The Impact of Sandblasting and Primer on the Bond Between Cements and Metal Framework

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Acta Stomat Croat
2005; 377-385

Summary

Disintegrating the adhesive bridge from the abutment is one of the most uncomfortable consequences for the patient, and especially for the therapeutist, as it arises a question on the justifiability of the applied method. The success of these appliances depends on the design of the metal skelet, the strenght of the cement itself, as well as its bonding with the etched enamel and the dental alloy. However, because of the weak affinity of one material to the other and higher strain at the interface cement-alloy, the bond cement-alloy is weak.

The aim of the undertaken investigation was to identify which combinations of sandblasting and primer achieve maximum torque strength values of the bond between cement and corresponding Ag-Pd part of sample.

In order to minimize the number of variables in the experiment, so that the strength of the bond cement-alloy represents a real indicator of the efficiency of the cement bond on the metal sample, the metal-cement-metal test model was used. 180 completely equal metal samples were tested, divided in groups and subjected to various methods of conditioning. Bonding strength values obtained through various combinations of mechanical-chemical type of bonds of three kinds of cement with Ag-Pd alloy were tested, while structural investigations of the break area were accomplished by means of the polarizing microscope and the microanalyzer of the view.

The bonding strength values of the cement-alloy bond were determined by measuring the load at the instant of the bond break. The results were statistically analyzed by three-way variance analysis, and then processed by one-way variance analysis and/or compared by means of the Tukey test.

The active group of the V-Primer and the functional monomers of Panavia 21 and Super-Bond improved the characteristics of the bond of adhesive cements on the semi-precious surface, sandblasted by abrasives, while the worst results and adhesive breaks characterise ABC cement.

Key words: *sandblasting, primer, cement, cement-metal bond.*

ORIGINAL SCIENTIFIC PAPER
Received: June 3, 2004

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Introduction

One of the major challenges of modern dentistry is undoubtedly how to solve the problem of one or two missing teeth in the frontal or lateral region exclusively by prosthodontical means. Removable and fixed appliances have been tried, but the problem of retention and stabilisation has remained an obstacle, or the aesthetics and functionality of the solutions found have been compromised. Experience implies that adhesive bridges are often the optimal solution. However, during their production, narrowed indication, precise work, and the possibility of weakening of the bond at the interface between the tooth and the alloy of adhesive bridge wings must be taken care of.

The bond between the cement and the tooth enamel is a mechanical bonding that, on the one hand, depends on the size of the basic area, and on the other on the retentions (secondary enlargement of the surface) by means of the tooth preparation and the etching technique. However, the cement-alloy interface is under the direct impact of chewing forces, humid environment, successive tension due to temperature variations in the oral cavity, polymerisation shrinkage, and differences in the thermal coefficient of expansion of different materials (1). A break usually occurs in the contact zone of the cement-alloy, which is always considered a critical part of the retention of the adhesive bridge system (2, 3).

In order to avoid weakening of the tooth-alloy interface, it is necessary to ensure greater bonding strength of the cement-alloy interface than the strength of the cement-enamel and cement-cement interface (4). In this respect, efforts have been undertaken to optimise the interface by various techniques of conditioning the metal framework surface and primers. Various treatments of the dental alloy surface have been developed as a precondition for successful bonding of cements to abutments. However, most of such methods are insufficient due to difficult control of the final stage of the preparation of the metal basis and sensitivity of the treatments which can be applied only on certain types of alloy . In addition, as many variables have an impact on the final result, and as the actual mechanism of bonding of the cement to the metal framework uses two hardly comparable basic bonding systems (mechanical and chemical) (5-7), the success of these treatments is difficult to predict. The problem is even more complex, because there are at least 250 alloys and about 30 cements available on the market, resulting in too many possibilities for combining them (8).

Aware of the fact that no means of bonding adhesive bridges is ideal, further investigations are under way, with the goal of discovering the best solutions. Efforts have been undertaken to simplify the technique of production of adhesive bridges and create the most useful bonding surface. The investigations are aimed at improving the bond with the dental base, extending the clinical application, and improving the durability of appliances, and also to lower the cost of expensive devices, as well as to eliminate the potential danger of depurifying the conditioned metal surface, with a view to ensuring the highest possible bonding strength values.

