European Journal of Prosthodontics and Restorative Dentistry (2020) **28**, 161-171

Bond Strength Durability of Adhesive Cements to Translucent Zirconia: Effect of Surface Conditioning

Keywords

Zirconia
Bonding
Sandblasting
Self-Adhesive
Hot Acid
Piranha

Authors

Amal A. Sakrana *
(DDS, PhD)

Walid Al-Zordk §
(BDS, MSc, PhD)

Heba Shoukry ‡
(BDS, MSc)

Mutlu Özcan ^
(DDS, PhD)

Address for Correspondence

Amal A. Sakrana *

Email: amal.sakrana@yahoo.com

- * *Professor, Department of Fixed Prosthodontics, Mansoura and Horus University, Egypt*
- § *Associate professor, Department of Fixed Prosthodontics, Mansoura and Horus University, Egypt*
- ‡ *Postgraduate graduate student, Department of Fixed Prosthodontics, Mansoura University, Egypt*
- ^ *Professor, University of Zurich, Division of Dental Biomaterials, Center for Dental and Oral Medicine, Clinic for Reconstructive Dentistry, Zurich, Switzerland*

Received: 23.01.2020
Accepted: 05.05.2020

doi: 10.1922/EJPRD_2036Sakrana11

ABSTRACT

Purpose: To evaluate the influence of airborne particle abrasion, Piranha acid and hot acid etching on bond strength of zirconia with self-adhesive resin cements after aging. Also, the effect of Silano-Pen treatment on the bond strength of zirconia to resin cements. Materials and Methods: Thirty-six zirconia blocks were cut, sintered and divided into three groups (n=12); Airborne particle abrasion, Piranha acid, and hot acid etching were then treated with Silano-Pen. Each zirconia block was bonded to its corresponding composite block utilizing either Panavia SA, TheraCem or Panavia F2.0. 360 micro -tensile test bars were obtained and half of them were subjected to 10000 thermal aging cycles. Each microtensile test bar was subjected to microtensile force until debonding. Scanning Electron Microscopic evaluation was performed. Results: There was a significant difference between the surface treatments. Hot acid showed the highest mean bond strength and the lowest was Piranha acid. Panavia SA significantly improved the bond strength compared to TheraCem and Panavia F2.0. The interaction between cement and Silano-Pen was non-significant (p=.067). Under SEM analysis, hot acid treatments showed homogenous granular texture with wide distribution of porous network. Conclusions: Pre-treatment, resin cement, and aging influences the effectiveness of bonding of zirconia. Silano-Pen after hot acid improved the bonding of zirconia.

INTRODUCTION

One of the limitations for the clinical durability of zirconia is its limited ability to bond with resin cement as zirconia has a glass-free polycrystalline microstructure which is non-etchable and chemically inert with low surface energy.[1-3] Various surface treatment methods were employed to enhance bonding with zirconia, such as airborne particle abrasion, hot chemical etching, and pyrochemical silica coating. Airborne particle abrasion increases the surface wettability, surface roughness and provides micromechanical undercuts.[4] However, airborne particle abrasion results in structural defects and induction of sharp cracks that enhance radial cracking during function.[5] Piranha etching solution on the other hand is a combination of hydrogen peroxide and sulfuric acid which is a strong oxidizing corrosive agent used to remove the organic impurities and hydroxylate surfaces.[1,6] Hot chemical etching improves the surface roughness through a corrosion controlled process which is based on removing the less well arranged and high energy peripheral atoms resulting in wider grain boundaries.[7,8] The use of hydrofluoric acid at different temperature and concentrations could produce modifications in zirconia surface.[9] Moradabadi *et al*[10] studied the effect of micromechanical and chemical surface treatments on bond strength of zirconia to resin cement and concluded that the airborne particle abrasion treatment prior to acid etching process enhanced the shear bond strength. Pyrochemical silica coating depends on formation of a silica layer through the chemical reactions of silane at high temperatures.[4,11]

Contemporary resin cements are classified as self-adhesive resin cements and conventional resin cements.[12] Self-adhesive resin cement contains acid functionalized monomers and conventional methacrylate monomers. Based on the functional acidic monomers, there are two common group of cements; methacrylate monomers with carboxylic acid groups such as 4-META based cements and PMGDM based cements, or with phosphoric acid groups such as MDP based cements and BMP based cements.[13] Oyagüe *et al*[14] evaluated the hydrolytic stability of different resin cements when bonded to zirconia and concluded that water aging played an important role in the degradation of the bond strength and the bond durability is mainly dependent on the cement selection rather than the applied surface treatment.

Adhesion of the resin cement to zirconia can be studied with various testing methods such as macroshear, microshear, macrotensile and microtensile tests. It is critical that the bonding interface must be the most stressed zone, regardless of the applied test methodology. With microtensile test, the small interfacial bonding zone (1 mm^2) and small dimension shows more homogeneous stress distribution; therefore, it presents more sensitive evaluation of bond performance when specimens are aligned correctly.[15,16]

The main limitation of zirconia based restorations is the low adhesive potential and that the conventional adhesive techniques do not produce a high enough bond strength.[17,18] In order to establish a reproducible, effective and applicable bonding protocol for zirconia restorations, the objective of the present study was to evaluate the influence of airborne particle abrasion, Piranha acid etching and hot acid etching pretreatments on bond strength of self-adhesive resin cements (Panavia SA Cement Plus and TheraCem) and conventional adhesive resin cement (Panavia F2.0) to zirconia before and after thermal aging and also to investigate the effect of Silano-Pen treatment on the bond strength of zirconia cemented with self-adhesive resin cements and conventional resin cements before and after thermal aging. Thus, the null hypotheses of this study were that there would be no difference in the effect of surface pre-treatment methods on the bond strength of adhesive resin cements to zirconia with before and after thermal aging.

MATERIALS AND METHODS

Partially sintered zirconia blocks (inCoris TZI C, Sirona Dental, Germany) were cut using precision cutting machine (Isomet 4000, Buehler Ltd, Lake Bluff, IL, USA) to obtain thirty-six zirconia blocks measuring 10 mm length, 10 mm width and 6 mm thickness. All zirconia blocks were sintered in zirconia sintering furnace (Sirona inFire HTC, Sirona Dental Systems, GmbH, Germany) according to manufacturer's instructions. After sintering, the dimension of each zirconia block (8 mm length, 8 mm width and 4.8 mm thickness) was measured using digital caliper (Mitutoyo, Tokyo, Japan) to verify the volumetric shrinkage after sintering. After finishing using a zirconia-specific finishing kit (Eve Ernst Vetter GmbH, Germany), all zirconia blocks were ultrasonically cleaned in distilled water for 10 minutes, then air dried.[19] A photo-polmyerized composite (Tetric N-Ceram, Ivoclar Vivadent) was used to fabricate thirty-six composite blocks using Teflon mold (8 mm length, 8 mm width and 4.8 mm thickness). After polymerization, the bonding surface of each composite block was polished, ultrasonically cleaned and air dried. Zirconia blocks were equally divided according to the surface treatment into three main groups (n=12): airborne particle abrasion group, Piranha group (airborne particle abrasion and Piranha acid etching) and hot acid group (airborne particle abrasion and hot acid etching). Each group was divided into two subgroups (n=6) either directly bonded with no further treatment or treated with Silano-Pen (Bredent GmbH, Senden, Germany) before bonding of zirconia with resin cements. Panavia SA Cement Plus self-adhesive resin cement (Kuraray Noritake Dental, Tokyo, Japan), TheraCem self-adhesive resin cement (BISCO Inc, USA) and Panavia F2.0 adhesive resin cement (Kuraray Noritake Dental, Tokyo, Japan) were the resin cements used for bonding.

