Durability of bond strength between titanium alloy and resin cement

Durabilidade da resistência de união entre uma liga de titânio e um cimento resinoso

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Summary

The aim of this study was to evaluate the effect of thermocycling on the bond strength between resin cement and titanium alloy with silica coating. Six titanium alloy blocks (Rematitan, Dentaurum) were cast with dimensions of 5x6x6mm. One of the faces measuring 5x6mm of each titanium alloy block was etched with the CoJet System (3M ESPE – silica coating) and luted with Panavia F (Kuraray) to another identical block made from composite resin Z100 (3M ESPE) under a constant 750g load. The six samples formed by titanium alloy, cement and composite resin were split up in a mechanical lathe and 30 samples measuring 10x1x1mm were achieved, with an adhesive surface area of $1mm^2 \pm 0.2mm^2$. The samples were divided into 2 groups (n=15): G1 (group 1) – stored for 1 day in distilled water at 37°C; G2 (group 2) – thermocycling for a total of 2,700 cycles (5°C – 55°C, dwell time: 30s). The microtensile test was accomplished in a universal testing machine (EMIC) at a crosshead speed of 1.0 mm/min. Means and standard deviations of bond strengths (MPa) were 44.50±8.41 for G1 and 38.03±7.63 for G2. Data were analyzed using the unpaired Student t test ($p<0.05$). There was a statistically significant difference between groups G1 and G2 ($t=2.206$; $df=28$; $p=0.036$). The bond strength values between the titanium alloy surface and the resin cement decreased after thermocycling.

Uniterms

Titanium alloy; resin cement; bond strength

Introduction

Titanium-based alloys have been widely employed in dental implants because of their excellent biocompatibility and resistance to corrosion. The development of titanium casting technologies allowed the prosthesis fabrication from titanium alloys. Titanium presents several advantages as a prosthetic material, such as excellent biocompatibility, good mechanical properties and low density [8, 15, 24, 25, 29].

Utilization of titanium as a metallic alloy for prosthetic devices requires a stable bond between metal and resin cement. The bond of resin compounds to metallic alloys has been improved during the past decades and several techniques have been developed in an attempt to achieve a stable bond. Sandblasting the metallic alloys with aluminum oxide is commonly employed for surface cleaning and a proper retentive topography, with a consequent increase in the adhesive bond [1, 12, 17].

In vitro simulations have evaluated the bond between resin cements and titanium and other metallic alloys [11, 13, 21, 25]. The stability and durability of certain adhesive systems under aging conditions may have an important influence on the absolute bond values. *In vitro* procedures for aging simulation of adhesive bonds may be applied, such as thermocycling, before bond strength testing. Whereas some authors observed that the adhesive bond between metallic alloy and resin cement is not affected after thermocycling [9, 12, 14], others found a decreased bond after aging of the specimens [6, 8]. With the widespread utilization of different luting cements, the influence of thermocycling on the bond durability of resin cements to titanium becomes fundamental.

The aim of this study was to evaluate the effect of thermocycling on the bond strength between resin cement and titanium alloy with silica coating.

Materials and methods

Six machined acrylic blocks measuring 4mm in length, 4mm in width and 4mm in thickness were employed as patterns for casting of six blocks from titanium alloy (Rematitan, Dentaurum, Ispringen, Germany). One face of each metallic block was planed with sandpaper grit 300, 600, 800, 1000 and 1200 in order to provide a flat and uniform surface. Thereafter, an impression of each metallic block was obtained with additional silicone (Express, 3M ESPE, St Paul, MN, USA) to create a mold for the fabrication of composite resin blocks with the same dimensions (Z100, 3M ESPE). Following block preparation, all metallic blocks had one of their faces submitted to 20 seconds of aluminum oxide sandblasting (particle size 110µm) at 2.8bars with a standard distance of 10mm with the CoJet-Sand system (3M ESPE). The initial sandblasting was perpendicular to the block surface and was accomplished with aid of a sandblasting machine (Micro Etcher™, Danville Engineering, Danville, California, USA). This was followed by further sandblasting with silica oxide (particle size 30µm) for the formation of a thin silica layer. Sandblasting was completed with application of a thin silane layer (Rocatec-Sil, 3M ESPE), which was left to dry for 5 minutes.

