Bond Strength of Resin Cements to Noble and Base Metal Alloys with Different Surface Treatments

Farkhondeh Raeisosadat1, Maryam Ghavam2, Masoomeh Hasani Tabatabaei2, Sakineh Arami3, Maedeh Sedaghati4

1Assistant Professor, Department of Operative Dentistry, School of Dentistry, Shahid Beheshti University of Medical Sciences, Tehran, Iran
2Associate Professor, Dental Research Center Dentistry Research Institute, Department of Operative Dentistry, School of Dentistry, Tehran University of Medical Sciences, Tehran, Iran
3Assistant Professor, Department of Operative Dentistry, School of Dentistry, Tehran University of Medical Sciences, Tehran, Iran
4Former Resident, Department of Operative Dentistry, School of Dentistry, Tehran University of Medical Sciences, Tehran, Iran

Abstract
Objectives: The bond strength of resin cements to metal alloys depends on the type of the metal, conditioning methods and the adhesive resins used. The purpose of this study was to evaluate the bond strength of resin cements to base and noble metal alloys after sandblasting or application of silano-pen.

Materials and Method: Cylinders of light cured Z 250 composite were cemented to “Degubond 4” (Au Pd) and “Verabond” (Ni Cr) alloys by either RelyX Unicem or Panavia F2, after sandblasting or treating the alloys with Silano-pen. The shear bond strengths were evaluated. Data were analyzed by three-way ANOVA and t tests at a significance level of P<0.05.

Results: When the alloys were treated by Silano-pen, RelyX Unicem showed a higher bond strength for Degubond 4 (P=0.021) and Verabond (P< 0.001). No significant difference was observed in the bond strength of Panavia F2 to the alloys after either of surface treatments, Degubond 4 (P=0.291) and Verabond (P=0.899).

Panavia F2 showed a higher bond strength to sandblasted Verabond compared to RelyX Unicem (P=0.003). The bond strength of RelyX Unicem was significantly higher to Silano-Pen treated Verabond (P=0.011). The bond strength of the cements to sandblasted Degubond 4 showed no significant difference (P=0.59).

RelyX Unicem had a higher bond strength to Silano-Pen treated Degubond 4 (P=0.035).

Conclusion: The bond strength of resin cements to Verabond alloy was significantly higher than Degubond 4. RelyX Unicem had a higher bond strength to Silano-Pen treated alloys. Surface treatments of the alloys did not affect the bond strength of Panavia F2.