In airborne particle abrasion group, the bonding surfaces of zirconia blocks were particle abraded with 50 μm Al_2O_3 particles at 2-bar pressure for 10 s/cm^2 at a distance of 10 mm and perpendicular to the surface.[20] In Piranha group, the bonding surfaces of zirconia blocks were particle abraded as in airborne particle abrasion group. Then, the zirconia blocks were immersed in a glass beaker containing Piranha acid solution ($3H_2SO_4$:$1H_2O_2$) for 4 days.[1] The acid solution was daily replaced by fresh solution. The Piranha solution was prepared from a mixture of 96% sulfuric acid (Al Nasr Pharmaceutical Chemicals Co., Egypt) and 30% hydrogen peroxide (Piochem Co., Egypt). As regards to hot acid group, the bonding surfaces were air abraded and immersed in polyethylene beaker containing the hot chemical etching solution ($1HNO_3$:1HF) which was heated up to 100°C in water bath for 25 minutes.[21] The hot chemical etching solution was prepared as a mixture of 69% nitric acid (Honeywell International Inc., Burdick and Jackson, Seelze, Germany) and 48% hydrofluoric acid (Honeywell International Inc., Riedel-de Haën, Seelze, Germany). Finally, all zirconia blocks were rinsed with distilled water, ultrasonically cleaned in distilled water for 10 minutes and air dried. For each group, a representative zirconia block was pre-treated for SEM evaluation of the surface pre-treatments. From each group, the bonding surface of three zirconia block was subjected to Silano-Pen treatment. The bonding surfaces of nine zirconia blocks were heated with the pale blue reactive flame zone of Silano-Pen device (Bredent GmbH, Senden, Germany) according to the manufacturer's instructions. After the surface was cooled down to room temperature, the silane coupling agent (Silane Haftvermittler, Bredent, Senden, Germany) was applied using a disposable brush and left for 30 seconds.

Each zirconia block was bonded to its corresponding composite block utilizing either Panavia SA Cement Plus, TheraCem or Panavia F2.0 resin cements according to manufacturer's recommendations. The bonding procedures were performed under a static load of 1 kg to ensure a uniform cement layer.[22] The photo-polymerization was performed from all directions for each specimen according to the recommendations of the manufacturers. The ceramic/cement/composite assemblies were stored in distilled water at 37°C for 24 hours.[23] Using a cutting machine (Isomet 4000), each assembly was sectioned perpendicular to the bonding interface area to obtain microbars of 1 mm^2 thickness. For each microbar, the cross-sectional area of the bond interface was verified using a digital caliper (Mitutoyo, Tokyo, Japan). Microbars were examined under stereomicroscope (MA 100 Nikon, Japan) at 50x magnification for selection of the intact specimens that were free from any microcracks.

To study the effect of thermal aging, half of microbars (n=180) were subjected to 10.000 thermal cycles (SD Mechatronics Thermocycler, Westerham, Germany) between 5°C and 55°C with a dwell time of 30 seconds.[24] Each microbar was subjected to tensile force through a universal testing machine (3345, Instron, 2519-104, 3345, Canton, MA, USA) at a crosshead speed of 0.5 mm/min until de-bonding. The mean value of the bond strength for each specimen was calculated in Mega Pascale (MPa) using the machine software (Bluehill Lite software, Instron, MA, USA) through dividing the load at failure (N) by the adhesive area (mm^2).

Statistical analysis was perfomed using statistical software (SPSS Statistics for Windows version 22). Normal and relative (marginal) distributions of data was tested by using Shapiro-Wilk's test and Levene's test which revealed normal data distribution.

RESULTS

Means and standard deviations of microtensile bond strength values before and after thermal aging are presented in Tables 1 and 2. Table 3 illustrates the results of Post Hoc multiple pair wise comparison of the test groups. Omnibus test *(Table 4)* showed that the main surface pre-treatment, the cement type, and the aging significantly affect the bond strength ($p<.05$). Also, the interaction between the main surface pre-treatment and cement, and the interaction between main surface pre-treatment and Silano-Pen was significant ($p<.05$).

The mode of failure was predominantly cohesive within ceramic or composite for groups without thermal aging *(Table 5)*. However, after aging, the predominant mode of failure was adhesive between resin cement and ceramic with less cohesive failure.

Table 1. Mean and standard deviation of µTBS values of the test groups before thermal aging.

			N	Mean	Stand. deviation
Airborne particle abrasion	Direct bonding	Panavia SA	10	33.5	2.8
		TheraCem	10	15.2	10.7
		Panavia F2.0	10	26.6	4.5
	Silano-Pen	Panavia SA	10	30.9	4.5
		TheraCem	10	18.4	7.3
		Panavia F2.0	10	21.1	6.2
		Total	60	24.3	8.9
Piranha	Direct bonding	Panavia SA	10	22.1	3.8
		TheraCem	10	21.7	8.9
		Panavia F2.0	10	17.1	3.2
	Silano-Pen	Panavia SA	10	16.2	8.9
		TheraCem	10	22.4	5.3
		Panavia F2.0	10	21.3	1.0
		Total	60	20.1	6.0
Hot acid	Direct bonding	Panavia SA	10	27.5	6.4
		TheraCem	10	24.5	4.9
		Panavia F2.0	10	26.8	4.2
	Silano-Pen	Panavia SA	10	33.5	4.4
		TheraCem	10	24.8	2.9
		Panavia F2.0	10	27.3	3.9
		Total	60	27.4	5.1

Scanning electron microscope images showed that with airborne particle abrasion surface pre-treatment, the bonding surface presents rough surface texture with wide distribution of sharp irregular edges and grooves *(Figure 1)*. However, with Piranha acid etching, the bonding surface showed less roughness with shallow edges and grooves *(Figure 2)*. Regarding hot acid surface pre-treatment, the bonding surface showed homogenous granular texture with wide distribution of porous network with different depth and width *(Figure 3)*. The effect of Silano-Pen application was presented in *(Figures 4-5)*. Additionally, Figure 7 presented the mixed mode of failure after µTBS test.

Table 2. Mean and standard deviation of µTBS values of the test groups after thermal aging.

