (Kuraray Medical Inc., Tokyo, Japan)	Resin cement	Paste A: MDP, hydrophobic aromatic dimethacrylates, hydrophobic aliphatic dimethacrylates, hydrophilic aliphatic dimethacrylates, silanated silica filler, silanated colloidal silica, dl-camphorquinone, initiators Paste B: Hydrophobic aromatic dimethacrylates, hydrophobic aliphatic dimethacrylates, hydrophilic aliphatic dimethacrylates, silanated barium glass filler, initiators, accelerators, pigments (61138)
RelyX Unicem (3M ESPE, St. Paul, MN)	Resin cement	Catalyst: Glass powder, substituted dimethacrylate, silane-treatead silica, sodium p-toluenesulfinate, calcium hydroxide Base: Glass powder, methacrylated phosphoric acid esters, triethylene glycol dimethacrylate, silane treatead silica, sodium persulfate. (240529)
Metaltite (Tokuyama Dental Corp.)	Primer	6-methacryloyloxyhexyl-2-thiouracil-5-carboxylate (MTU-6), ethanol, initiator (019)
Metal Primer II (GC Corp.)	Primer	Thiophosphoric methacrylate (MEPS), methylmethacrylate (MMA) (612073)
Alloy Primer (Kuraray Medical Inc.)	Primer	6-(4-Vinylbenzyl-N-propyl) amino-1,3,5-triazine-2,4-dithione, MDP, acetone (224A)
Ceramic Primer (3M ESPE)	Primer	Ethyl alcohol, water (4147)

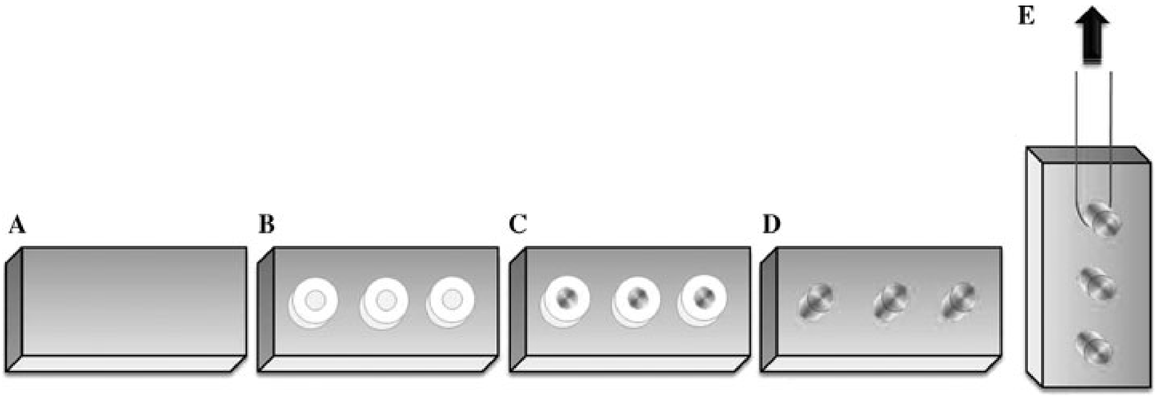

Figure 1 Specimen preparation: (A) cast plate, (B) three cylindrical molds positioned over surface of cast plate, (C) resin cements filling the internal space of the molds, (D) resin cement cylinders, (E) shear test.

all resin cylinders were checked under an optical microscope (30X) for bonding defects.

Micro-shear testing

Each metal plate was attached to the testing device with cyanoacrylate glue (Super Bonder, Loctite, Itapevi, Brazil) and tested in a universal testing machine (4411, Instron Corp., Canton, MA). A shear load was applied to the base of the resin cement cylinder with a thin wire (0.20-mm diameter) at a crosshead speed of 0.5 mm/min until failure (Fig 1E). Shear bond strengths were obtained in kgf, and the means expressed in MPa, according to the inverse ratios: 1 MPa = 10.2 kgf/cm^2 (0.02 cm^2 of bonding area).[23] Three bond strength measurements were recorded for each metal plate, and the mean bond strength was determined for each experimental unit.