Key Words:Resin Cements; Silano-Pen; Sand Blast

INTRODUCTION
Indirect restorations are used in a variety of clinical situations among which loss of tooth structure due to caries and trauma is of utmost importance [1]. Some of indirect restorations are fabricated using metal alloys. The composition of alloys used in metal based indirect restorations varies.
Base metal and noble alloys are examples of the currently used alloys [2-6]. Base metals possess higher free surface energy compared to noble alloys resulting in thicker oxide layer formation and higher reactivity [2]. Reports indicate that enhancement of alloy nobility decreased the adhesive strength [7]. On the other hand, noble alloys have a number of advantages over base metal alloys including esthetics and the ability of bonding to ceramics and they are also less technique sensitive [8]. Adhesion of the cements to the intaglio surface of indirect restorations is imperative to durability of the restoration, particularly when there are difficulties during the restoration process due to shortness of the tooth and/or tapering caused by preparation [2]. Additionally, adhesion highly depends on the surface treatment of both the tooth and the indirect restoration and also the chemical composition of the cement [9]. Practically, adhesion can be reached via chemical reaction, luting or micromechanical retention [1]. In order to enhance bonding strength, various surface treatments are performed including i) sandblasting, ii) application of metal primers, iii) tin plating and iv) silicoating [3, 8]. Since the debris on the surface is removed during sandblasting, this technique improves adhesiveness and it is an inexpensive technique [2]. Studies have shown excellent bonding of resins to sandblasted base metals [10-12]. Since 1984 it has been possible to create a chemical bond between dental alloys and composite resins resembling the metallo-ceramic bond (silicoater), and since then some researchers have evaluated its performance[13-15]. The mechanism is to place an intermediate layer of silicon dioxide (SiO2) providing sufficient bonding to resin via silane application. The phenomenon introduces a durable and reasonably strong bond between resin and noble alloys as well as resin and base metals [15]. Silano-Pen is an easy to use and inexpensive device, basically designed on the silicoater technique [3,14-16]. In the past decade researchers have tried to improve the adhesion of resins to dental alloys. Dual cure resin cements are polymerized via light or chemical reactions [1,17,18]. Combination of these two mechanisms makes it possible to provide resin luting materials for permanent cementation of indirect restorations fabricated by base metals. Moreover, these cements have high mechanical strengths compared to zinc phosphate and glass ionomer [19]. Studies have shown that a newer version of phosphate resins, RelyX Unicem (3M ESPE), can chemically interact with treated surfaces of metals and increase the retention of restorations [1,19, 20]. To achieve optimum bond strength of cements to indirect restorations, multiple factors should be considered. Bond strength of alloys and cements are reported to vary depending on the type and composition of the alloy, surface treatment, type of cement and the testing methods [2, 16]. The aim of this study was to evaluate the effect of sandblasting or applying Silano-Pen on the bond strength of resin cements to base and noble metals. MATERIALS AND METHODS The composition of resin cements and metal alloys used in this study is summarized in Table 1. Eighty discs, 6 mm in diameter and 2 mm in thickness from two different alloys of nickel chrome (Verabond; Alba Dent, USA) and gold palladium (Degubond 4; DeguDent GmbH, Germany) were prepared according to the manufacturers’ instructions. Consequently, the discs were mounted in self-cure acrylic (Acropars, Marlak, Tehran, Iran) to enhance the accuracy of preparing the samples. All the samples were polished by 600 grit silicon carbide abrasive paper. Half of the samples were selected randomly from both alloys and sand-blasted with 50μ Al2O3 under 3 bar pressure at the distance of 10...
mm for 14 seconds, followed by cleaning with 96% isopropyl alcohol via ultrasonication. Then they were air dried.

The remaining samples were sandblasted with 110µ AL203, then flamed (5sec/cm²) with Silano-Pen device (Bredent GmbH Senden Germany) based on the manufacturer’s instruction. After cooling down to room temperature, the Silano-Pen bonding agent was brushed on and air dried for 3 minutes.

Plastic tubes (3 mm inner diameter, 3 mm height) were filled with shade A3.5 of resin composite (FiltekZ 250, 3M ESPE) and covered with glass slide to achieve a uniform surface. Then both sides of the composite were light cured for 40s using LED Bluephase 16i Ivoclar_Vivadent with minimum intensity of 600 mw/cm².

Afterwards, the composite cylinders were perpendicularly bonded to the pre-treated substrates with either Panavia F2 or RelyX adhesive resin cements. A primary curing was done and the excess marginal cement was removed. An oxygen blocking gel (Oxyguard) was applied for 3 minutes when Panavia F2 was used. Final curing was done along all four sides for 20 seconds for each side and the samples were kept at 37°C in distilled water for 24 hours.

Table 1. Compositions of Resin Cements and Metal Alloys

| Material                  | Composition                                                                 | Lot no  | Manufacturer        |
|---------------------------|-----------------------------------------------------------------------------|---------|---------------------|
| Panavia F2.0              | **Paste A:** MDP, hydrophobic aromatic dimethacrylates, hydrophobic aliphatic dimethacrylates, hydrophilic aliphatic dimethacrylates, silanated silica filler, silanated colloidal silica, dl-camphorquinone, initiators | 61138   | Kuraray (Japan)     |
|                          | **Paste B:** Hydrophobic aromatic dimethacrylates, hydrophobic aliphatic dimethacrylates, hydrophilic aliphatic dimethacrylates, silanated barium glass filler, initiators, accelerators, pigments |         |                     |
| RelyX Unicem             | **Catalyst Paste:** Methacrylate monomers                                  | 240529  | 3M ESPE (Germany)   |
|                          | Alkaline (basic) fillers                                                  |         |                     |
|                          | Silanated fillers                                                         |         |                     |
|                          | Initiator components                                                      |         |                     |
|                          | Stabilizers                                                                |         |                     |
|                          | Pigments                                                                   |         |                     |
|                          | **Base paste:** Methacrylate monomers containing phosphoric acid groups     |         |                     |
|                          | Methacrylate monomers                                                     |         |                     |
|                          | Silanated fillers                                                         |         |                     |
|                          | Initiator components                                                      |         |                     |
|                          | Stabilizers                                                                |         |                     |
| Verabond (casting alloy) | Ni 77.95%, Cr 12.60%, Mo 5.00 %, Al 2.90%, Co 0.45%, Be 1.95%              |         | Alba Dent (USA)     |
| Degubond 4 (casting alloy)| Au 49.60%, Pd 29.00 %, Ag 17.5%, Sn 3.00%, Ir 0.10 %, Ga 0.50, Ta 0.10%, Re 0.20% |         |Degu Dent (Germany) |
The final products were subjected to 2000 thermal cycles in water baths (5-55°C) with 30 seconds dwell time and 10 seconds transfer time.

