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The Effect of Nano-silica -Coating on Micro-Shear Bond Strength of CAD/CAM PEEK to Resin Cement: (An In Vitro Study

Nourhan H. Tawfik[1], Ibrahim M. El-Sherbiny[2], Tamer E. Shokry[3], Hanaa H. Zaghloul[4]

ABSTRACT

Background: PEEK is a polymer with lots of significant potentials making it an important candidate in dental applications; however, strong durable bond of PEEK restorations with resin cement is still questionable. ***Aim:*** Evaluating the effect of different surface treatment protocols on the bond strength of PEEK surface with resin cement in comparison to Lithium Disilicate ceramic. ***Methodology:*** PEEK (P) and Lithium Disilicate discs (LD) were fabricated using CAD/CAM technique. A total of 40 samples were divided into four groups according to surface treatment protocol (n=10): Group (LD): hydrofluoric acid etching followed by silane application. Group (PP): 110 µm alumina particles sandblasting followed by Piranha solution acid etching. Group (PNsi): 110 µm alumina particles sandblasting followed by nano-silica coating and silane coupling agent respectively. Group (PN): 110 µm alumina particles sandblasting followed by nano-silica coating. All specimens underwent thermocycling. All specimens were cemented using universal resin cement. Micro-shear bond strength (µSBS) test was performed using a universal testing machine and the mode of failure was assessed using digital microscope. Surface roughness was assessed before and after surface treatment using optical profilometer. ***Results:*** There was no statistically significant difference between (LD) and (PP); both showed the highest (µSBS). No statistically significant difference between (PNsi) and (PN); both showed the lowest (µSBS). However, statistically significant difference was found between (LD, PP) groups and (PNsi, PN) groups. (P-value = 0.028). ***Conclusion:*** PP group showed a comparable µSBS results to LD group, whereas, nano-silica coated group showed the lowest bond strength values.

Keywords: CAD/CAM PEEK, surface treatment, nano silica coating, micro-shear bond strength, and CAD/CAM Lithium Disilicate ceramic.

1. Postgraduate student, Department of Fixed Prosthodontics, Faculty of Oral and Dental Medicine, Misr International University, Cairo, Egypt.
2. Professor and head of Nanomedicine Research Labs, Center for Materials Science (CMS), Zewail City of Science and Technology, 6th October City, 12578 Giza, Egypt.
3. Professor and head of Fixed Prosthodontics Department, Faculty of Dental Medicine, Al-Azhar University, Cairo, Egypt.
4. Professor of Fixed prosthodontics, Department of Fixed Prosthodontics, Faculty of Oral and Dental Medicine, Misr International University, Cairo, Egypt.

INTRODUCTION

Dental ceramics and different processing technologies have been in continuous evolution during the past few years, focusing on new microstructures, pressing and CAD-CAM techniques.[1] Research recent advances and techniques have developed several combinations between ceramic materials themselves. Their aim was to develop a material with modulus of elasticity near dentin, easier to mill, adjust and repair.[1] However, as the main aim has always been trying to resemble and imitate tooth structure properties, new materials with higher and improved properties have been continuously introduced to dental market. Polyether ether ketone (PEEK) is a member of polyaryl ether ketone family (PAEK), an important class of high performance thermoplastics that has been recently introduced and spread into the dental field, showing promising success.[2]

Polyether ether ketone is a poly aromatic semi crystalline polymer. It is synthesized by the reaction between 4-difluorobenzophenone and disodium salt of hydroquinone in a polar solvent as diphenylsulphonates at 300 °C. PEEK can be modified either by addition of a functionalized monomer or by chemical reaction, making it a high performance thermoplastic polymer with superior chemical, thermal and mechanical properties in addition to excellent bio-compatibility.[3] The combination of these properties have made PEEK an effective alternative for different dental procedures such as replacing metal implants, implant abutments, temporary crowns and orthodontic wires construction of single crowns, fixed dental prostheses and removable dental prosthesis.[4]

Among other thermoplastic polymers, PEEK is a highly bio inert and biocompatible material that can resist degradation and does not induce any harmful effect on human tissue. It has high thermal and chemical stability (melting point= 335°C). It is stable against hydrolysis even at high temperatures and is not affected by long term water exposure even at high temperatures with lowest solubility and water sorption values under different aging solutions.[3] PEEK has a shock absorbing quality that acts as a stress breaker and provides better forces distribution.[3–6]

Strong durable bond of PEEK restorations either with resin cement or with tooth structure is still limited, making it a major drawback in the material. Bond strength of PEEK is considered low because of its chemical inertness and its poor surface energy.[7,8] Recently several studies have been

conducted trying to modify PEEK surface, and aiming to achieve a strong, durable bond. Most of these studies concluded that no adequate bonding to non-conditioned/modified PEEK surface could be achieved.[7,9]