After the etching procedures, the metallic blocks of each group were luted to composite resin blocks with resin cement (Panavia F, Kuraray CO., Tokyo, Japan), prepared according to the manufacturer's instructions and applied on the surface of both blocks. The assembly was positioned on a Gutemberg press and a load (0.750kgf) was applied perpendicular to the adhesive bond for 10 minutes. Before complete curing, the excess cement was removed with proper instruments, followed by light curing (XL 3000 - 3M ESPE) with a light intensity of 450mW/cm^2 for 40 seconds in each margin and the application of an oxygen inhibitor (Oxyguard, Kuraray CO., Tokyo, Japan) for 5 minutes in all interfaces. After the time recommended for cementation, the assemblies were washed with air-water spray and stored in distilled water at 37°C for 24 hours.

This led to the creation of two groups of samples with three assemblies of metallic blocks cemented to resin blocks, which were attached by cyanoacrylate adhesive (Super-Bonder, Henkel Ltda., Itapevi, SP, Brazil) to a cylindrical acrylic base connected to a machine especially designed by Andreatta Filho et al (2003)[1] for sectioning with carborundum discs measuring 0.15mm in thickness and 22mm in diameter, to the nearest 0.1mm.

Initially, the assemblies had approximately 0.5mm of their external faces sectioned, to avoid any interference from the excess cement on the bond strength values. Thereafter, sectioning was performed to achieve slices measuring 8x4x1mm.

Each slice was positioned and connected with the 8x1mm surface turned towards the acrylic base, for further sectioning and final completion of the specimens.

This allowed the creation of five specimens from each assembly of blocks, with the following characteristics: (a) rectangular shape; (b) quadrangular (symmetrical) transverse section; (c) adhesive surface area of 1±0.01mm2; and (d) length of ±8mm.

The specimens were then divided into two groups:

Group 1 – fifteen specimens stored in distilled water at 37±2ºC for 24 hours.

Group 2 – fifteen specimens submitted to 2,700 thermal cycles (Etica, Vargem Grande Paulista, SP) in water at 5ºC and 55ºC with a dwell time of 30 seconds in each bath.

The specimens of each group were attached to a device by cyanoacrylate adhesive for microtensile testing, on which they could be positioned parallel to the axis of application of tensile force with a view to reduce possible lateral forces on the adhesive area. Each specimen attached to the device was submitted to tension in a universal testing machine (Model DL-1000, EMIC - Equipamentos e Sistemas Ltda, Sao José dos Pinhais, PR, Brazil) at a crosshead speed of 1mm/min up to bond failure.

The bond failure values (MPa) achieved in the microtensile testing were submitted to the Student t test for independent samples (unpaired test), $p<0.05$.

Results

The bond strength values displayed the same variability (Levene's Test, $p=0.798$) and their mean tensions were statistically different ($t=2.206$; $df=28$; $p=0.036$). As indicated by the Student t test for independent samples (unpaired test, $p<0.05$), the group not submitted to thermocycling exhibited better bond strength performance than the group submitted to thermocycling (Table 1).

Discussion

Many studies have been conducted to verify the bond strength between titanium alloys and resin cements, with variations in the surface treatment [13, 15, 24, 28, 29] cements employed [25] and the effects of thermocycling and mechanical cycling with a view to assess the adhesive durability [8, 9].

This study observed the effect of thermocycling on the microtensile strength of the adhesive bond between the resin cement Panavia F (Kuraray, Japan) and the titanium alloy Rematitan (Dentaurum, Germany), etched with the CoJet system (3M ESPE). Several methods may be employed for evaluation of the bond strength between substrates such as dental structures and metallic, resin or ceramic materials. Many studies have been employing the shear strength test for evaluation of the bond strength between metallic alloys and substrates such as resin cements [25, 29] or indirect ceramics and composite resins with variations in the adhesive systems [8, 24, 29]. However, the shear strength test should not be considered an ideal mechanical test for that purpose, since it leads to non-uniform distribution of the stresses in the adhesive area, with maximum occurrence of tensile forces close to the point of load application, therefore affecting the substrate more than the adhesive interface itself [5, 20, 27].