The goal of the experimental investigations, with the results presented in this paper, was to identify the values of the bonding torsion strength of three types of cement and the corresponding samples of the Ag-Pd alloy, after various sandblasting treatments (abrasive and polisher), as well as conditioning (with primer and without primer), and finally, to check the hypothesis that sandblasting and conditioning do not significantly affect the strength of the cement - Ag-Pd alloy interface.

Materials and method

In this experiment dental alloy Auropal S (Ag-Pd) (Aurodenta, Zlatarna Celje), adhesion promoter V-Primer (VBATDT) (Sun-Medical, Kyoto Japan), and three types of cement - Panavia 21 - MDP (Kuraray, Osaka, Japan), Super-Bond C&B - 4-META (Sun-Medical, Kyoto, Japan) and ABC cement (Vivadent, Schaan, Liechtenstein), as well as three different types of corund sand of the same diameter - Cobra, Sanita and Rolloblast (Refrent, Hilzingen, Njemačka), were used.

(1). Wax samples

Following the directions of the manufacturers, 180 samples of Ag-Pd alloy were created. Blue inlay wax (Inlay Wax, Galenika - Zemun, SCG) was input by dropping it into wetted, polished, chromised metal, which was round in shape with diameter d2 = 11.3 mm, in order to obtain mutually equal samples(Figures 1 and 2-a) (9). Once the wax had cooled down, on the back of each wax sample, mechanical retention in a cross shape was planted, thus also enabling better attachment and centering of the metal sample on the metal handler.

(2). Investing and casting

The obtained wax samples were laid into the investing material: Neoduroterm (Bayer -Leverkusen, Germany), following the directions of the manufacturer. The prescribed ratio was applied - 30 grams of water and 100 grams of powder, mixed in the vacuum device Vakumat (Zlatarna Celje, Slovenia). The investing is done in accordance with the manufacturer's instructions on the investing material. Preheating and burning was done between 12 to 24 hours after investing, while casting was done in the device for centrifugal casting CF - 2 (Zlatarna Celje, Slovenia). Ten wax samples were cast into each cylinder and the new alloy was used for each sample.

Once the metal samples had cooled down to room temperature, they were taken out of the flask and sandblasted in the sandblaster PK-N (Zlatarna Celje, Slovenia) with circular flow of the corund sand of 250-micron particles, so as to remove the investing material. By means of cutting pincers, samples were removed from the casting channels and treated by the carbide milling machine, Drendel + Zweiling (Diamant, Berlin, Germany).

Metallic samples were cleaned by a metal comb (brush?) and acetone and by means of mechanical retention and the bond (Tikso K-10 - single-component cyano-acrilate adhesive) (Henkel, Wien, Austria) attached to the metal handler (Figures 1 and 2-b). Each sample was cleaned for at least three minutes, washed in running water, dried with hot air and preserved until the testing time.

(3). Treatment of the metallic sample surfaces

Parallelism of the metallic sample working surfaces was ensured through levelling by means of sandpaper, type 400, on the milling bar, while sandblasting of the metallic surface was accomplished in the sandblasting device Basic - Duo (Refrent, Hilzingen, Germany) with use once of corund sand of 110-micron particles under the following conditions: sandblasting pressure was 0.4 MPa at a distance of 5 mm from the gusher, during 15 seconds and perpendicular with respect to the bonding surface.

In order to minimize the number of variables in the experiment, and also to enable bonding strength values to realistically represent the efficiency of bonding cement to the alloy, the test model metal-to-metal (10) was used. Ninety coupled samples were divided into three groups of 30 couples each, depending on the method of sandblasting the metal surface. (Table 1). The method of micromechanical retention was used, i.e. Cobra, Sanita abrasives and Rolloblast polisher with particles diameter of 50 microns. Cobra is a pure abrasive, Sanita is a 1:1 mix of abrasive and glass balls, and is insignificantly coarser than the Roloblast polisher, which is made of glass balls. The first group of samples was sandblasted with Cobra abrasive, the second with Sanita abrasive and the third with Rolloblast polisher.