Several surface treatment protocols have been introduced and evaluated to improve the bonding capabilities of PEEK. These protocols include chemical treatments, sandblasting, plasma spraying and laser treatment.[3,10,11] Chemical treatment (acid etching by sulfuric acid, hydrofluoric acid, piranha solution) is a process aiming to increase surface roughness. This creates a new chemical/functional group at surface to achieve better micromechanical bonding.[11–15] Mechanical processes such as sandblasting by alumina particles in combination with piranha solution have shown improvement in bonding ability of PEEK.[16–19] Nevertheless, sandblasting is advantageous over others as it is of low cost and convenience. Its aim is to create micro roughness to improve mechanical interlocking with adhesive materials.[11]

A recently introduced trend is coating PEEK surface by the aid of nanotechnology. Nanotechnology attracts more attention nowadays due to its unique properties resulted from its nano-structure. Coating peek implants with different nano components such as TIO_2 and hydroxyapatite crystals were introduced in order to improve PEEK osteoconductive properties.[5] However, by reviewing the literature, there was lack of efficient data about whether this technique increases the bond strength between PEEK surface and resin cement. So, the aim of the present study is to evaluate the effect of different surface treatment protocols including nano-silica coating on the micro-shear bond strength of PEEK surface with resin cement in comparison to Lithium Disilicate ceramic. The null hypothesis is that there's no difference between various PEEK surface treatments protocols in enhancing micro-shear bond strength compared to Lithium Disilicate ceramic.

MATERIALS AND METHODS

Sample size calculation was performed using IBM® SPSS® Sample Power® Release 3.0.1. This power analysis is for a one-way fixed effect analysis of variance. The computed effect size for micro-shear bond strength was found to be (0.6), using alpha (α) level of (5%) and Beta (β) level of (20%) i.e. power = 80%; the minimum estimated sample size is a total of 36 specimens (9 specimens per group). Sample size was increased to 10 specimens per group to fulfill the requirements of micro-shear testing. The

compositions and details of the materials used in this study are shown in **Table (1)**. A total 40 samples (30 PEEK and 10 Lithium Disilicate) were divided into four equal groups according to the surface treatment protocols applied. Sample grouping is shown in **Table (2).**

PEEK samples were constructed using CAD/CAM technique in accordance with the manufacturer's instructions, and Lithium Disilicate samples were cut using Isomet into discs (six discs for PEEK and two discs for Lithium Disilicate) with 10mm diameter and 2 mm thickness. For Lithium Disilicate

Table (1): List of brand names, material descriptions, manufactures and lot numbers.

Brand name	Material description	Manufacturer	Lot number
IPS.e.max	Lithium disilicate glass ceramic CAD-CAM block LT/A1L/I12	Ivoclar Vivadent AG, Schaan, Liechtenstein	W95765
PEEK	PEEK milling disc (brecam.biohpp) Shaded, white	Bredent GmbH & co. KG, Weissenhorner, Senden Germany	482047
Porcelain etch	Hydrofluoric acid etch	Ultradent, South Jordan, UT, USA	BGZ9W
Silane	Silane coupling agent		
50µm aluminum oxide	Sandblasting abrasive powder	Renfert GmbH, Hilzingen, Germany	A722A30
110µm aluminum oxide	Sandblasting abrasive powder		
Sulphuric acid	Sulphuric acid for surface etching	Merck KGaA, 64271 Darmstadt, Germany	7664-93-9
Hydrogen peroxide	30% hydrogen peroxide	Sigma-Aldrich, St.Louis, MO, USA	7722-84-1
Piranha sol	Sulphuric acid+ hydrogen peroxide for etching	-	-
Silica particles	Tetraethoxysilane (TEOS,99%.chemlab	Nano gate company ,Cairo, Egypt	-

Table (2): Sample grouping.

Group	Surface treatment
Control (LD)	According to manufacturer recommendations
PEEK (PP)	Sandblasting by 110 microns aluminum oxide followed by piranha acid etching
PEEK (PNsi)	Sandblasting by 110 microns aluiminum oxide followed by nano-silica coating then silane
PEEK (PN)	Sandblasting by 110 microns aluiminum oxide followed by nano-silica coating

samples serving as control group (LD), the IPS e.max CAD block was rounded then cut into 2 circular discs (2mm thickness each) using (Isomet 4000 linear precision saw, Buehler, IL, USA) which is A low speed cutting saw with 0.7 mm thickness abrasive disc, at a speed of 2500 rpm, under continuous water-cooling.[20] A digital caliper (Mitutoyo, Kanagawa Prefecture, Japan) was used to confirm the required thickness of each disc. The specimens were fired through the crystallization process in a press/firing furnace, (Programat EP 3010, Ivoclar Vivadent, Schaan, Liechtenstein) at 850°C for 25-30 minutes, following the manufacturer's recommendations. Then the two ceramic discs were etched with hydrofluoric acid, (Ultradent, South Jordan, UT, USA), with a brush for 20 seconds. Then the etched surfaces were thoroughly rinsed for one minute under continuous running water, to remove any hydrofluoric acid etchant remnants, and dried with oil-free air for 30 seconds. Silane coupling agent (Ultradent, South Jordan, UT, USA) was then applied to the specimens with a brush and left to dry for one minute, following the manufacturer's recommendation.