After drying at room temperature, all specimens were mounted in universal testing machine (Zwick/RoellZo 50) at a crosshead speed of 0.5 mm/min until failure occurred. The diameter of bonding surface was measured in three different areas and the average was recorded.

The shear bond strength was calculated by dividing the failure load over the bonding area and was recorded as MPa. The mode of failure was studied via stereomicroscope (Nikon SMZ 800) with a magnification of 40 and identified as i) adhesive failure in the interface of metal-resin and ii) mixed failure (visible remnants of cements and/or composites on the metal surfaces). The data were analyzed by three-way ANOVA (α=0.05) followed by t tests. The primary error was corrected by Bonferroni method.

RESULTS

The bonding strength of resin cements to Verabond alloy was significantly higher than Degubond 4, irrespective of surface treatment methods (P< 0.001).

When the alloys were treated by Silano-Pen, RelyX Unicem showed a higher bond strength to both alloys, Degubond 4 (P=0.021) and Verabond (P< 0.001).

On the other hand no significant difference was observed in the bond strength of Panavia F2 to both alloys, Degubond 4 (P=0.291) and Verabond (P=0.899), with either of the surface treatments.

When Verabond alloy was sandblasted, Panavia F2 showed a significantly higher bond strength compared to RelyX Unicem (P=0.003).

In case of surface treatment by Silano-Pen, the bonding strength of RelyX Unicem cement was significantly higher (P=0.011).

When Degubond 4 was sandblasted, the bond strength of both cements was the same (P=0.59).

On the other hand, when the surface was treated with Silano-Pen, RelyX Unicem cement had a higher bonding strength (P=0.035) compared to Panavia F2.

![Table 2. Bond Strength of Resin Cements to Metal Alloys After Using Silano-Pen or Sandblasting](image-url)
Inspection of the failed surfaces by stereomicroscope revealed that the majority of failures in Verabond alloy were mixed. However, in Degubond 4 alloy the failure mode was both adhesive and mixed. (Figures 1 and 2)

DISCUSSION
Choosing a better combination of available cements and surface treatments to get a reliable bond of cements to metals is a main concern in dental research. In this study, it was observed that compared to Degubond 4, Verabond alloy had a stronger bond to both cements irrespective of surface treatment. It was concluded that the type of alloy is a determinant factor for bonding.

This conclusion is in agreement with various reports that have studied the role of alloys in alloy-resin bond strength [6, 21-23]. However, Abreu et al. have reported that the type of metal did not affect the bond strength of resin cements [2, 24]. The disagreement between the findings of this research with the study conducted by Abreu et al. may be due to the different alloys used [2, 24]. Base metals are oxidized rapidly at room temperature [6]. The oxides formed on the surface of the alloy play an important role in wettability, resulting in the formation of chemical bonds with resin cements [7, 23].

Stereomicroscopic images confirm this phenomenon, for example the mode of failure in Verabond group was dominantly mixed. Sandblasting causes complex morphological changes at the surface of metal along with accumulation of particular ions on its surface [25]. Additionally, mechanically removing debris can improve the wettability of cements [26, 27]. This procedure is relatively inexpensive and does not have the sensitivity of other alloy surface treatments [24]. Therefore, all the samples in this study were sandblasted prior to bonding. 50 µm aluminum oxide is reported to be the best sandblasting material that creates high mechanical bond strength [10, 28].