			N	Mean	Stand. deviation
Airborne particle abrasion	Direct bonding	Panavia SA	10	21.5	7.3
		TheraCem	10	15.4	1.8
		Panavia F2.0	10	20.6	2.5
	Silano-Pen	Panavia SA	10	20.2	4.2
		TheraCem	10	10.6	4.1
		Panavia F2.0	10	10.1	4.3
		Total	60	16.4	6.2
Piranha	Direct bonding	Panavia SA	10	23.1	5.1
		TheraCem	10	11.4	3.8
		Panavia F2.0	10	5.7	0.8
	Silano-Pen	Panavia SA	10	13.0	4.3
		TheraCem	10	19.7	7.1
		Panavia F2.0	10	17.4	3.4
		Total	60	15.0	7.1
Hot acid	Direct bonding	Panavia SA	10	25.1	4.6
		TheraCem	10	17.5	8.8
		Panavia F2.0	10	22.2	6.9
	Silano-Pen	Panavia SA	10	23.0	3.0
		TheraCem	10	20.8	5.5
		Panavia F2.0	10	23.2	4.6
		Total	60	22.0	5.9

DISCUSSION

There are several methods for achieving high bond strength of resin cements to zirconia but the achieved bond should be able to withstand the surrounding oral environment over years.[25] Recently, adhesive strategies that combine mechanical and chemical pre-treatment have been developed to improve the bond durability between resin cement and zirconia.[26] Airborne particle abrasion with aluminum oxide particles with a particle size of 50 µm is a common and simple procedure to produce micro-mechanical roughness.[3,27] Also, the use of 50 µm aluminum oxide particles has a less harmful effect of the surface topography of zirconia when compared with 120 µm aluminum oxide particles.[28] In the present study, Piranha acid etching solution was prepared according to Lohbauer *et al*[1] who observed that 96% sulfuric acid and 30% hydrogen peroxide with ratio of 3:1 for four days exhibited effective chemical preconditioning with effective hydroxylation of abraded zirconia surface. Also, hot acid etching solution was prepared according to Liu *et al*[21] who found that 69% nitric acid and 48% hydrofluoric acid with ratio of 1:1 at 100°C for 25 minutes resulted in improving the dissolution rate of zirconia grains with increased roughness. In the present study, airborne particle abrasion was applied before hot acid etching to get the advantages of both methods.

Hot acid etching pre-treatment showed the highest microtensile bond strength values (22.0±5.9 MPa) followed by airborne particle abrasion (16.4±6.2 MPa). The Piranha acid etching resulted in the lowest micro-tensile bond strength value (15.0±7.1 MPa). The rank of micro-tensile bond strength from lowest was Piranha < airborne particle abrasion < hot acid. Therefore, the first part of null hypothesis was rejected. The results of the present study were coincided with that of Casucci *et al*[22] who found that zirconia treated with hot acid solution recorded higher bond strength than those treated with airborne particle abrasion. Another study showed higher bond strength with hot acid etching than airborne particle abrasion.[29] The hot acid etching improves the surface roughness and removes the superficial ceramic layer resulting in a homogenous granular and porous texture of zirconia.[8] Studies showed that the bond strength and durability after Piranha acid etching was lower than that after airborne particle abrasion.[6,30] The inferior bond strength and durability is related to the unstable bond between the resin cement and the hydroxyl groups produced by Piranha solution.[6] Additionally, surface conditioning with Piranha solution cleans and hydroxylates the surface without formation of undercuts which are particularly important in micromechanical interlocking with the resin cement.[30]

On the contrary, Moradabadi *et al*[10] showed that the zirconia treated with airborne particle abrasion recorded higher bond strength than that treated with airborne particle abrasion and HF/HNO_3 etching at room temperature for two minutes. The addition of this etching solution to the abraded zirconia surface leading to deformation of surface roughness created by airborne particle abrasion leading to deformation of this roughness to be rounded which results in reduction of the micromechanical retention.[10] In the current study, the acid solution was performed for 25 minutes at 100°C. That temperature with hot acid etching has an essential role in molecular motion as the higher the temperature, the protons become more easily ionized leading to more acidic effect.[8] Another study reported that the addition of Piranha solution to the abraded zirconia resulted in higher bond strength than airborne particle abrasion using 110 µm particle size.[1] The possible explanation is that the aggressive air abrasion using bigger particle size could result in ditching between resin cement and zirconia surface.[31]

Table 3. Post Hoc pair wise comparison of the tested groups without and with thermal aging.

				Mean difference (I-J)	Std. Error	Sig.
Airborne Particle Abrasion	Panavia SA	Direct Bonding	Without (I)	11.97484*	3.39322	.001
			With (J)			
		Silano-Pen	Without (I)	10.66904*	3.39322	.002
			With (J)			
	Thera Cerm	Direct Bonding	Without (I)	-.14433	3.39322	.966
			With (J)			
		Silano-Pen	Without (I)	7.79259*	3.39322	.023
			With (J)			
	Panavia F2.0	Direct Bonding	Without (I)	5.92899	3.39322	.083
			With (J)			
		Silano-Pen	Without (I)	11.06271*	3.39322	.001
			With (J)			
Piranha Acid	Panavia SA	Direct Bonding	Without (I)	-1.00528	3.39322	.767
			With (J)			
		Silano-Pen	Without (I)	3.22836	3.39322	.343
			With (J)			
	Thera Cerm	Direct Bonding	Without (I)	10.30017*	3.39322	.003
			With (J)			
		Silano-Pen	Without (I)	2.65492	3.39322	.435
			With (J)			
	Panavia F2.0	Direct Bonding	Without (I)	11.43031*	3.39322	.001
			With (J)			
		Silano-Pen	Without (I)	3.94645	3.39322	.247
			With (J)			
Hot Acid	Panavia SA	Direct Bonding	Without (I)	2.36590	3.39322	.487
			With (J)			
		Silano-Pen	Without (I)	10.46069*	3.39322	.002
			With (J)			
	Thera Cerm	Direct Bonding	Without (I)	7.02535*	3.39322	.040
			With (J)			
		Silano-Pen	Without (I)	4.02524	3.39322	.237
			With (J)			
	Panavia F2.0	Direct Bonding	Without (I)	4.61783	3.39322	.176
			With (J)			
		Silano-Pen	Without (I)	4.09506	3.39322	.229
			With (J)			

Table 4. Results of four-way ANOVA-Omnibus test of variance of study groups.

Source of variation	Type II Sum of Squares	Df	Mean Square	F value	p value
Main surface treatment (A)	1535.418	2	767.709	26.671	.000
Silano-Pen treatment (B)	1.819	1	1.819	.063	.802
Cement (C)	1010.371	2	505.186	17.550	.000
Aging (D)	1693.684	1	1693.684	58.839	.000
(A) * (B)	256.909	2	128.454	4.463	.013
(A) * (C)	788.371	4	197.093	6.847	.000
(A) * (D)	69.431	2	34.716	1.206	.302
(B) * (C)	158.229	2	79.115	2.748	.067
(B) * (D)	4.112	1	4.112	.143	.706
(C) * (D)	19.004	2	9.502	.330	.719
(A)* (B)* (C)	697.073	4	174.268	6.054	.000
(A)* (B)* (D)	111.732	2	55.866	1.941	.147
(A)* (C)* (D)	257.545	4	64.386	2.237	.068
(B)* (C)* (D)	53.008	2	26.504	.921	.401
(A)* (B)* (C)* (D)	203.944	4	50.986	1.771	.138
Error	4145.015	144	28.785		
Total	89412.664	360			

Table 5. Failure mode of the study groups.