For PEEK specimens two disc-shaped objects were designed in (3-D BUILDER CAD) software, with 2 mm thicknesses and 10 mm diameter.[21] The designs were sent as Standard Transformation Language (STL) files to the computer-Aided-Manufacturing (CAM) software (SHERA ECO-MILL-CAM, Lemförde, Germany), where construction of the specimens followed by dry-milling of the PEEK blank (Bio-HPP, Bredent, GmbH & co. KG, Weissenhorner, Senden, Germany) using a dental milling machine (VHF S1 SHERA ECO-MILL 5-axis, Lemförde, Germany). Digital caliper was used for confirming the desired diameter and thickness of the disc. PEEK discs were polished using polishing kit (Bredent, GmbH & co. KG, Weissenhorner, Senden, Germany) after being milled, then they were ultrasonically cleaned in distilled water (Toption Digital Ultrasonic Cleaner, Shaanxi, China) for 10 min.

For ease of handling and support of the specimens, each specimen was embedded in a block of cold cure acrylic resin (Acrostone, Egypt) with about only 0.5 mm of specimen surface elevated over the acrylic surface. To standardize the effect of sandblasting in PEEK groups, two needle holders were used to stabilize the mold in place while the sandblaster nozzle was fixed on another separate needle holder. The three needle holders were properly stabilized on the base of the sandblasting unit. The nozzle of the

sandblaster was fixed at a 90° angle to the disc surface and applied in a circular motion for 15 seconds.

For PEEK etched with piranha solution (PP) group, both discs were sandblasted with 110 μm cobra white aluminum oxide (Al_2O_3) particles in a dental sandblasting unit (Renfert, Hilzingen, Germany), followed by etching with piranha solution (H2SO4:H2O2 = 1:1) (98% sulphuric acid (Sigma-Aldrich, St. Louis, MO, USA) (10ml) mixed with 35% hydrogen peroxide (Sigma-Aldrich, St. Louis, MO, USA) (10ml) for 30 sec.[22] The acid was rinsed off with distilled water for 60 s and then dried with oil-free compressed air. Silane coupling agent was added with a brush and left to dry for one minute, following the manufacturer's recommendation.

For peek groups coated with nano-silica with silane (PNsi) and without silane (PN), each of the four specimens was subjected to 110 μm cobra white aluminum oxide (Al_2O_3) particles in a dental sandblasting unit using the same standardization method then ultrasonically cleaned and nano-silica particles was coated to the surface by using Sol/gel method. Tetraethoxysilane (TEOS,99%. chemlab), absolute ethanol and ammonia 25% (Meck, Germany) and distilled water were used to prepare silica sol-gel with nano-sized particles.[23]

PEEK discs were added to the sol-gel container throughout the whole preparation method of silica, followed by autoclaving for 6 hours at a temperature of 160 ^{0}C for the mean of compressing the nanoparticles on PEEK specimen disc.[23,24] Silane coupling agent was added to group PNsi with a brush and left to dry for one minute, following the manufacturer's recommendation.

Surface roughness was measured before and after surface treatments for all specimens. All discs were photographed using USB digital microscope with a built-in camera connected with compatible personal computer (U500X Digital Microscope, Guangdong, and China). A 3D image of the surface profile of cropped images for the specimens was created and analyzed using (WSxM) software (Ver 5 develop 4.1, Nanotec, Electronia, SL) to calculate average of heights (Ra) expressed in μm. Background was set to have the same color during measuring before and after to standardize the results.[25,26]

For nano-silica coated groups SEM analysis (Quanta 250 FEG, ThermoFisher Scientific, MA, USA) was performed to confirm the presence of nano- silica particles on PEEK surface. This was operated at magnification 500x and 2500x. Prior to SEM imaging, the samples were ultrasonically

washed for 30 s and sputter-coated with gold in a sputter-coating device (Emitech K550X Sputter Coater, Quorum Technologies, Kent, UK).