In the current study, Panavia F2 strongly bonded to sandblasted Verabond alloy (18 MPa). Various studies also have shown high bond strengths of Panavia cement to sandblasted base metal alloys [10-12]. Adhesives with acidic groups such as phosphoric acid, triphosphoric acid or carboxylic acid can form bonds with oxides on the surface of metals. Panavia F2 contains a phosphate monomer [10-Methacryloxydecyl dihydrogen phosphate (MDP)] that is extremely effective for bonding to enamel, dentin and metal alloys.

Fig 1. Depicts the adhesive failure between the cement and alloy.

Fig 2. Mixed failure. C represents the cement and Co represents the composite.
Moreover, researchers believe that a covalent bond forms between adhesive and the remaining alumina deposited on the surface after sandblasting [29, 30]. Nowadays the use of self-adhesive cements has increased. These systems are made to combine the advantages of various available cements, facilitate luting and reduce the vulnerability of the material to probable mishandlings [31-33]. RelyX Unicem, a self-adhesive cement, is made of a monomer, filler and a novel initiator [34]. Based on the manufacturer’s claim, the organic matrix is made of multipurpose phosphoric acid methacrylate. Phosphoric acid methacrylates react with basic fillers in the luting cement and dental hydroxyapatite [34, 35]. That explains the satisfactory bonding (13 MPa) of sandblasted Verabond with RelyX Unicem cement. A lot of studies have evaluated the bond strength of resin cements [36-38]. However, the outcomes may vary due to the different metals used as well as preparation methods and the type of adhesives. Another important factor would be the testing methods that differ from one study to the other. Therefore, comparison of the exact values may not reflect the reality [39]. Since the bond strength of enamel to resin systems is within the range of 13-20 MPa; therefore, bond strengths within this range are defined as amenable [38]. Durable bonding in clinic is defined to be within the range of 10 to 13 MPa [40]. In this respect, although the bond strength of RelyX Unicem to Verabond was stronger than Panavia F2, the range of both was within the acceptable clinical range of bonding strengths. Our study demonstrated that when sandblasted Degubond 4 was used, the bond strength did not depend on the cement type. This finding is in agreement with the study conducted by Piwowarczyk et al. [1]. The other type of surface treatment that was used in this study was silicoating with Silano-Pen. The instrument is a chair side silicoater that can be used with a hand-held igniter [14, 15]. The preparation in this method is via flame. Ignition of the surface starts a reaction in which tetra etoxy silane is decomposed to organic Si (SiOx-C) and covers the surface. This layer has glass like qualities that can silanate with (3- Methacryloyloxy Propyl trimethoxy Silane (MPS). Simultaneously, Silane is capable of polymerizing with other acrylic and methacrylic functional groups and a strong bond can form [41]. This phenomenon explains the stronger bond formed when using Silano-Pen compared to sandblasted alloys, although this difference was not significant when using Panavia F2 cement. There is lack of available information regarding the nature of both Silano-Pen surface treatment and its impact on bond strength. Further studies are required to elucidate these phenomena. In addition, studies on the impact of fatigue and cyclic loads are required to understand the long-term durability of this technique.

CONCLUSION
The alloy, resin cement and the surface treatment were important factors in achieving a strong and durable bond. The bond strength of RelyX Unicem to both Verabond and Degubond 4 alloys treated by Silano-Pen was higher compared to sandblasting. As for Panavia F2, the bond strength did not depend on the surface treatment technique.