The samples were then brushed with a clean, sharp brush-pencil and sorted into a carrier, specially made for this occasion. Care was taken to ensure that the activated surface of the metallic sample did not get polluted. For a period of 15 seconds a thin layer of V-Primer was placed by a clean brush onto half of the sandblasted samples (15 pairs), and the rest were not treated (15 even control samples).

V-Primer consists of 0.5% of the 6-(4-vinylbenzyl-n-propyl) amino-1,3,5-triazine-dithiol or 2.4-dithione tautomer in the 95% acetone .

(4). Investing of cement and bonding of samples

Because of the test sample tube centring and hardening of the cement, the whole procedure was done in an appropriate flask (Figures 1 and 2-c), where firstly the handle with the sample and polyurethane handler stuck together, was mounted, and then, on the opposite side of the flask, another handle, stuck together with the even sample, was inserted. Handler space with thickness of about 25 microns and central aperture of about 5 mm was used to determine the thickness of the cement layer and the size of the contact surface of the final bond. Three cements were mixed according to the manufacturer's directions and used for cementing the metallic samples (5 pairs).

One pair of screws on the centering device were (tuned (turned?) so holding the first handle with the sample stuck together with it and the mounted handler at the centre of the bond in the block, while the other handle with the even sample stuck together with it, was kept in contact with the handler. The contact obtained was marked by a thin felt-tip pen at the end of the other handler next to the margin of the device for cementing and centering samples. The handler and the second handle with the even sample stuck together with it were removed from the centering device and the mixed cement put onto the conditioned surface of the sample in the area of the handler aperture. The handle without the handler was then returned to the marked position in the cementing and centering device. In that way a 25-micron thick cement layer was achieved.

ABC cement is based on urethane dimethacrylate, and is a combination of a special microfiller and metal primer, which contains phosphate groups. Equal quantities of the basic paste and catalyst were mixed in the course of 30 seconds with a plastic spatula, until a cream-like paste was formed. Firstly, a thin layer of primer (Contact Cement Primer) is applied by a paintbrush on the metal surface.

Super-Bond cement consists of three components: the initiator is partially oxidized tri-n-buythl-borane derivative, the monomer is 4-methacryloxyethyl trimellitate anhydride in methyl methacrylate (MMA) (4-META), while the powder is a mixture of 80% finely pulverized poly (methyl methacrylate)(PMMA) and 20% coated titanium dioxide. In the course of 15 seconds, one drop of catalyst and 4 drops of monomer were added into a container and cooled down to a temperature of 12 to 14 degrees Celsius. One part of the activated fluid is applied with a paintbrush onto the dried surface of the metal framework, while the rest of it is mixed with a plastic spatula for 30 seconds with two teaspoons of powder until a cream-like paste is formed.

Panavia 21 is BiS-GMA based cement that contains acide phosphate ether type monomer MDP (10-Methacryloyloxydecyl dihydrogen phosphate), activator - aromatic triple amine - DMPT (N,N-dimethyl-p-toluidine) and initiator BPO (benzoylperoxide). It is equipped with enamel and dentin primer (ED Primer) which contains HEMA (2-hydroxyethyl methacrylate) and salicylic acid derivative 5-NPSA (n-methacrylolyl 5-aminosalicylic acid). A slight turn of the handle in a clockwise direction all the way until it clicks was used for pressing out the same quantities of paste (Universal and Catalist), which were mixed with a plastic spatula for 20 to 30 seconds until a cream-like consistency was formed.

Complete hardening of Panavia 21 and ABC cements around the bond of samples is more difficult in the presence of oxygen, so that anaerobic conditions were achieved putting the layer of the polyethylene glycol gel (Oxyguard gel - Kurary, Osaka, Japan), while before the application of the Super-Bond, the alloy surface was oxygenized for two minutes by (drowning (rinsing?) the sample in 10% water solution of potassium permanganate.