For micro-shear bond strength test (μSBST), five transparent polyethylene microtubules were cut using a sharp blade #15 from a 6 FG nelaton catheter, with internal diameter of 0.9mm and 1 mm height.[27,28] Five microtubules were placed on each disc surface giving a total of 40 microtubules (6 peek specimens and 2 ceramic specimens X 5 microtubules = 40). Resin cement capsules (relyX unicem, 3M Deutschland GmbH, Neuss-Germany) were activated and filled into microtubules, using the 3M mixing tip to fill each micro tubule. A glass microscopic slide was gently pressed on the top surfaces of the microtubules to remove excess cement and obtain a flat surface. All resin cement-filled microtubules were light cured with a dental light cure unit of 1200 mW/cm^2 for three seconds of tack curing, following the manufacturer's recommendations. After tack curing, a sharp dental explorer was used to remove excess, then each microtubule was light cured for 40 seconds on each specimen, following the manufacturer's recommendation. After curing, the microtubules were cut using a surgical blade size 15 by making a vertical cut along the microtubule wall and each was carefully removed leaving the resin cement micro-cylinders properly bonded on the ceramic surface disc.[20,27] All specimens containing the five resin cements micro-cylinders (n=40) were subjected to thermocycling in distilled water in a thermocycling unit (Robota automated thermal cycle; BILGE, Turkey) for 5000 cycle's equivalent to 6 months clinically[29] with dwell times 25 s. in each water bath and a lag time 10 s. The low-temperature point was 5 ^{0}C. The high temperature point was 55 ^{0}C.[29]

Test procedure

The μ-Shear bond strength test was performed using universal testing machine. A circular interface μ-shear test was designed to evaluate the bond strength. All samples were individually and horizontally mounted on a computer-controlled materials testing machine (Model 3345; Instron Industrial Products, Norwood, USA) with a load cell of 5 kN and data were recorded using computer software (Bluehill Lite; Instron Instruments). Samples were fixed to specially designed sample holder [hollowed metal tube with central hole for acrylic block housing] secured to the lower fixed compartment of testing machine by tightening screws. A loop prepared from an orthodontic wire (0.014 in

diameter) was wrapped around the bonded micro-cylinder assembly as close as possible to the base of the microcylinder and aligned with the loading axis of the upper movable compartment of the testing machine. A shearing load with tensile mode of force was applied via materials testing machine at a crosshead speed of 0.5 mm/min. The load required to debonding was recorded in Newton.

μ-Shear bond strength calculation: The load at failure was divided by bonding area to express the bond strength in MPa :$\tau = P/ \pi r2$ where ; τ = μ-shear bond strength (in MPa), P =load at failure (in N), π =3.14 and r = radius of micro-cylinder (in mm).

To identify the failure mode after microshear bond strength test, disc specimens of each group were analyzed under a USB digital-microscope with magnification x35, and the images were captured and transferred to an IBM personal computer equipped with the Image-tool software (Image J 1.43U, National Institute of Health, USA). Failure pattern was characterized as adhesive failure between cement and ceramic surface, cohesive failure within cement or ceramic surface, and mixed failure; both cohesive and adhesive.

Numerical data were explored for normality by checking the distribution of data and using tests of normality (Kolmogorov-Smirnov and Shapiro-Wilk tests). Micro-shear bond strength data showed non-normal (non-parametric) distribution while surface roughness (Ra) data showed normal (parametric) distribution. Data were presented as mean standard deviation (SD), median and range values. For non-parametric data, Kruskal-Wallis test was used to compare between surface treatment protocols. Dunn's test was used for pair-wise comparisons when Kruskal-Wallis test is significant. For parametric data, repeated measures ANOVA test was used to study the effect of surface treatment protocol, application and their interactions on mean surface roughness values. Bonferroni's post-hoc test was used for pair-wise comparisons when ANOVA test is significant. Failure mode data were presented as frequencies and percentages. Fisher's exact test was used to compare between failure modes of different surface treatment protocols. The significance level was set at $P \leq 0.05$. Statistical analysis was performed with IBM SPSS Statistics for Windows, Version 23.0. Armonk, NY: IBM Corp.

RESULTS

Micro-shear bond strength (MPa)

The mean standard deviation (SD) values and the results of Kruskal-Wallis test

for comparison between micro-shear bond strength (MPa) of the four groups were listed in table (3) There was a statistically significant difference between the groups (*P*-value = 0.028, Effect size = 0.274). Pair-wise comparisons between groups revealed that there was no statistically significant difference between Control and Piranha solution; both showed the statistically significantly highest values. There was no statistically significant difference between Nano-coating with and without Silane; both showed the statistically significantly lowest micro-shear bond strength.