REFERENCES
1- Piwowarczyk A, Lauer HC, Sorensen JA. In vitro shear bond strength of cementing agents to fixed prosthodontic restorative materials. J Prosthet Dent. 2004 Sep;92(3):265-73. 2- Abreu A, Loza MA, Elias A, Mukhopadhyay S, Looney S, Rueggeberg FA. Tensile bond strength of an adhesive resin cement to different alloys having various surface treatments. J Prosthet Dent. 2009 Feb;101(2):107-18.
3- Matlininna JP, Vallittu PK. Silane based concepts on bonding resin composite to metals. J Contemp Dent Pract. 2007 Feb 1;8(2):1-8. Review.
4- Fonseca RG, Martins SB, de Oliveira Abirached F, Dos Santos Cruz CA. Effect of different airborne-particle abrasion/bonding agent combinations on the bond strength of a resin cement to a base metal alloy. J Prosthodont Dent. 2012 Nov;108(5):316-23.
5- Muraguchi K, Minami H, Minesaki Y, Suzuki S, Tanaka T. A study of self-adhesive resin cements for bonding to silver-palladium-copper-gold alloy -- effect of including primer components in cement base. Dent Mater J. 2011;30(2):199-205.
6- Capa N, Ozkurt Z, Canpolat C, Kazazoğlu E. Shear bond strength of luting agents to fixed prosthodontic restorative core materials. Aust Dent J. 2009 Dec;54(4):334-40.
7- Sen D, Nayir E, Pamuk S. Comparison of the tensile bond strength of high-noble, noble, and base metal alloys bonded to enamel. J Prosthodont Dent. 2000 Nov;84(5):561-6.
8- McConnell RJ. Metal-resin bonding. J Calif Dent Assoc. 1993 Jun;21(6):38-42. Review.
9- Hill EE, Lott J. A clinically focused discussion of luting materials. Aust Dent J. 2011 Jun;56 Suppl 1:67-76. Review.
10- Dixon DL, Breeding LC, Hughie ML, Brown JS. Comparison of shear bond strengths of two resin luting systems for a base and a high noble metal alloy bonded to enamel. J Prosthodont Dent. 1994 Nov;72(5):457-61.
11- Pegoraro LF, Barrack G. A comparison of bond strengths of adhesive cast restorations using different designs, bonding agents, and luting resins. J Prosthodont Dent. 1987 Feb;57(2):133-8.
12- Fonseca RG, de Almeida JG, Haneda IG, Adabo GL. Effect of metal primers on bond strength of resin cements to base metals. J Prosthodont Dent. 2009 Apr;101(4):262-8.
13- Capa N, Leinfelder KF, Lacefield WR, Bell W. Effectiveness of a method used in bonding resins to metal. J Prosthodont Dent. 1990 Jul;64(1):37-41.
14- Janda R, Roulet JF, Wulf M, Tiller HJ. Resin/Resin bonding: a new adhesive technology. J Adhes Dent. 2002 Winter;4(4):299-308.
15- Janda R, Roulet JF, Wulf M, Tiller HJ. A new adhesive technology for all-ceramics. Dent Mater. 2003 Sep;19(6):567-73.
16- Janda R, Roulet JF, Latta M, Damerau G. Spark erosion as a metal-resin bonding system. Dent Mater. 2007 Feb;23(2):193-7.
17- Faria-e-Silva A, Boaro L, Braga R, Piva E, Arias V, Martins L. Effect of immediate or delayed light activation on curing kinetics and shrinkage stress of dual-cure resin cements. Oper Dent. 2011 Mar-Apr;36(2):196-204.
18- Jongsma LA, Kleverlaan CJ, Pallav P, Feilzer AJ. Influence of polymerization mode and C-factor on cohesive strength of dual-cured resin cements. Dent Mater. 2012 Jul;28(7):722-8.
19- Ferracane JL, Stansbury JW, Burke FJ. Self-adhesive resin cements - chemistry, properties and clinical considerations. J Oral Rehabil. 2011 Apr;38(4):295-314.
20- Piwowarczyk A, Lauer HC, Sorensen JA. The shear bond strength between luting cements and zirconia ceramics after two pretreatments. Oper Dent. 2005 May-Jun;30(3):382-8.
21- Ergin S, Gemalmaz D. Retentive properties of five different luting cements on base and noble metal copings. J Prosthodont Dent. 2002 Nov;88(5):491-7.
22- Krabbendam CA, ten Harkel HC, Duijsters PP, Davidson CL. Shear bond strength determinations on various kinds of luting cements with tooth structure and cast alloys using a new testing device. J Dent. 1987 Apr;15(2):77-81.