Statistical analysis

As part of the data analysis, the data were initially evaluated to ensure they met the assumptions for an analysis of variance (ANOVA) model (adequate response scaling, no outliers, constant variance, and no influential outliers). The assumptions of homogeneity of variance and normal distribution were checked by Hartley's test and Kolmorov–Smirnov's test, respectively. Having met these assumptions, data were statistically analyzed by fitting a two-way (cementing system and metal alloy factors) ANOVA model. Given that the two-way interaction effect was statistically significant ($p < 0.05$), comparisons between the individual means were performed using Tukey's studentized range test to control the experiment-wise error rate. All calculated p-values were two-sided, and p-values less than 0.05 were considered statistically significant. Analysis was performed using SAS software version 8.0 (SAS Institute, Cary, NC).

Results

The mean shear bond strength and standard deviation values are presented in Table 2 and Figure 2. Two-way ANOVA revealed that there were statistically significant differences for the factor "cementing system" ($F = 24.14$, $p < 0.001$), for the factor "metal alloy" ($F = 19.73$, $p < 0.001$) and for the interaction between factors "cementing system and metal alloy" ($F = 5.19$, $p < 0.001$). The coefficient of variation for this study was 17.1%.

The Tukey post hoc test showed that the application of Metal Primer II increased the bond strength of LinkMax resin cement to both metal alloys, when compared to non-application of AP. Conversely, the bond strength of Bistite II DC, RelyX Unicem, and Panavia F 2.0 was not enhanced by the use of APs. The bond strength of cementing systems to Cr-Co was higher for most experimental groups, except for RelyX Unicem, Panavia F 2.0, and LinkMax + Metal Primer II.

Discussion

Although the manufacturers suggested using adhesive or alloy primers before application of resin cement, the results of this study indicate that only one cementing system had its bond strength increased by primed metal surface preparation. Thus, the null hypothesis was only partially confirmed, because one

Table 2 Bond strength means (SD) (MPa) of cementing systems to metal alloys (n = 6)

	Metal alloys	
Cementing system	Ni-Cr	Co-Cr
Panavia F 2.0 + Alloy Primer	37.2 (9.2) A b	44.9 (4.1) ABC a
Panavia F 2.0	41.0 (4.5) A a	46.3 (3.0) AB a
LinkMax + Metal Primer II	45.1 (8.0) A a	50.3 (6.7) A a
LinkMax	18.4 (3.2) B b	28.4 (6.3) D a
Bistite II DC + Metaltite	19.3 (4.5) B b	33.3 (3.4) D a
Bistite II DC	22.4 (9.4) B b	36.5 (4.9) BCD a
RelyX Unicem + Ceramic Primer	38.2 (7.2) A b	30.8 (3.8) D a
RelyX Unicem	39.6 (6.3) A a	34.8 (6.8) CD a

Mean values followed by different lowercase letters in rows (comparison among metal alloys within the same cementing system) or uppercase letters in columns (comparison among cementing systems within the same metal alloy) differ statistically by Tukey test ($p < 0.05$).

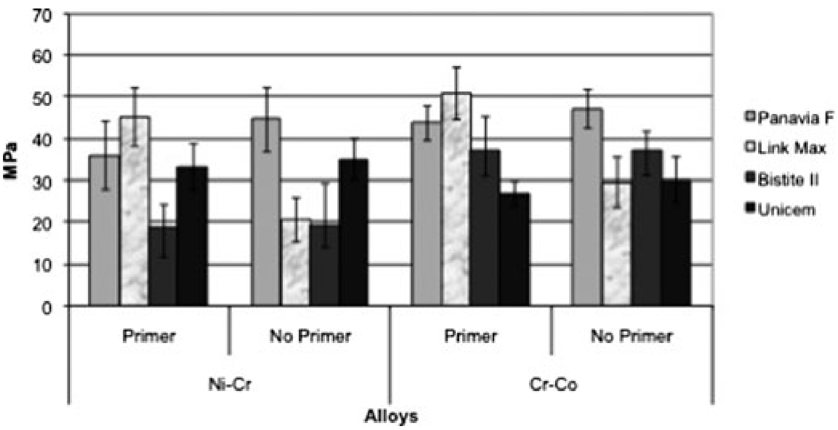

Figure 2 Bond strength of resin cements to metal alloys (mean values).

cementing system tested was influenced by the application of the AP on the metal alloy surface.