The mean standard deviation (SD) values and results of Kruskal-Wallis test for comparison between micro-shear bond strength (MPa) are shown in **Table (3).** A box plot representing median and range values for micro-shear bond strength in the four groups is shown **(Figure 1).**

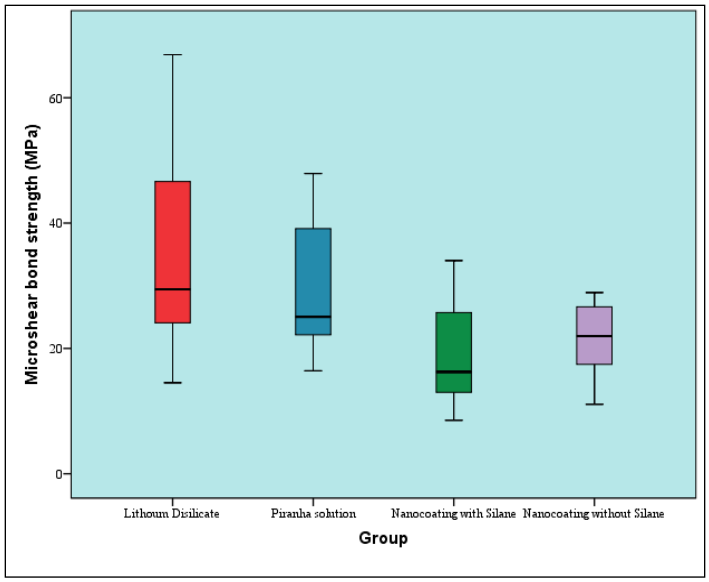

Figure (1): Box plot representing median and range values for micro-shear bond strength in the four groups.

Surface roughness

Comparison between Ra values before and after surface treatment: repeated measures ANOVA test for comparison between Ra values (µm) with different interactions of variables is recorded and listed in **Table (4)**. A bar chart representing mean and standard deviation values for Ra with different interactions of variables is shown in **(Figure 2).** As regards LD (control

Table (3): The mean, standard deviation (SD) values and results of Kruskal-Wallis test for comparison between microshear bond strength (MPa).

Group	Median	Min.	Max.	Mean	SD	*P*-value	Effect size *(Eta squared)*
Control (LD)	29.4 [A]	14.5	66.9	34.7	16.5	0.028*	0.274
PEEK (PP)	25 [A]	16.4	47.9	29.1	10.2		
PEEK (PNsi)	16.2 [B]	8.5	34	18.4	8.1		
PEEK (PN)	22 [B]	11.1	28.9	21.3	6.7		

**: Significant at P ≤ 0.05.*
Different superscripts indicate statistically significant difference between groups.

Table (4): Comparison between Ra values before and after surface treatment: repeated measures ANOVA test for comparison between Ra values (µm) with different interactions of variables.

Surface treatment protocol	Before surface treatment		After surface treatment		*P*-value	Effect size *(Partial eta squared)*
	Mean	SD	Mean	SD		
Control (LD)	0.2754 ^{C}	0.0051	0.2855 ^{B}	0.0045	<0.001*	0.591
PEEK (PP)	0.2859 ^{A}	0.0032	0.2952 ^{A}	0.0035	<0.001*	0.73
PEEK (PNsi)	0.2827 ^{B}	0.0012	0.2846 ^{B}	0.0016	0.269	0.049
PEEK (PN)	0.2806 ^{B}	0.0009	0.2835 ^{B}	0.0051	0.095	0.107
P-value	<0.001*		<0.001*			
Effect size *(Partial eta squared)*	0.752		0.79			

**: Significant at P ≤ 0.05.*
Different superscripts in the same column indicate statistically significant difference between groups.

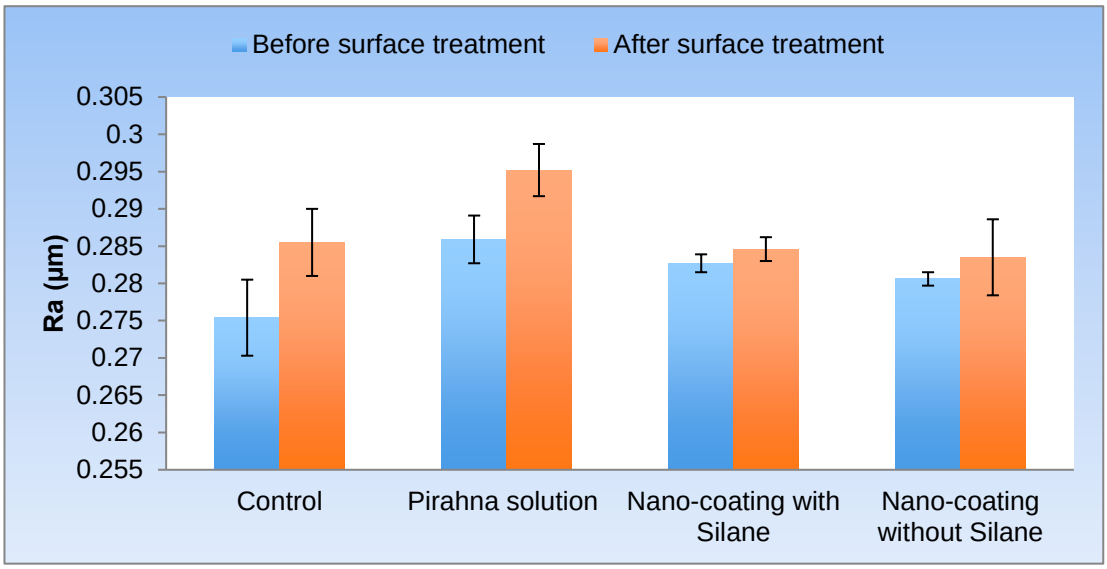

Figure (2): Bar chart representing mean and standard deviation values for Ra with different interactions of variables.