		Without aging			With aging		
		C	M	A	C	M	A
Airborne particle abrasion	Panavia SA (Direct)	2	6	2	6	2	2
	Panavia SA (Silano-Pen)	2	4	4	6	0	4
	TheraCem (Direct)	6	2	2	4	2	4
	TheraCem (Silano-Pen)	6	0	4	6	2	2
	Panavia F2.0 (Direct)	2	6	2	6	2	2
Piranha acid	Panavia F2.0 (Silano-Pen)	4	2	4	6	0	4
	Panavia SA (Direct)	4	4	2	4	2	4
	Panavia SA (Silano-Pen)	6	0	4	6	0	4
	TheraCem (Direct)	2	4	4	6	2	2
	TheraCem (Silano-Pen)	4	4	2	4	2	4
	Panavia F2.0 (Direct)	4	2	4	10	0	0
Hot acid	Panavia F2.0 (Silano-Pen)	2	2	6	6	2	2
	Panavia SA (Direct)	2	6	2	4	2	4
	Panavia SA (Silano-Pen)	2	4	4	4	0	6
	TheraCem (Direct)	6	0	4	6	2	2
	TheraCem (Silano-Pen)	6	2	2	6	2	2
	Panavia F2.0 (Direct)	2	4	4	4	2	4
	Panavia F2.0 (Silano-Pen)	0	8	2	4	2	4

A: Adhesive failure at the interface between resin cement and ceramic.
C: Cohesive failure within composite or within ceramic.
M: Mixed failure.

Concerning Silano-Pen, the results showed that the interaction between main surface pre-treatment and Silano-Pen was significant, while no significant interaction was detected between Silano-Pen and cement. The heat treatment using Silano-Pen could improve the surface hydroxylation resulting in a more reactive zirconia surface.[31] Moreover, Silano-Pen enhances the surface wettability and produces a dense scattering nanosilica grains leading to a stratified surface topography.[32,33] Additionally, the role of airborne particle abrasion with hot acid etching in creation and improving the surface roughness could not be neglected.[20]

In the present study, a comparison was made between MDP-containing conventional resin cement (Panavia F2.0) which is commonly used in researches and two self-adhesive resin cements which are methacrylate-based (TheraCem) and MDP-containing (Panavia SA) self-adhesive resin cements. The results of the present study showed that Panavia SA Cement Plus showed high bond strength. These results could be related to the high content of acidic phosphate functional monomers in self-adhesive resin cement which could increase the hydrophilicity of the cement resulting in hydrolytic degradation due to the higher water sorption.[34] Tanis *et al*[35] showed that using of MDP-containing resin cement improved the bond strength with airborne particle abrasion. Another study reported that the abraded zirconia specimens bonded with methacrylate-based cement showed lower bond strength than bonded with MDP-containing resin cement as the MDP monomers creates a chemical interaction with zirconia.[36] Also, the results of the present study revealed that the highest bond strength with hot acid etching. The hot acid etching improves the surface roughness by dissolving the less well arranged peripheral atoms of zirconia surface resulting in larger grain boundaries formation which increase mechanical interlocking with resin cement with no phase transformation.[23]

With Panavia F2.0, there was significant decrease in the bond strength (5.7±0.8 MPa) after aging with Piranha group. This bond strength value is considered a very low value for acceptable clinical bonding as the range of 10-13 MPa was suggested as the minimum clinically acceptable bond

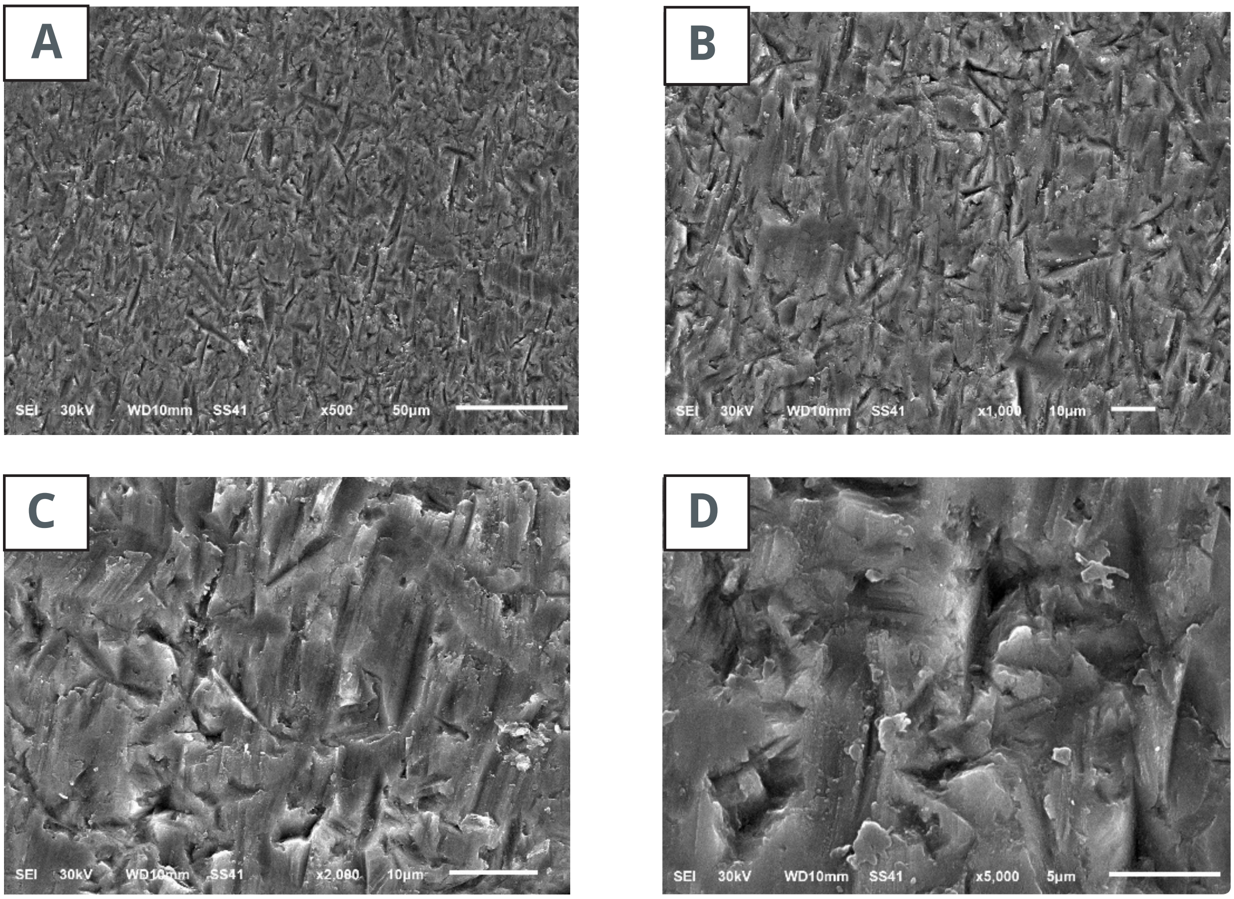

Figure 1: SEM micrograph of airborne particle abrasion surface pre-treatment at x500 (A), x100 (B), x2000 (C), and x5000 (D).