The tensile test has also been employed in some studies [12, 14, 19] and is able to provide information on the global bond strength of adhesive materials, even though it has some restrictions related to the difficulty of aligning the samples in the testing machine and the tendency towards unequal distribution of the tensions on the interface [4]. On the other hand, the microtensile test suggested by Sano el al (1994) [20] assesses the bond strength of specimens with reduced adhesive areas ranging from 0.3 to 1.5mm^2. With the reduction in the testing area, fractures occur basically in the adhesive interface, since the specimens will have less structural defects such as surface irregularities, presence of bubbles and variations secondary to the procedures of application of luting agents. Moreover, the bond strength values are higher when compared to tests employing larger specimens. Other advantages of the microtensile test are the possibility of achievement of several samples from a single substrate and easier analysis of the surfaces in scanning electron microscopy [18]. In the present study, the bond strength values were higher compared to investigations employing other testing methods [15, 8, 28] with small standard deviation for both groups (Table 1).

Resin cements have been enhanced in the past decades and currently have some advantages, such as better physical properties, less deleterious effects to the pulp, less post-operative sensitivity, less solubility and better marginal adaptation when compared to other cements, such as zinc phosphate and glass ionomer cements [1, 2, 11, 16, 30]. In the present study, the resin cement Panavia F was employed after surface treatment of the titanium alloy with the CoJet system. Many studies have been demonstrating better results for the Panavia applied on metallic alloys when compared to other cements [12, 14, 30]. The Panavia F cement

Table 1 – Bond strength, formation of groups after the *t* test (*Student*)

Groups	Mean (standard deviation) – MPa	Homogeneous groups *
Without cycling	44.50 (±8.41)	a
With cycling	38.03 (±7.63)	b

* Means followed by different letters are statistically different

contains a modified MDP in its composition and presents better bonding to aluminized surfaces because of the occurrence of chemical bonding between MDP and alumina, since the phosphate ester groups of these cements are directly bonded to metallic oxides. Thus, the presence of chemical bonding between MDP and alloys sandblasted with aluminum oxide is suggested [14, 15, 23, 24].

Many surface treatments have been advocated for titanium alloys with a view to increase the bond strength, such as application of acidic compounds, primers and adhesives, and sandblasting. The sandblasting of titanium influences the bond strength, since it removes surface debris and leads to formation of an oxide layer that yields physicochemical changes in the surface, affecting the surface energy and the wetting ability. Moreover, sandblasting allows the remaining aluminum particles to chemically bond to cements containing MDP in their composition. Many authors have been reporting good results with utilization of the Rocatec system (3M ESPE, Germany) on the surface of metallic alloys [15, 17, 19, 24, 28]. According to Robin et al (2002) [19], the Rocatec system combines the formation of a rough surface due to sandblasting with 110μm aluminum oxide and further blasting with silica coating with the application of silane on the sandblasted metallic surface. As indicated by Kern e Thompson (1994b) [13], the alumina particles are firmly attached to the titanium surface and the silica particles are also deeply attached. By utilization of an EDS microscope after the second sandblasting and ultrasound cleaning, the authors observed the presence of 20% of alumina, an important compound affecting the bond to the Panavia F cement. Even though Lim el al (2003) [15] have indicated problems such as contamination and distortion of the prostheses after sandblasting, Kern e Thompson (1994a) [12] evaluated the volume of titanium lost after sandblasting and concluded that abrasion was not critical for adaptation of the restorations. The CoJet system employed in the present study is a treatment method similar to the Rocatec system: a) silica coating; b) silanization with ESPE-Sil. This system was designed to allow intraoral silicatization of ceramics and metal for the direct repair of porcelain fused to metal and metal-free fractured crowns [7, 10]. The bonding mechanisms assigned to the Rocatec and CoJet systems are identical, since both employ silicatization followed by silanization. However, the CoJet system may be regarded as a more versatile method for clinical application (assisted silicatization), whereas the Rocatec system is a larger laboratory system. Moreover, the CoJet system is also indicated for intraoral repair of indirect restorations, which is not feasible with the Rocatec system.