group) and PEEK; (PP; Piranha solution), there was a statistically significant increase in (Ra) values after surface treatment (*P*-value <0.001, Effect size = 0.591) and (*P*-value 0.001, Effect size = 0.73), respectively, while for PEEK; (PNsi, PN) groups; there was no statistically significant difference between Ra values before and after surface treatment

(*P*-value = 0.269, Effect size = 0.049) and (*P*-value = 0.095, Effect size = 0.107), respectively. **(Figure 3)**

Failure mode

Frequencies (n), percentages (%) and results of Fisher's exact test for comparison

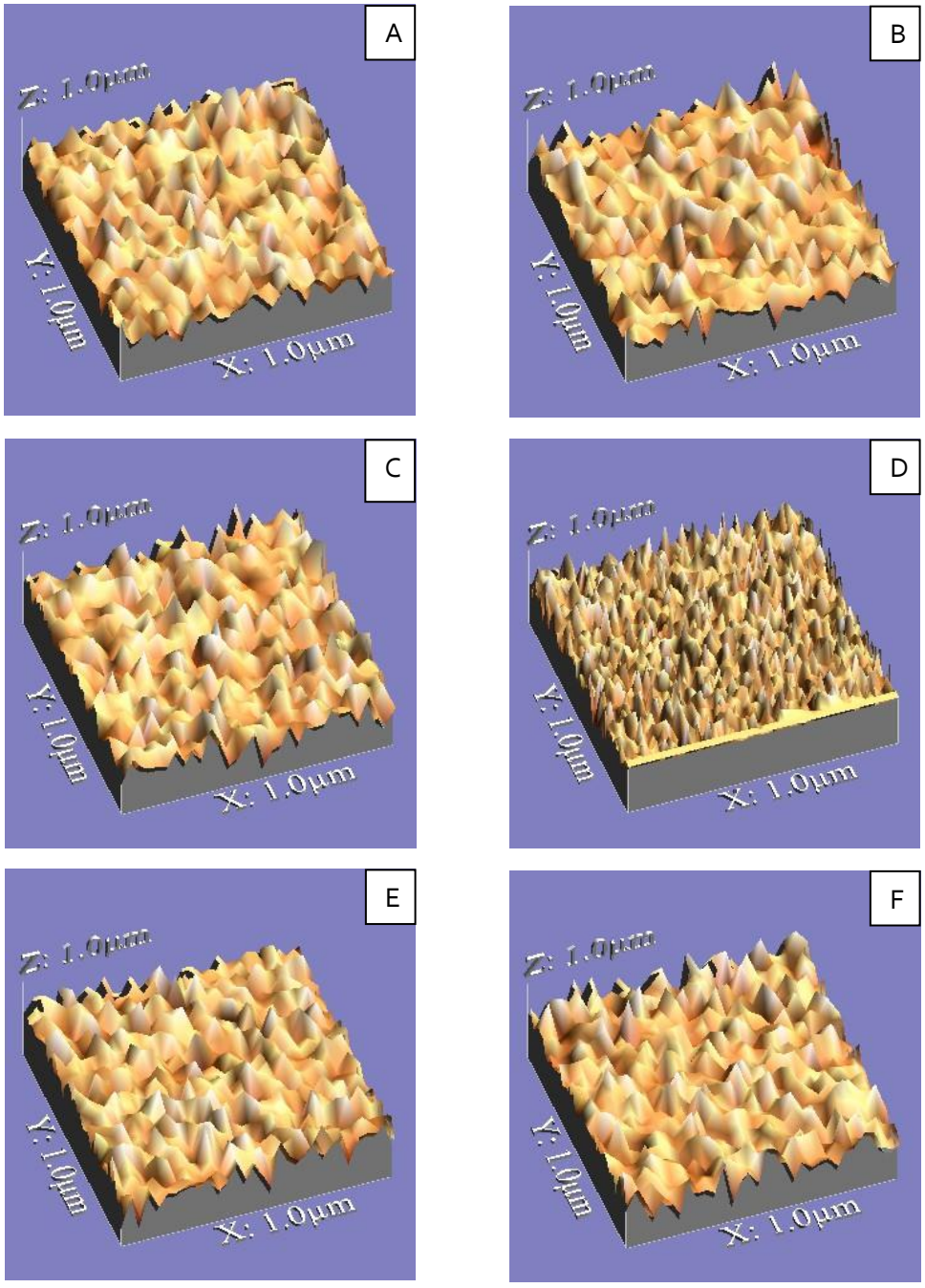

Figure (3): 3D images representing the difference in peaks and valleys before and after surface treatment protocol. **A:** before hydrofluoric acid etching, **B:** after hydrofluoric acid etching, **C:** before piranha surface treatment, **D:** after piranha surface treatment, **E:** before 110 microns sandblasting, **F:** after 110 microns sandblasting.