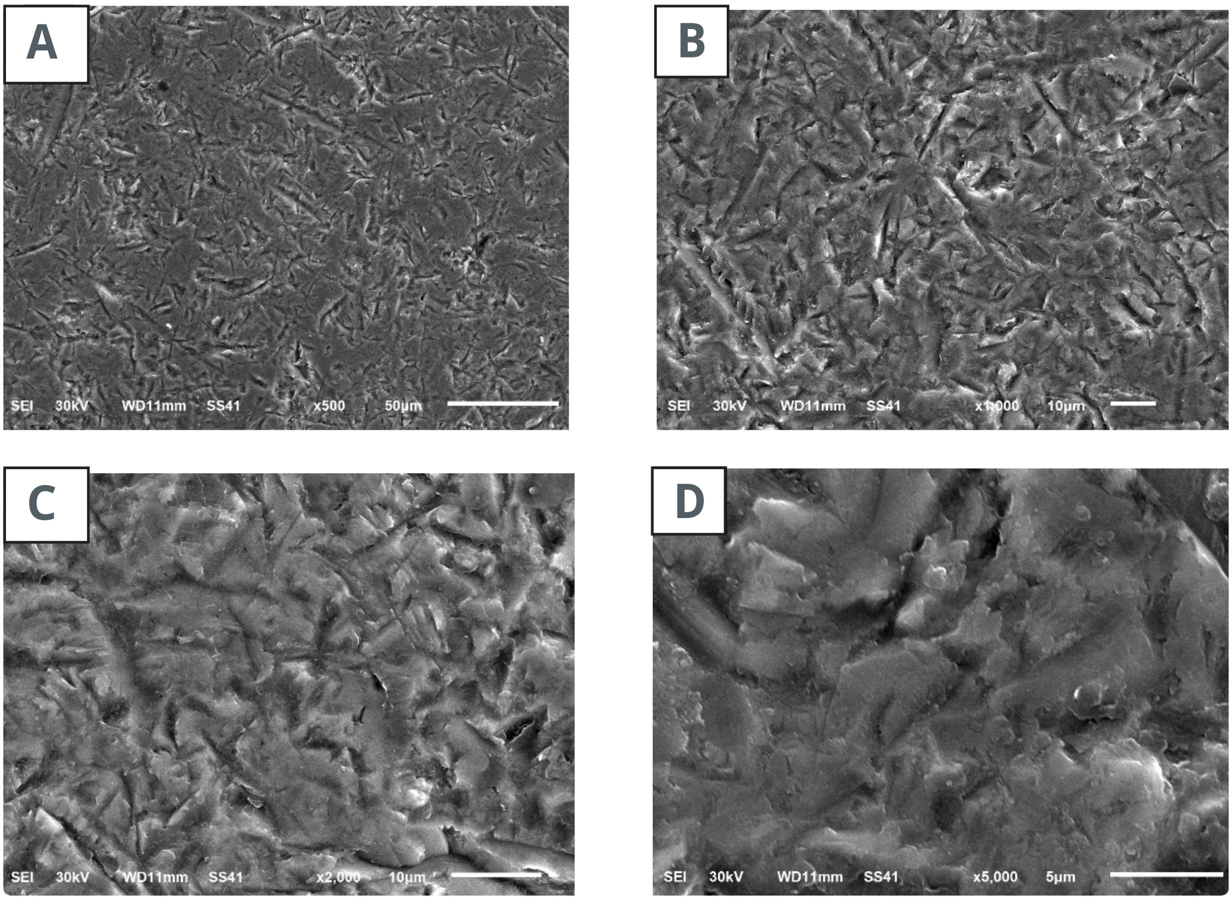

Figure 2: SEM micrograph of Piranha acid surface pre-treatment at x500 (A), x100 (B), x2000 (C), and x5000 (D).

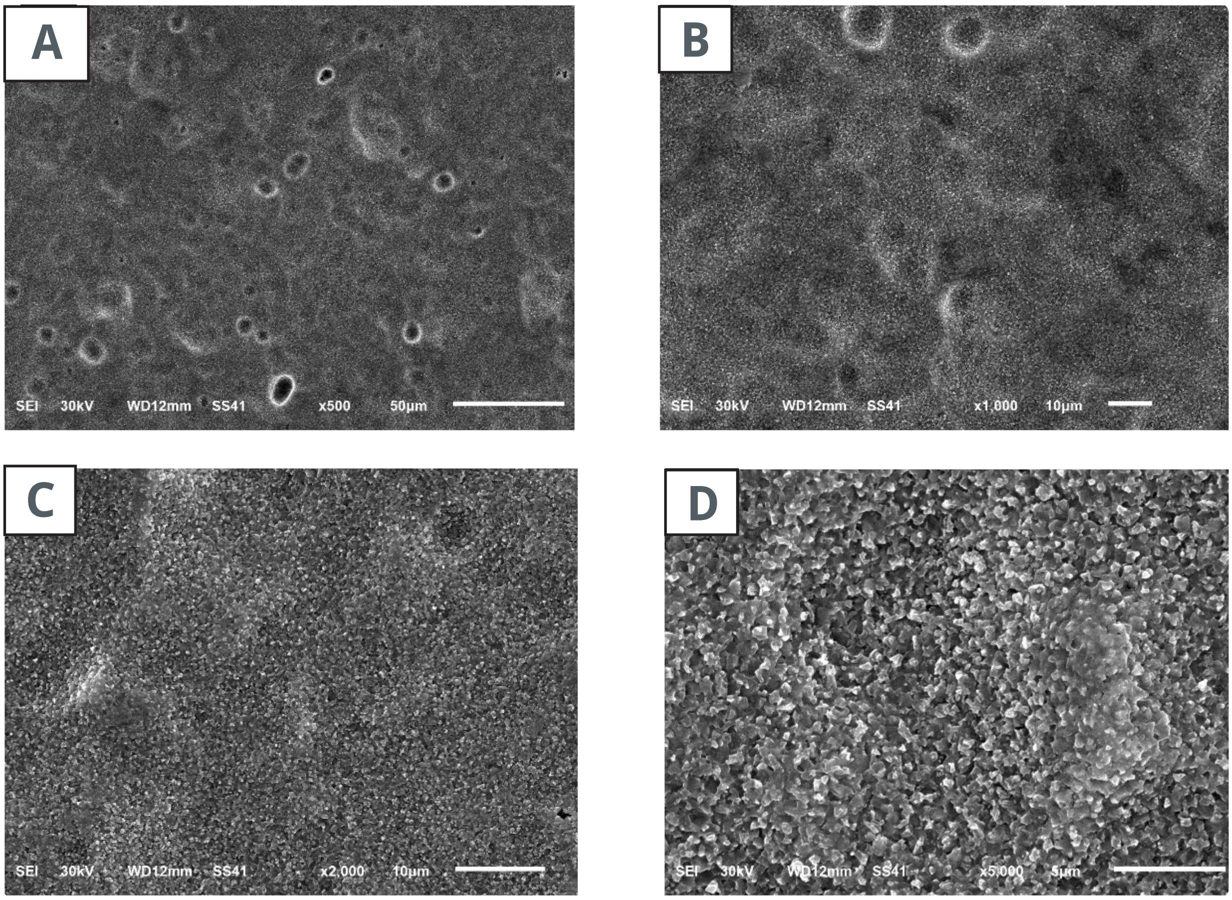

Figure 3: SEM micrograph of hot acid surface pre-treatment at x500 (A), x100 (B), x2000 (C), and x5000 (D).