The device holding the prepared samples enabled centering and cementing of samples under constant load, but not their mutual contact, while the static load, directed on the upper lever of the centering device, provided constant pressure of 1 kg/cm2. After hardening, the surplus of cement from the edge of the bonded metal samples was removed by a sharp metal milling machine.

(5). Break testing

A test sample (Figures 1 and 2-d) was mounted in the appropriate apertures in the device (Figure 3), where one end is made firm by a screw, and at the other end there is a lever of ten centimeters in length transferring the force. The resistance to torsion was measured in a universal testing machine (Zwick 1439, Ulm, Germany), while the speed of force which breaks the samples was 0.5 cm/min.

The bonding strength value of the cement-alloy interface (i.e. between the cement and the metal part of the sample) was expressed by the value of the load at the instant when the bond location disintegrated. The force (expressed in MPa) needed to break the sample was registered as a break on torque moment, which was calculated from the known sample area, lever length and force (9).

The strength of the cement-alloy interface under the torque moment is proportional to the force, so that all comparisons could be undertaken on the basis of the values of the force alone.

On three randomly selected samples of an each combination, by means of a polarizing microscope (Nikon Microphot, Tokyo, Japan), the break at the bond cement alloy was qualified as: cohesive (within cement), adhesive (between cement and alloy) and combined-mixed (remaining particles of cement on the alloy surface), while the percentage of the residual cement on the interrupted surface of the samples was identified with a microanalyser (JXA 613 Superprobe, Tokyo, Japan). When more than 75% of the bonding area was pure metal it was considered that the sample breaks adhesively, while the samples were considered to break cohesively when more than 75% of breaks were within the cement. Mixed break was considered between 25% and 75% adhesive and cohesive breaks.

(6). Statistical analysis of the measurements results

Analysis of the measurement results is based on the variance analysis. The results of the torque moment measurements were subject to factorial analysis of variance (three-way, two-way and one-way classification) (11), and the statistical significance of results was determined by means of the Tukey test (12). The differences of the arithmetical means which are greater than the Tukey-Kramer intervals were considered statistically significant ($p<0.05$). The strength of the cement-alloy bond was a dependent variable, while sandblasting, cement and primer were the changing conditions.

In this paper, the data systematisation and variance analysis follows the Cohen-Holliday method (13).

Results

The results of measurements and statistical analysis of data are presented tabularly . Arithmetical means and standard deviations are presented in Table 1, while the results of the three-way and one-way variance analysis are presented in Tables 2-5. In Table 6 breaks and the percentage of the remaining cement on the metal sample are classified.

Three-way variance analysis showed that the method of sandblasting, type of cement and primer significantly impact the bonding strength values ($p<0.05$). The variable having maximum F value is primer, followed by cement and primer. Two-way mutual dependence between cement and primer differs significantly ($p<0.0001$), while two-way (sandblasting and primer, and sandblasting and cement) as well as three-way mutual dependence (sandblasting, cement and primer) show little difference ($p>0.05$) (Table 2). Tukey intervals for the comparison of significant arithmetical means, at the significance level of 0.05, are: 1.6 MPa between sandblasting and cements, 1.3 MPa between primers (i.e. without primer and with primer) and 2.8 MPa between cement and primer.

The results are then statistically analysed by one-way variance analysis and/or compared on the basis of the Tukey test (Table 3). Before application of primer, bonding strength values were in the range between 28.0 to 38.0 MPa, and can be sorted into two groups: (a) with the range from 34.2 to 38.0 MPa, and (b) with the range from 28.0 to 34.2 MPa (Table 4). The samples that were sandblasted by means of Rolloblast polisher show statistically significant lower bonding values with respect to Cobra and Sanita abrasives ($p>0.05$), while Panavia 21 and Super-Bond have considerably superior bonding strength values compared to ABC cement ($p<0.05$). The best results were achieved through sandblasting with abrasives and Panavia 21 cement (Group a)($p<0.05$), and the poorest with ABC cement, regardless of sandblasting (Group b) ($p>0.05$). Bonding strength values of Panavia 21 cement and Super-Bond significantly ($p<0.05$) differed after sandblasting with Sanita abrasive (Group a and Group b).