between failure modes of surface treatment protocols are recorded and listed in **Table (5).** A bar chart representing failure modes with different surface treatment protocols is shown in (**Figure 4).**

coating with Silane protocol. Cohesive failure was only found with control group. The highest prevalence of mixed failure was found with Nano-coating without Silane protocol followed by piranha.

Table (5): Frequencies (n), percentages (%) and results of Fisher's exact test for comparison between failure modes of surface treatment protocols.

Group	Adhesive		Cohesive		Mixed		*P*-value	Effect size *(v)*
	n	%	n	%	n	%		
Control	2	20	3	30	5	50	0.025*	0.457
Pirahna solution	4	40	0	0	6	60		
Nano-coating with Silane	8	80	0	0	2	20		
Nano-coating without Silane	3	30	0	0	7	70		

**: Significant at P ≤ 0.05.*

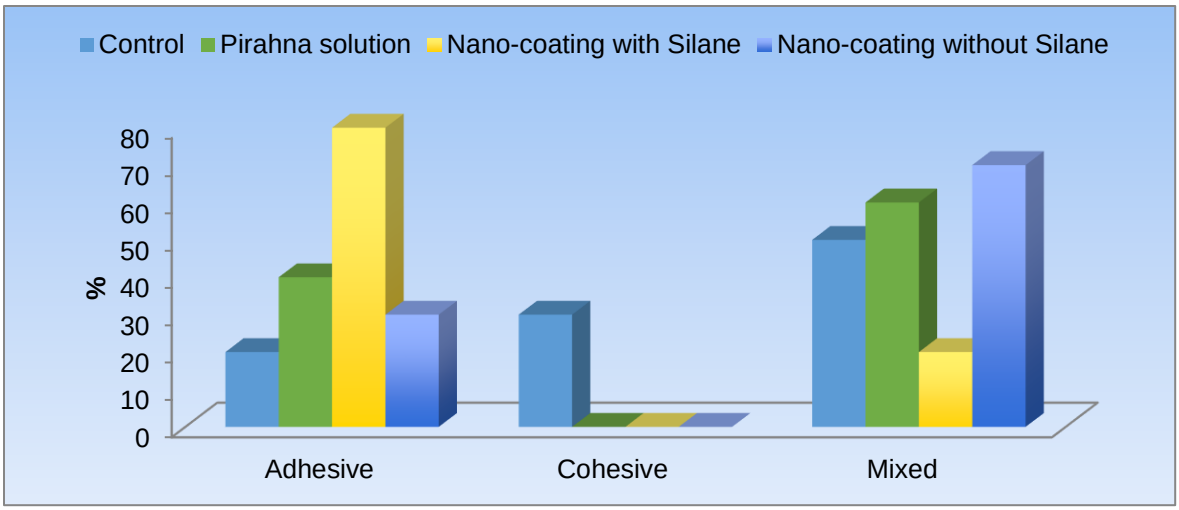

Figure (4): Bar chart representing failure modes with different surface treatment protocols.

There was a statistically significant difference between failure modes of different surface treatment protocols (*P*-value = 0.025, Effect size = 0.457). The highest prevalence of adhesive failure was found with Nano-

DISCUSSION

This in vitro study examined the effect of different surface treatment protocols on micro-shear bond strength of PEEK to a resin cement in comparison to Lithium Disilicate.

According to the results obtained, the null hypothesis of the present study was partially accepted. Micro-shear bond strength values obtained with piranha solution (25 MPa) treated group were non statistically significant compared to Lithium Disilicate group (29.4MPa). Whereas the nano-silica coated groups showed lower bonding values compared to Lithium Disilicate (PNsi=16.2MPa, PN=22MPa). In addition, surface roughness analysis revealed the increase in surface roughness for all groups with the highest mean value for PP group. In the present study, the mean bond strength value for the PEEK PP group showed the only comparative results to Lithium Disilicate among all other groups evaluated. The increased bond strength of this group could be attributed to its strong oxidizing capability due to its combination of highly-concentrated sulfuric acid (98%) and hydrogen peroxide (30%), chemically termed peroxymonosulfuric acid. Piranha solution reacts with PEEK surface through removing organic remnants, increasing surface polarity, and breaking aromatic structures. These led to an increase in the number of functional groups. Moreover, the atomic oxygen (which emerges during the reaction of sulfuric acid and hydrogen peroxide) in piranha acid reacts directly with the benzene ring on PEEK surface. This results in more functional groups available to bond to components of the adhesive system.[30–32] Previous studies have shown piranha etching significantly increases the strength of the bond between PEEK and dental adhesives.[16,33–36] However, they did not compare piranha solution with Lithium Disilicate. The surface roughness results obtained by piranha solution group scored the highest value. This could be explained by the strong oxidizing behavior of piranha along with the use of adjunctive sandblasting protocol that may have resulted in increasing roughness features and non-uniform increase in peaks and valleys (Figure 3d), while hydrofluoric acid etching in lithium disilicate group only removes the glass matrix forming homogenous porosities of uniform size, thus increasing the resin tag infiltration and promoting the bond strength.[37]