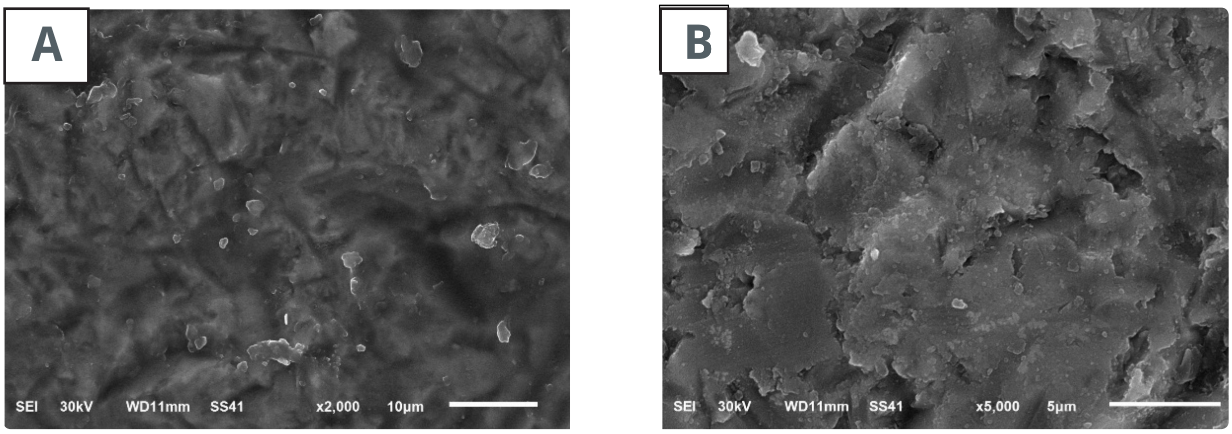

Figure 4: SEM micrograph of Airborne particle abrasion surface pre-treatment after Silano-Pen application at x2000 (A), and x5000 (B).

strength.[37,38] Although the increased inorganic filler (59 v%) has a significant role in improving wear resistance, mechanical properties and reducing polymerization shrinkage, it affects the proper viscosity and the suitable film thickness.[39] Moreover, this cement needs hand mixing which possibly leads to incorporation of air bubbles and resulting in reduction of the mechanical properties.[40]

The results of the present study revealed that the bond strength between resin cement and zirconia reduced after aging. These results were in agreement with other studies.[6,29,32,36] This may be attributed to several factors such as the exposure of a wide surface area of the microbars to the effect of thermocycling.[25] The expansion of the cement layer due to water sorption may result in degradation of resin cement.[8]

In the present study, before microtensile bond strength test, the microbars were examined carefully at 50x magnification for selection of the intact specimens that were free from any microcracks. Moreover, the bonding area was checked carefully and any defective specimen was excluded. The mode of failure of the specimens without aging was predominantly cohesive within ceramic or composite while it was predominantly adhesive after aging. The failure mode analysis showed exclusively adhesive failure with Piranha acid pre-treatment before and after aging. The bond

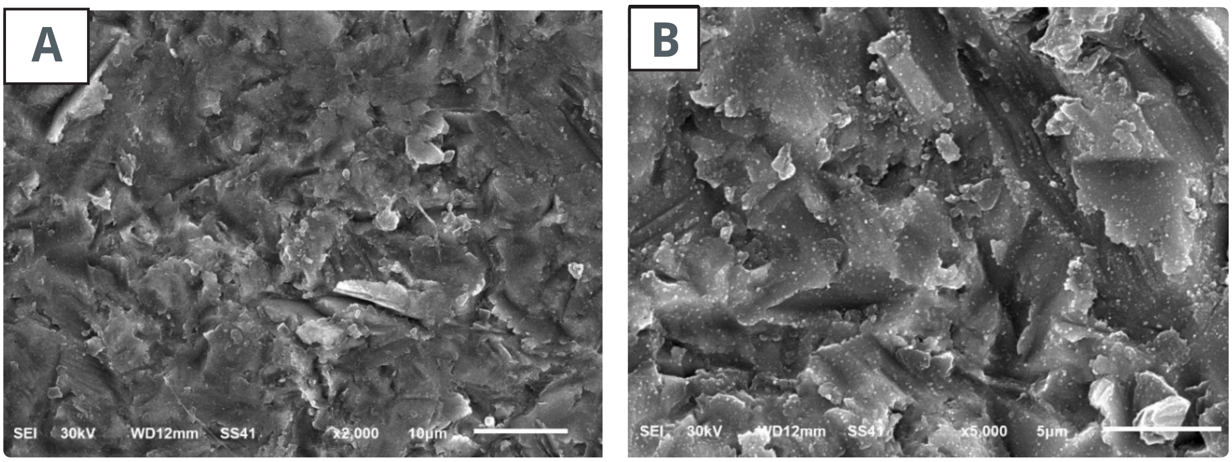

Figure 5: SEM micrograph of Piranha acid surface pre-treatment after Silano-Pen application at x2000 (A), and x5000 (B).

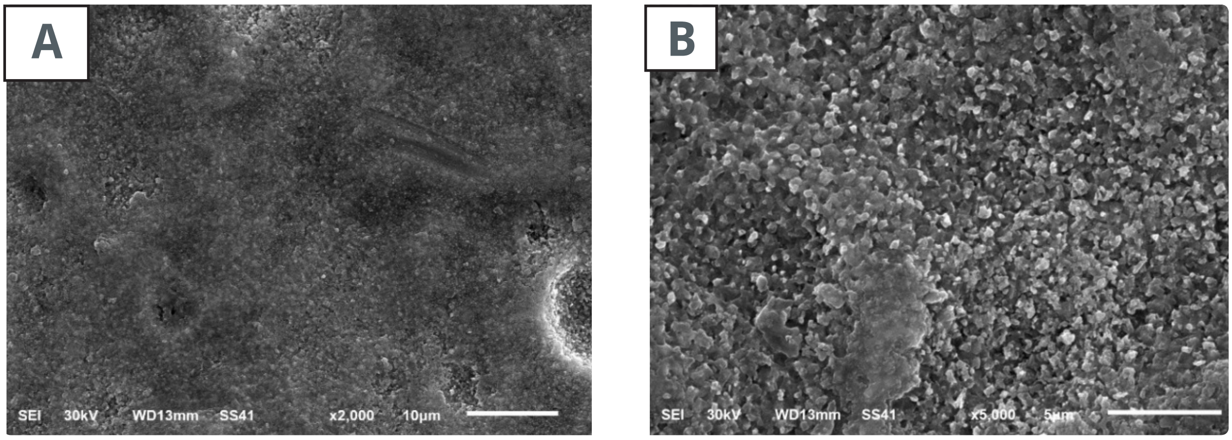

Figure 6: SEM micrograph of hot acid surface pre-treatment after Silano-Pen application at x2000 (A), and x5000 (B).