According to Tjan et al (1980) [26] and Taira el al (2000) [25], the durability of bond strength depends on factors such as bonding of the interface between resin cement and metal, physical properties of the cement and linear thermal expansion coefficient of the cement and metal. There are many ways to simulate the aging of adhesive bonds *in vitro*, such as storage in distilled water or artificial saliva for different time periods or thermocycling. Many investigations make use of thermocycling for evaluation of the bond strength of metallic alloys, with conflicting outcomes. Some authors did not observe statistically significant differences in the bond values after thermocycling. Kern e Thompson (1994a,b, 1995) [12, 13, 14] evaluated the effect of different surface treatments and the influence of thermocycling on Ni-Cr and Co-Cr alloys and observed similar bond strength for samples submitted to sandblasting or application of the resin cement Panavia either at the onset or after 37,500 cycles. According to the authors, the silica layer left by blasting is not influenced by water and yields a water-resistant bond between silane and resin. Moreover, in the samples cemented with Panavia, there was a bond between MDP and the aluminum from sandblasting, which was not reduced after thermocycling. However, an increased bonding could be observed after 7,500 cycles, with reduction at study completion. GaRey el al (1994) [9] observed a small decrease in the retention of cemented titanium implants after thermocycling, yet with no statistically significant difference from the control, even though the authors conducted just 400 cycles. Robin el al (2002) [19] also did not observe any difference before and after thermocycling with utilization of noble alloys and the Rocatec system.

In the present study, thermocycling negatively influenced the bond strength values between the titanium alloy and the resin cement. The present results corroborate other investigations [6, 8, 24, 29]. The decreased bonding may be explained by several factors According to Kern e Thompson (1995) [14], the water absorption due to thermal variations may weaken the bonding between the resin matrix and the fillers within the resin cement. Moreover, resin cements may undergo hydrolysis after contact with water.

Another important aspect is the linear thermal expansion coefficient of the materials. The differences in this coefficient between metal, resin matrix and fillers lead to different occurrences of shrinkage and dilation, yielding material fatigue and ultimately leading to bond failure [3, 26].

Another aspect that may have influenced the decrease in the bond strength values was the dimension of the specimens, since Shono et al (1999) [22] observed that specimens with smaller adhesive areas are more susceptible to the action of storage in aqueous solutions.

The 2,700 cycles employed in thermocycling in the present study is clinically equivalent to approximately 2.5 years. The bond strength between titanium and the resin cement was reduced in this period; however, the bond strength values after thermocycling remained high and probably proper for clinical application.

Conclusion

The bond strength values between the titanium alloy surface and the resin cement were reduced after thermocycling.

Resumo

O objetivo desse estudo foi avaliar o efeito da termociclagem na resistência adesiva entre uma liga de titânio tratada com depósito de sílica e um cimento resinoso. Seis blocos de titânio (Rematitan, Dentaurum) foram fabricados com dimensões de 5x6x6mm. Uma das faces medidndo 5X6mm foi condicionada com o sistema CoJet System (3M ESPE, deposição de silica) e cimentada com Panavia F (Kuraray) a outro bloco identico de resina composta Z100 (3M ESPE) sobre constante carga de 750g. Os seis corpos-de-prova formados pela liga de titânio, cimento e resina composta foram seccionados e 30 amostras foram obtidas medindo 10x1x1mm, com área adesiva de $1mm^2 \pm 0.2mm^2$. As amostras foram divididas em 2 grupos (n=15): G1 (grupo 1) – estocadas por 1 dia em água destilada a 37°C; G2 (Grupo 2) – termociclagem (2700 ciclos, 5°C – 55°C, tempo de cada banho: 30s). O teste de microtração foi realizado em máquina de teste universal (EMIC) com velocidade de 1,0 mm/min. Médias de resistência adesiva (MPa) e desvio padrão foram de 44,50±8,41 para G1 e 38,03±7,63 para G2. Os dados foram analisados pelo o teste t Student ($p<0,05$). O teste estatístico indicou diferença estatisticamente significante entre G1 e G2 ($t=2.206$; $gl=28$; $p=0.036$). A resistência adesiva entre a liga de titânio e o cimento resinoso diminuiu após a termociclagem.

Unitermos

Liga de titânio; cimento resinoso; resistência adesiva

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