The resulting values significantly increase after the application of primer ($p<0.05$), and range from 28.4 to 46.2 MPa. Tukey-Kramer intervals are sorted into three groups: from 42.2 to 46.2 MPa (c), from 39.8 to 42.2 MPa (a), from 28.4 to 29.8 MPa (b) (Table 5). Samples bonded with Super-Bond and Panavia show statistically significantly better results with respect to ABC cement ($p<0.05$), while sandblasting with the Rolloblast polisher is significantly worse with respect to Cobra and Sanita abrasives ($p>0.05$). Bonding strength values achieved by means of the Rolloblast polisher sandblasting and two adhesive cements (Super-Bond and Panavia 21) do not significantly differ from the samples which were sandblasted with abrasives (Cobra and Sanita), and so Panavia 21 cement (group a)($p>0.05$) was used. The best results have been achieved by means of sandblasting with abrasives bonded with Super-Bond (Group c) ($p<0.05$), and the worst with ABC cement regardless of sandblasting (Group b) ($p>0.05$). Bond strength values mutually differed ($p<0.05$) after sandblasting with Sanita abrasive and bonding by means of Super-Bond and Panavia 21 cement (Group c and Group a).

By investigating the incidence of failure and the percentage of residual cement on the metal sample, it was determined that the samples of Ag-Pd alloy without primer break adhesively (ABC - 100%, Super-Bond - 71.7% and Panavia 21 - 60%), but after conditioning - cohesively (Panavia 21 and Super-Bond - 56.7%) and adhesively (ABC - 96.7%). All samples of Ag-Pd alloy sandblasted with Rolloblast polisher, regardless of cement and primer, break adhesively (96.7% and 91.6%), while the samples of alloy without primer, sandblasted by Cobra and Sanita abrasives and bonded by Panavia 21 and Super-Bond cements, break adhesively (66.7% and 68.3%), and when the primer is used, cohesively (60% and 53.3%) (Table 6).

Discussion

Within the oral cavity, fixed prosthetic appliances are exposed to the combined influence of shear forces, compression and stretching, and consequently in this study the method of torque testing was used (14), and the metal-to-metal testing model, since the problems with controlled testing are far less than those associated with enamel-cement-alloy bonding interface. A total of 18 combinations of samples were analyzed (three types of sandblasting, three kinds of cement and one primer - without the primer and with the primer), and the validity of the results was evaluated against the informal standard applying to the interface of adhesive cements on etched enamel (7-20 MPa) (4) and sandblasted alloy (10-40 MPa) (2). Three-way variance analysis rejects the null hypothesis of equal arithmetic means for primer, cement and sandblasting, which implies that the type of sandblasting, kind of cement and primer significantly influence the values of the bonding strength of the cement bond on the alloy.

Based on the results of this study, it can undoubtedly be concluded that abrasives (Cobra and Sanita) are significantly better than the Rolloblast polisher ($p<0.05$), and the mixture of abrasives and glass balls (Sanita) weaker with respect to pure abrasive ($p>0.05$) (Tables 3 and 4). By making micromechanical retention, Cobra and Sanita abrasives improved the bonding, while the Rolloblast polisher reduced it by 30%. The surface treated by Rolloblas was irregular, although smooth and grey with characteristic spots, and hardly forming any retention. One could say that glass balls smooth the alloy surface while abrasive roughens it. Obviously, there is a direct relationship between maximal bond strength values and the maximal number of cohesive breaks (66.7% and 68.3%), as well as between the poorest results and adhesive breaks (96.7%), (Table 6). This is in agreement with the results of other investigations (15,16), and implies that on all occasions it is necessary to correctly sandblast and use the well known diameter and type of corund sand, as otherwise the dental alloy could be entirely roughened and, consequently, cause early de-cementing of the wings of the adhesive bridge.