Studies stated that sandblasting increases bond strength by decontaminating and improving the surface roughness, thus, promoting micromechanical interlocking between the treated surface and resin cement.[1,8,17,18,37–40] In the present study combining both methods have created high surface roughness that slightly hinder the full depth resin infiltration due to high peaks and narrow valleys formed **(Figure 3d).**

This is attributed to achieving a slightly lower bond strength values for PP group (25MPa) in comparison to LD group (29.4MPa). Rely x Unicem is a self-adhesive resin cement with relatively high viscosity,[41] preventing its effective infiltration through highly roughened surface created by piranha etching. However, additional research after bonding protocol may be needed to confirm this theory. Moreover, using piranha solution for PEEK surface treatment should be avoided whenever possible because of its chemical hazard effects.[11]

Experimental nano-coated silica groups were investigated in this study after being subjected to 110 microns aluminum oxide sandblasting**.** Considering that the composition of PEEK will affect not only the mechanical properties but also the bond strength, the influence of coating the surface with nano sized silica instead of embedding it in the composition not to alter its mechanical properties was the technique experimented. Pretreatment with silane coupling agent greatly contributes to attaining a reliable bond between silica based restoration material and resin cement.[42] Considering the high reactivity between silica and silane coupling agent, it can be expected that reliable adhesion of the PEEK prosthesis can be successfully achieved. However, this was not verified in the present study. The results have shown the lowest micro-shear bond strength values (16 MPa) for nano-silica coated with silane.

The results came in disagreement with ***Rikitoku, et al. (2019)***[43] that stated that bond strength values increased significantly with an increase in silica content followed by silane coupling agent step that helped in improving and facilitating durable bond between PEEK and resin cement . However, this was not implied in this study.

Experimental nano-silica coating without silane was added to evaluate the silane effectiveness on bond strength when compared to the silane treated group. According to the obtained results, silane application negatively affected the nano-silica coated PEEK surface. Non silane added group had a slightly higher bond strength (22 MPa) even though there was no statistically significant difference between them.

Surface roughness analysis can be a possible explanation for the attained results which scored lowest surface roughness values (0.282 for PNsi, 0.283 for PN). There were low surface roughness values for both group. This can be explained by the presence of alumina particles along with the nano-sized silica particles found on the air-abraded PEEK surface. This may have caused a few

weak points at the bonding interface. Even though no significant difference was found in surface roughness values between them and that of the control group (0.28), bond strength values was significantly different. This can be attributed to the presence of both aluminum oxide and nano-sized silica particles that might clogged the surface micro porosities, resulting in less infiltration of resin tags thus decreased the resin cement penetration and decreasing the bond strength.

This result is comparable to that achieved by ***Stawarczk B, et al.***[39] who observed that even though highest values were achieved in surface roughness in air abraded group, the greatest bond strength was observed with acid-etched group. Here in the present study control group had shown a high bond strength (29.4MPa) compared to these 2 groups. This is explained by homogenous porosities and glass matrix removal by the use of hydrofluoric acid previously explained in various literature.[30,37,44]

LIMITATION OF THE STUDY

- Surface treatment protocols used in this study such as piranha solution cannot be used clinically as they need special precautions while usage and at disposal.
- Simulation of other factors in oral environment other than thermocycling are needed to be further investigated to assess bond strength better.
- Nano-coating with a method other than sol-gel should be experimented on PEEK surface.
- SEM analysis after cementation should be conducted to evaluate the depth of resin infiltration**.**

CONCLUSION

Within the limitation of this study, the followings could be concluded:

- Piranha treated group showed comparable micro-shear bond strength results to Lithium Disilicate values obtained.
- Nano-silica coated groups showed lower bond strength values compared to Lithium Disilicate and further investigations are required.
- Sandblasting obtained best results in combination with chemical treatment method.
- Piranha treated group showed the highest surface roughness values in comparison to all other groups.

CONFLICT OF INTEREST: The authors declare no conflict of interest concerned with this research.

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