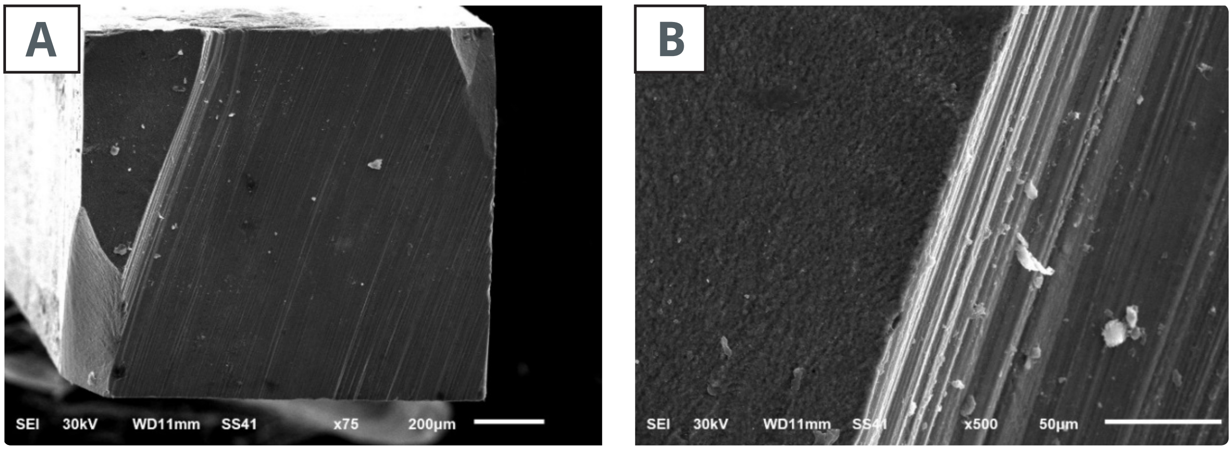

Figure 7: SEM micrograph of the mixed mode of failure at x75 (A), and x500 (B).

strength results were reflected on the failure mode of the debonded specimens. In the present study, the cohesive failure was mainly within composite and this may be caused by the induction of microcracks during the cutting procedures. The adhesive failure mode may be explained by the fact that the microtensile bond strength test estimates a small interfacial bonding zone.

New zirconia ceramics for dental restorations are continually under development; only one type of zirconia was tested in the present study. The results obtained should be verified in future studies in comparison with more surface condition methods and with more prolonged aging. The specimens were produced and examined under ideal conditions which may not reflect actual clinical conditions. Further clinical studies are needed to confirm the relationship between surface pre-treatment, Silan-Pen and cement to confirm the durability of the bonding protocol for zirconia restorations.

CONCLUSIONS

From this study, the following could be concluded:

1. The surface pre-treatment method, type of adhesive resin cement and aging influence the effectiveness of bonding of resin cements to with zirconia.
2. The hot acid etching pre-treatment recorded the highest bond strength, whereas the lowest bond strength was obtained with Piranha acid etching.
3. Silano-Pen treatment after hot acid etching improved the bonding of adhesive resin cement to zirconia more than with airborne particle abrasion.
4. Thermal aging had an important role in the degradation of the bond strength between resin cements and zirconia.
5. Among the tested adhesive resin cements, the self-adhesive MDP-containing resin cement (Panavia SA Cement Plus) enhanced the effectiveness of the bond strength to zirconia.