Today, we can only speculate on the processes which happen on the sandblasted surface. The sandblasting enlarges the surface of the adherent for chemical bonding with activated functional groups of adhesives, it improves the capacity of wettability, and/or changes the structure of its surface, yet it is necessary to improve the chemical bonding of cement and particles of corund, as well as the bonding of the particles of corund on the surface of the metal structure (17, 18).

It is universally accepted that the bonding at the interface of two different materials can be achieved through physical or chemical means. However, it is usually impossible to draw a sharp line between the two. The mechanical component of retention makes a distinction between the geometrical (which can be matematically calculated), real (the result of microroughness), and active (wetting) bonding surface, and the chemical component or specific adhesion is assured through the inter-molecular or chemical forces of bonding, and is defined by the chemical structure of adhesives and adherents (19,20). However, it is universally accepted that the chemical adhesion is the most important part of the bonding mechanism (21), which has also been confirmed by the results of this research.

Differences in bond strength values of the three cement bonds with the metal part of the sample are statistically significant ($p>0.05$), and can be explained by the fact that adhesive groups within cements show different affinity to the sandblasted surface of the Ag-Pd alloy, and also that physical and chemical changes in the cement and outside factors can be the cause of a weaker bond on the interface surface. The strength of the adhesive bond between cements and Ag-Pd alloy decrease if the following is applied: phosphate ester group of the Panavia 21 cement (bonded the best way), 4-META group of the Super-Bond (bonded well) and phosphate group of the metal primer of the ABC cement (weakly bonded).

The samples of Ag-Pd alloy, bonded by nonadhesive ABC cement, provided the weakest bonding values and 100% of adhesive breaks, regardless of sandblasting (Tables 4 and 6). This is in accordance with other investigations that have confirmed the superiority of adhesive cements on sandblasted alloys (22, 23), but not in accordance with some other claims that both kinds of cements bond better on sandblasted Ni-Cr alloy (24). The reason for such poor results probably arises because of inconsistency of action of the chemically active group within the molecule of the metal primer, which has the potential of forming an ionic bond with the alloy and the covalent bond with cements. The mechanism of the action is equivalent to that of the Metal Primet primer (both are bifunctional groups), which was confirmed in a study by Tay (25). Low viscosity and apparently weak flow feature of the ABC cement consequently cause bad wettability (22), while low elastic modulus (1/4 Comspan) (26), as well as the presence of cracks, gaps and porosities at the interface cement-alloy (become the source of concentration of strain and reduction of fatigue strength) represent a possible explanation of the adhesive break (27). Greater elastic modulus of the cement distributes the strain more uniformly over the bonding surface and directs it towards the point of reduced load, consequently shrinking the cement at the point of load, while the shear strength of the bond of orthodontic cements is directly related to the elastic modulus (28). Retention of the ABC cement on the surface of the Ag-Pd alloy is determined by the value of micromechanical interlocking and the amount of metal framework wetting.

The samples bonded with Super-Bond show great variations of the results, so that the standard deviation is accordingly larger (Tables 4). Methodology of the work is more complicated, the technic is sensitive and hard to manage. The mixture of oxygenizers has to be used a couple of hours after preparation, or after 24 hours at the latest. Otherwise, potassium manganate reduces to maganese dioxide and weakens the oxygenizing effect. It is better to use a combination of the paste-paste system cement (Panavia 21), rather than the paste-liquid system (Super-Bond). In this way the possibility of influencing the measurement results due to incorrect measurement of equal parts of catalyst and universal paste, as well as due to infiltration of air-bubbles within the cement during its mixing, is eliminated (29, 30). It is well known that the air can be infiltrated into some materials, which, consequently, causes the creation of gaps between the cement and the alloy and/or within the cement layer itself, which results in weakening the bond and cohesive break (31). Back in 1988, Tanaka explained the mechanism of bonding Super-Bond cement on nonprimer Ag-Pd alloy as the ability of bonding of the functional monomer (4-META) of the cement onto the passive layer of the copper oxyde of the surface of non-precious alloys (29), which other investigations confirmed (32).