23- El-Guindy J, Selim M, El-Agroudi M. Alternative pretreatment modalities with a self-adhesive system to promote dentin/alloy shear bond strength. J Prosthodont. 2010 Apr;19(3):205-11.
24- Abreu A, Loza MA, Elias A, Mukhopadhyay S, Rueggeberg FA. Effect of metal type and surface treatment on in vitro tensile strength of copings cemented to minimally retentive preparations. J Prosthet Dent. 2007 Sep;98(3):199-207.
25- Kern M, Thompson VP. Sandblasting and silica-coating of dental alloys: volume loss, morphology and changes in the surface composition. Dent Mater. 1993 May;9(3):151-61.
26- Gargari M, Gloria F, Napoli E, Pujia AM. Zirconia: cementation of prosthetic restorations. Literature review. Oral Implantol (Rome). 2010 Oct;3(4):25-9.
27- Pazinatto FB, Lopes FA, Marquezini Junior L, de Castro FL, Atta MT. Effect of surface treatments on the spreading velocity of simplified adhesive systems. J Appl Oral Sci. 2006 Dec;14(6):393-8.
28- Petridis H, Garepis P, Hirayama H, Kafantaris NM, Koidis PT. Bonding indirect resin composites to metal: part 2. Effect of alloy surface treatment on elemental composition of alloy and bond strength. Int J Prosthodont. 2004 Jan-Feb;17(1):77-82.
29- Cobb DS, Vargas MA, Fridrich TA, Bouschlicher MR. Metal surface treatment: characterization and effect on composite-to-metal bond strength. Oper Dent. 2000 Sep-Oct;25(5):427-33.
30- Fonseca RG, Dos Santos Cruz CA, Adabo GL, Vaz LG. Comparison of the tensile bond strengths of cast metal crowns luted with resin cements. J Oral Rehabil. 2004 Nov;31(11):1080-4.
31- Mak YF, Lai SC, Cheung GS, Chan AW, Tay FR, Pashley DH. Micro-tensile bond testing of resin cements to dentin and an indirect resin composite. Dent Mater. 2002 Dec;18(8):609-21.
32- De Munck J, Vargas M, Van Landuyt K, Hikita K, Lambrechts P, Van Meerbeek B. Bonding of an auto-adhesive luting material to enamel and dentin. Dent Mater. 2004 Dec;20(10):963-71.
33- Ibarra G, Johnson GH, Geurtsen W, Vargas MA. Microleakage of porcelain veneer restorations bonded to enamel and dentin with a new self-adhesive resin-based dental cement. Dent Mater. 2007 Feb;23(2):218-25.
34- Viotti RG, Kasaz A, Pena CE, Alexandre RS, Arrais CA, Reis AF. Microtensile bond strength of new self-adhesive luting agents and conventional multistep systems. J Prosthet Dent. 2009 Nov;102(5):306-12.
35- Hikita K, Van Meerbeek B, De Munck J, Ikeda T, Van Landuyt K, Maidt T, Lambrechts P, Peumans M. Bonding effectiveness of adhesive luting agents to enamel and dentin. Dent Mater. 2007 Jan;23(1):71-80.
36- Gates WD, Diaz-Arnold AM, Aquilino SA, Ryther JS. Comparison of the adhesive strength of a BIS-GMA cement to tin-plated and non-tin-plated alloys. J Prosthet Dent. 1993 Jan;69(1):12-6.
37- Chang JC, Powers JM, Hart D. Bond strength of composite to alloy treated with bonding systems. J Prosthodont. 1993 Jun;2(2):110-4.
38- Kern M, Thompson VP. Influence of prolonged thermal cycling and water storage on the tensile bond strength of composite to NiCr alloy. Dent Mater. 1994 Jan;10(1):19-25.
39- Quaas AC, Heide S, Freitag S, Kern M. Influence of metal cleaning methods on the resin bond strength to NiCr alloy. Dent Mater. 2005 Mar;21(3):192-200.
40- Thurmond JW, Barkmeier WW, Wilwerding TM. Effect of porcelain surface treatments on bond strengths of composite resin bonded to porcelain. J Prosthet Dent. 1994 Oct;72(4):355-9.
41- Ozcan M, Nijhuis H, Valandro LF. Effect of various surface conditioning methods on the adhesion of dual-cure resin cement with MDP functional monomer to zirconia after thermal aging. Dent Mater J. 2008 Jan;27(1):99-104.