For Bistite II DC, RelyX Unicem, and Panavia F 2.0, the application of AP did not increase the bond strength. Panavia F 2.0 resin cement contains MDP monomer (10-Methacryloyloxydecyl dihydrogen phosphate), which can react chemically with chromium oxide created on the casting surface and produce similar bond strength without Alloy Primer application.[9] Even though Alloy Primer contains MDP, this AP is only indicated to increase the bond strength of composite and acrylic resins to gold, base and semi-precious metals, and titanium.[8,10,14]

A silane coupling agent (Ceramic Primer) was used as AP for RelyX Unicem resin cement. Silane is indicated for application on conditioned surfaces of ceramics prior resin cement; however, it did not affect the bond strength of RelyX Unicem to metal alloys. Even though the silane improves the contact between alloy surface and resin cement, this additional step of priming can be eliminated. RelyX Unicem resin cement is considered self-adherent and does not need the separate dental etching, priming, or bonding steps required by conventional cementing systems; however, the pretreatment of metal surface is not established yet. As the basic chemistry and setting reactions of RelyX Unicem are close to characteristics of zinc polycarboxilate and glass ionomer cements, it is possible to speculate that good adhesion on metal alloy surfaces can be obtained by cementation with RelyX Unicem.[15,24,25]

The bond strengths of most of experimental groups to Co-Cr metal alloy were higher than to Ni-Cr, except for RelyX Unicem, Panavia F 2.0 and LinkMax + Metal Primer II. The bonding between casting alloy surface and adhesive resin composite cement is created by micromechanical retention promoted by sandblasting[9,21] and the layer of chromium oxides that is easily created on the casting Co-Cr metal surface.[9] Thus, APs and some resin cements containing adhesive monomers with an ability to produce a chemical reaction with oxides were developed in an attempt to enhance the bonding of resin-based materials to non-precious metal alloys.[6,9,18,26,27]

Metaltite is a primer indicated for improvement of the adhesion between Bistite II DC resin cement and precious metals such as gold and titanium, semiprecious metals, and other dental alloys. It contains MTU-6, a thiouracil monomer that promotes a chemical bond between resins and precious metals;[8] however, in this study, Metaltite was applied in non-precious metal alloys and did not improve the bond strength. Also, this cementing system showed lower bond strength than Panavia F 2.0 and RelyX Unicem. Similar values of bond strength results were related by Lisboa et al[14] using two Ni-Cr alloys and the same metal primer.

Metal Primer II contains methyl-methacrylate and MEPS (thiophosphoric metacrylate), which promotes bonding of LinkMax resin cements to different types of metal alloys.[8,9,18,19,27] The results of this study showed that independent of the non-precious metal alloy type used, the application of Metal Primer II increased the bond strength of resin cement to metal surfaces. Studies have shown that the functional monomer of Metal Primer II has an affinity with the layer of oxides created on the casting surface, which can be responsible for increasing bond strength.[9,19]

In 1987, Kojima et al[28] reported on the use of VBATDT (6-[(4-vinylbenzyl)propylamino]-1,3,5-triazine-2,4-dithione), a thione-thiol tautomer, as a metal primer to bond composite resins to precious metals with good results. The coupling mechanism of this monomer has been assigned to the transformation of thione to thiol groups on noble metal surfaces, subsequent to primary bond formation and to the copolymerization of vinyl groups with the methacrylate-based resins.[29] Thus, the adhesive metal primers were created to promote an adhesion to noble metal alloys;[17-20,29,30] however, in this study, the bond strength to non-precious or alternative alloys, which present low chemical affinity with resin cements and APs, was evaluated.[9-12,26] The interaction between adhesive metal primers and methacrylate-based resin cements remained the same, but the bonding mechanism of APs to metal alloys and the interaction between resin cements and metal alloys changed according to the composition of Co-Cr and Ni-Cr non-precious alloys.

The thermocycling method was not used in this study. The implications that it could have to the results are related to reduction of bond strength of resin cements to metal alloys, because of the lack of durable bonding to alloys for some cementing systems, as shown by Yoshida et al.[8,9] Regarding significance, as the results showed that the use of APs did not increase the bond strength for most cementing systems evaluated, the use of primers can be avoided depending on cementing system. On the other hand, the use of Metal Primer II, which contains the functional monomer MEPS, was essential to increase the bond strength of resin cement to both metal alloys.

Conclusions

The results suggested that the bond strengths of resin cements to Ni-Cr and Co-Cr metal alloys were not increased by AP applications, except for the use of Metal Primer II and LinkMax resin cement. Four cementing systems presented higher bond strengths in Co-Cr metal alloy than in Ni-Cr alloy, while three systems showed no differences on bond strength between the metal alloys.

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