Panavia 21 cement enabled the best results, regardless of the method of sandblasting the Ag-Pd alloy (Tables 3 and 4). The functional (MDP) monomer of Panavia 21 cement bonded better onto copper oxyde Ag-Pd alloys with respect to 4-META monomer Super-Bond, and shows a high percentage of cohesive breaks (60% and 71.7%) (Table 6). This is consistent with the investigation results of other authors on Ag-Pd alloy, but without using different methods of controlling aging of the material (23, 33-35). However, after thermocycling, the bond between Super-Bond and Panavia 21 cement and the sandblasted surface weaken, even though the latter has somewhat better results. (36). Panavia 21 cement posseses the best mechanical features and greater elastic module than ABC cement (5.2 GPa - 3.4 GPa) (37). The system weight contains 72% of filler parts, and is of brittle and cross-linking structure (facilitates the uniform transfer of forces on the bonding surfaces) (23), while the Super-Bond is without a filler, and exibits a significant plastic deformation feature which has been recognized as a potential cause of cement fracture and contains long flexible PMMA chains of great molecular weight, which have weaker cross-links and absorb water, so that the concentration of the strain is distributed along the adhesive interface (33,37-40). Certainly the choice of filler in the cement can also play a role in the method of more durable cementing of the adhesive bridge, and its amount and content influence the compressive strength of the cement. However, the results of various investigations on the presence and type of filler and its impact on bonding strength values of the cement-alloy bond are questionable. According to some sources, there is no correlation between the mechanical features of cements and the bonding strength values of the cement-alloy interface (41), and according to the others, which is in line with this investigation, semiporous fillers increase the interfacial area between the organic and non-organic components, and facilitate the penetration of cement and micromechanical interlocking (42).

Groups of Ag-Pd alloy samples, where V-Primer was used, showed significantly greater bonding strength values with respect to unconditioned ones ($p<0.05$) (Tables 3 and 5). Additional step in the sense of the use of primer, ensured significantly better result than the purely adhesive cements. The best was Super-Bond and Cobra combination, somewhat worse Super-Bond and Sanita, and the worst Panavia and Sanita combination. Lower bonding values always accompanied the adhesive failure mode (ABC - 96.7%), while the best results were associated with cohesive failure mode (Panavia 21 and Super-Bond - 56.7%) (Table 6).

These findings are in accordance with the investigations of other authors who consider that the thiol primer, i.e. the active component of the V-Primer, improves the bond of adhesive cements and polymers on precious and non-precious alloys before and after thermocycling, and that storing it in a humid environment significantly reduces the bond strength (43-47). However, other investigations demonstrated opposite results for the conditions of artificial aging. Regardless of the use of V-Primer, no significant statistical differences in terms of Super Bond cement - Ag-Pd-Cu alloy bonding strength values have been noticed (45), as well as Ag-Pd-Au alloy -Super Bond Opaque Ivory wax bonding, regardless of the use of 4-META monomer (48). The authors assume that the effectiveness of the cement (polimer) - alloy bonding, depends on the interaction of the active group of the primer with the functional monomer (4-META) Super Bond, and/or the latter covers the activity of V-Primer.

In addition, the bond between Ag-Pd alloy and Viso-Gem composite is improved by means of Super-Bond cement and thiofosforic methacrylate-containing primer (49), and by combining the active group of primer and functional (4-META) monomer of the Super-Bond cement of the M-TBB epoxy connection onto Au and Ag-Pd alloys (50). By means of electron spectroscopy for chemical analysis (ESCA), the electron spectroscopy for chemical analysis, mercapta group was discovered in the thiol, which chemically bonds with palladium, and the strong connection at the interface cement-alloy is associated with possible thiol-tinon tautometric structure of the functional monomer (VBATDT) of the V-Primer (43). It can be concluded that free mercapta group of the primer chemically react with precious alloys, while 4-META monomer of the cement bonds onto the oxydes (Cr, Sn and Cu) of non-precious alloys. So, the bonding mechanism of the used primer in this investigation is equal to the above mentioned, as the active group of the V-Primer has two mercapta groups per molecule of monomer, and semi-precious Auropal S (Ag-Pd) alloy contains copper.