REFERENCES

1. Lohbauer, U., Zipperle, M., Rischka, K., Petschelt, A. and Müller, F.A. Hydroxylation of dental zirconia surfaces: characterization and bonding potential. *J. Biomed. Mater. Res. B. Appl. Biomater.*, 2008; **87**: 461-467.
2. He, M., Zhang, Z., Zheng, D., Ding, N. and Liu, Y. Effect of sandblasting on surface roughness of zirconia-based ceramics and shear bond strength of veneering porcelain. *Dent. Mater. J.*, 2014; **33**: 778-785.
3. Tzanakakis, E.G., Tzoutzas, I.G. and Koidis, P.T. Is there a potential for durable adhesion to zirconia restorations? A systematic review. *J. Prosthet. Dent.*, 2016; **115**: 9-19.
4. Matinlinna, J.P., Lung, C.Y.K. and Tsoi, J.K.H. Silane adhesion mechanism in dental applications and surface treatments: A review. *Dent. Mater.*, 2018; **34**: 13-28.
5. Wang, G., Zhang, S., Bian, C. and Kong, H. Effect of zirconia surface treatment on zirconia/veneer interfacial toughness evaluated by fracture mechanics method. *J. Dent.*, 2014; **42**: 808-815.
6. Hallmann, L., Ulmer, P., Lehmann, F., Wille, S., Polonskyi, O., Johannes M. and *et al*. Effect of surface modifications on the bond strength of zirconia ceramic with resin cement resin. *Dent. Mater.*, 2016; **32**: 631-639.
7. Lv, P., Yang, X. and Jiang, T. Influence of hot-etching surface treatment on zirconia/resin shear bond strength. *Materials.*, 2015; **30**: 8087-8096.
8. Xie, H., Chen, C., Dai, W., Chen, G. and Zhang F. In vitro short-term bonding performance of zirconia treated with hot acid etching and primer conditioning etching and primer condioning. *Dent. Mater. J.*, 2013; **32**: 928-938.
9. Cho, J.H., Kim, S.J., Shim, J.S. and Lee, K.W. Effect of zirconia surface treatment using nitric acid-hydrofluoric acid on the shear bond strengths of resin cements. *J. Adv. Prosthodont.*, 2017; **9**: 77-84.
10. Moradabadi, A., Roudsari, S.E.S., Yekta, B.E. and Rahbar N. Effects of surface treatment on bond strength between dental resin agent and zirconia ceramic. *Mater. Sci. Eng. C. Mater. Biol. Appl.*, 2014; **34**: 311-317.
11. Radovic, I., Monticelli, F., Goracci, C., Vulicevic, Z.R. and Ferrari, M. Self-adhesive resin cements: a literature review. *J. Adhes. Dent.*, 2008; **10**: 251-258.
12. Ferracane, J.L., Stansbury, J.W. and Burke, F.J. Self-adhesive resin cements - chemistry, properties and clinical considerations. *J. Oral. Rehabil.*, 2011; **38**: 295-314.
13. Manso, A.P. and Carvalho, R.M. Dental cements for luting and bonding restorations: self-adhesive resin cements. *Dent. Clin. North. Am.*, 2017; **61**: 821-834.
14. Oyagüe, R.C., Monticelli, F., Toledano, M., Osorio, E., Ferrari, M. and Osorio, R. Effect of water aging on microtensile bond strength of dual-cured resin cements to pre-treated sintered zirconium-oxide ceramics. *Dent. Mater.*, 2009; **25**: 392-399.
15. Pashley, D.H., Carvalho, R.M., Sano, H., Nakajima, M., Yoshiyama, M., Shono Y. and *et al*. The microtensile bond test: a review. *J. Adhes. Dent.*, 1999; **1**: 299-309.
16. Smith, R.L., Villanueva, C., Rothrock, J.K., Garcia-Godoy, C.E., Stoner, B.R., Piascik, J.R. and *et al*. Long-term microtensile bond strength of surface modified zirconia. *Dent. Mater.*, 2011; **27**: 779-785
17. Negreiros, W.M., Ambrosano, G.M.B. and Giannini, M. Effect of cleaning agent, primer application and their combination on the bond strength of a resin cement to two yttrium-tetragonal zirconia polycrystal zirconia ceramics. *Eur. J. Dent.*, 2017;**11**: 6-11.
18. Li, R.W.K., Chow, T.W. and Matinlinna, J.P. Ceramic dental biomaterials and CAD/CAM technology: state of the art. *J. Prosthodont. Res.*, 2014; **58**: 208-216.
19. Larabi, H., Cetik, S., Ha, H., Atash, R. and Ha, H.T. In vitro study of bonding strength of zirconia on dentin using different adhesive systems. *Int. J. Prosthodont.*, 2018; **31**: 135-137.
20. Grasel, R., Santos, M.J., Rêgo, H.C., Rippe, M.P. and Valandro, L.F. Effect of resin luting systems and alumina particle air abrasion on bond strength to zirconia. *Oper. Dent.*, 2018; **43**: 282-290.
21. Liu, D., Tsoi, J.K., Matinlinna, J.P. and Wong, H.M. Effects of some chemical surface modifications on resin zirconia adhesion. *J. Mech. Behav. Biomed. Mater.*, 2015; **46**: 23-30.
22. Casucci, A., Monticelli, F., Goracci, C., Mazzitelli, C., Cantoro, A., Papacchini, F. and *et al*. Effect of surface pre-treatments on the zirconia ceramic-resin cement microtensile bond strength. *Dent. Mater.*, 2011; **27**: 1024-1030.
23. Keshvad, A. and Hakimaneh, S.M. Microtensile bond strength of a resin cement to silica-based and Y-TZP ceramics using different surface treatments. *J. Prosthodont.*, 2018; **27**: 67-74.
24. Chen, C., Niu, L.N., Xie, H., Zhang, Z.Y., Zhou, L.Q., Jiao, K., Chen, J.H., Pashley, D.H. and Tay, F.R. Bonding of universal adhesives to dentine–Old wine in new bottles? *J. Dent.*, 2015; **43**: 525-536.
25. Özcan, M. and Bernasconi, M. Adhesion to zirconia used for dental restorations: a systematic review and meta-analysis. *J. Adhes. Dent.*, 2015; **17**: 7-26.
26. Melo, R., Souza, R., Dursun, E., Monteiro, E., Valandro, L. and Bottino, M. Surface treatments of zirconia to enhance bonding durability. *Oper. Dent.*, 2015; **40**: 636-643.
27. Lundberg, K., Wu, L. and Papia, E. The effect of grinding and/or Airborne particle abrasion on the bond strength between zirconia and veneering porcelain: a systematic review. *Acta. Biomater. Odontol. Scand.*, 2017; **28**: 8-20.

28. Wang, H., Aboushelib, M.N. and Feilzer, A.J. Strength influencing variables on CAD/CAM zirconia frameworks. *Dent. Mater.*, 2008; **24**: 633-638.
29. Sakrana, A.A. and Özcan, M. Effect of chemical etching solutions versus air abrasion on the adhesion of self-adhesive resin cement to IPS e. max ZirCAD with and without aging. *Int. J. Esthet. Dent.*, 2017; **12**: 72-85.
30. Zandparsa, R., Talua, N.A., Finkelman, M.D. and Schaus, S.E. An in vitro comparison of shear bond strength of zirconia to enamel using different surface treatments. *J. Prosthodont.*, 2014; **23**: 117-123.
31. Özcan, M., Nijhuis, H. and Valandro, L.F. 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; **27**: 99-104.
32. Yenisey, M., Dede, D.Ö. and Rona, N. Effect of surface treatments on the bond strength between resin cement and differently sintered zirconium-oxide ceramics. *J. Prosthodont. Res.*, 2016; **60**: 36-46.
33. Oguri, T., Tamaki, Y., Hotta, Y. and Miyazaki, T. Effects of a convenient silica-coating treatment on shear bond strengths of porcelain veneers on zirconia-based ceramics. *Dent. Mater.*, 2012; **31**: 788-796.
34. Samran, A., Al-Ammari, A., El Bahra, S., Halboub, E., Wille, S. and Kern, M. Bond strength durability of self-adhesive resin cements to zirconia ceramic: An in vitro study. *J. Prosthet. Dent.*, 2018.
35. Tanış, M.Ç. and Akçaboy, C. Effects of different surface treatment methods and MDP monomer on resin cementation of zirconia ceramics an in vitro study. Lasers. Med. Sci., 2015; **6**: 174-181.
36. Aboushelib, M.N., Kleverlaan, C.J. and Feilzer, A.J. Selective infiltration-etching technique for a strong and durable bond of resin cements to zirconia-based materials. *J. Prosthet. Dent.*, 2007; **98**: 379-388.
37. Akay, C., Çakırbay, T.M. and Şen, M. Effects of hot chemical etching and 10-metacryloxydecyl dihydrogen phosphate (MDP) monomer on the bond strength of zirconia ceramics to resin-based cements. *J. Prosthodont.*, 2017; **26**: 419-423.
38. Lüthy, H., Loeffel, O. and Hammerle, C.H. Effect of thermocycling on bond strength of luting cements to zirconia ceramic. *Dent. Mater.*, 2006; **22**: 195-200.
39. Furuichi, T., Takamizawa, T., Tsujimoto, A., Miyazaki, M., Barkmeier, W. and Latta, M. Mechanical properties and sliding-impact wear resistance of self-adhesive resin cements. *Oper. Dent.*, 2016; **41**: E83-E92.
40. Higashi, M., Matsumoto, M., Kawaguchi, A., Miura, J., Minamino, T., Kabetani, T. and *et al.* Bonding effectiveness of self-adhesive and conventional-type adhesive resin cements to CAD/CAM resin blocks. Part 1: Effects of sandblasting and silanization. *Dent. Mater., J* 2016; **35**: 21-28.