The poorer results of the Panavia 21 cement were caused by the incompatibility of the active group (VBATD) of the V-Primer and the functional monomer (MDP) of the Panavia 21 cement, or by the method of its hardening. TBB initiator of the Super-Bond directs shrinkage towards the adhesive interface, and the homogenized free radicals of the BPO initiator of Panavie directs shrinkage away from the surface and deeper into the cement (51). Therefore, shrinkage of the Panavia 21 cement occurs in the opposite direction from the adhesive interface, which should weaken the bond. However, during the first phase of this investigation, high bond strength values were achieved with this cement, so this citation can be excluded as a potential cause of weakening of the bond. In addition, the presence of DMPT activator and BPO initiator are important, because they help polymerization of the primer, especially on the heated surface of precious and non-precious alloys, while a higher concentration of initiators significantly improves the cement-alloy interface (50,52). In recent literature, conditioning of the dental alloy with V-Primer is not recommended when Panavia 21 cement is used (53).

The application of ABC cement lead to equally poor results obtained during the first phase of this study. This is in accordance with investigations that lead to the conclusion that after thermocycling and V-Primer treatment, Ag-Pd alloy bonded well with SB cement, which is not the case for the interface between ABC cement and oxygenized precious alloy (54).

The results of measurements of torque bonding strength values of the cement-alloy bond in this study range from 28.0 to 46.2 MPa. Non-formal standards of the bonding strength values for the interface cement-etched enamel are satisfied by all combinations of materials, while this is the case for just 5 conditioned bonding strength values for the interface between cement and sandblasted alloy. The clinically acceptable combinations of bond strength values are listed from the best to the worse as follows: Super-Bond - Cobra - V-Primer = 46.2 MPa, Super-Bond - Sanita - V-Primer = 42.2 MPa, Panavia 21 - Cobra - V-Primer = 41.4 MPa, Panavia 21 - Sanita - V-Primer = 41.0 MPa and Super-Bond - Rolloblast - V-Primer = 40.8 MPa. When the literature dealing with interface cement-alloy is considered, it is clear that that differences among the results exist from study to study. Using the universal testing machine only, it is not possible to precisely identify the exact point where the cement bond breaks or is subject to permanent deformation. Bearing in mind the imprecision of the tool for the creation of samples, i.e. the positioning of the metal parts opposite each other in the course of the cementing procedure, a likely consequence could be non-uniform thickness of the cement layer between the metal samples, which affects the final result. Thus, it is necessary to test other areas of the complex enamel-cement-alloy bonding interface, which can also be a point- -of - -failure: the bond cement-dentin, cohesive strength of cement and their mutual relationship, and finally, such obtained results complement long-term clinical investigations, which, finally is the only way to obtain reliable results.

Conclusion

Based on the obtained results of the study, the following conclusions can be made:

1. The primer, kind of cement and type of sandblasting, as well as two-way cross-correlation between the type of cement and primer, influence the strength of the cement-alloy bond.
2. Bonding strength values vary from 28.0 to 38.0 MPa without primer, and after conditioning, from 28.4 do 46.2 MPa, and chemical adhesion is a more important part of the bonding mechanism than mechanical retention.
3. Direct correlation was determined between the maximal values of the bonding strength and the maximal number of cohesive breaks, as well as between the worst results of bonding strength and adhesive breaks.
4. Cobra and Sanita corund sand sandblasting gives better results than Rolloblast corund sand sandblasting, and (non-adhesive) ABC cement displays weaker bonding values than the (adhesive) cements Panavia 21 and Super-Bond.

Acknowledgements

The author would like to express his thanks to doc. Vlado Mitković, D.D.S., Ph.D. and Jadranko Jahić, M.Sc, B.Eng. from the Mechanical Engineering Faculty of the University of Sarajevo, for their help during the technical support of this study, as well as to Prof. Vlatko Lipovac from the University of Dubrovnik, for help regarding the statistical data analysis, and, finally, to Mr. Y. Oka and the company J. Morita, for the donated material.