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Original Article

Efficacy of Two Surface Treatment Methods of PEEK on The Shear Bond Strength to Veneering Composite: An In-Vitro Study

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Abstract

Aim: To evaluate the efficacy of sulfuric acid treatment of PEEK's surface on the shear bond strength to veneering composite compared to air abrasion.

Subjects and methods: 20 disc-shaped samples (10 mm diameter - 2 mm thickness) were produced from breCAM BioHPP blank and were randomly and equally divided into 2 groups according to the surface treatment; group H_2So_4: treatment with 98% sulfuric acid (etching), group Al_2O_3: treatment with 110 μm aluminum oxide particles (air abrasion). Visio-link primer was applied to samples followed by Crea.lign veneering composite. Scanning electron microscope (SEM) was used for the measurement of surface roughness. Universal testing machine was used to perform the shear bond strength (SBS) test. Elemental analysis was done after surface treatment and after shear bond strength test using energy dispersive X-ray analysis (EDX).

Results: Statistical analysis showed that group Al_2O_3 (30.26 ± 3.97 μm) had significantly higher surface roughness than group H_2So_4 (22.95 ± 2 μm). While group H_2So_4 (11.72 ± 2.93 MPa) had significantly higher shear bond strength than group Al_2O_3 (9.07 ± 1.63 MPa). Elemental analysis showed increase in sulfur and oxygen in group H_2So_4 and increase in carbon and silica in group Al_2O_3.

Conclusion: 98% sulfuric acid surface treatment of PEEK enhances SBS more than aluminium oxide air blasting.

Keywords: PEEK, shear bond strength, sulfuric acid, air blasting, air abrasion, aluminum oxide, composite, surface treatment, surface roughness, BioHPP.

I. INTRODUCTION

In prosthodontics, restorations are skilfully constructed to mimic and replace missing dental tissues in order to provide function and aesthetics (Al-Juaila et al., 2018).

Patients are increasingly selecting metal-free restorations. PEEK has superior mechanical and biological capabilities that provide several applications in different clinical situations. However, PEEK's poor translucency and grey or white hue still restrict its application as a monolithic restoration. Consequently, veneering is needed to provide acceptable aesthetics (Stawarczyk et al., 2014; Kumar R et al., 2019).

To provide a functional restoration that is stable over the long term, durable bonding of veneering material to substrate must be established. Depending on the nature of the materials used and how they interact, either chemical adhesion, micromechanical retention, or a mix of the two may be able to fulfil this need. Bonding PEEK to resin-based materials may be challenging due to PEEK's chemical composition and low surface energy (Hallmann et al., 2012).

This study's scope was to assess how chemical and mechanical surface treatments affect PEEK's shear bond strength (SBS) to the composite veneering material, and their correlation with surface roughness of PEEK and elemental composition.

The first null hypothesis was that there would be no difference between two tested surface treatments on the surface roughness of PEEK. The second null hypothesis stated that there would be no difference in shear bond strength of PEEK to the composite veneering material with both tested surface treatments.

II. SUBJECTS AND METHODS

a. Sample size:

A power analysis was created to perform 2-sided statistical test to the null hypothesis of research which assume that there was no difference between the evaluated treatments regarding shear bond strength. Effect size (d) had been calculated to be (1.32) based on the findings of (Zhou et al., 2014). By considering 0.05 (5%) alpha (α) level, and 0.20 (20%) beta (β) level (power=80%). The actual sample size (n) came out to be (20) samples in total. Sample size calculation was done by G*Power version 3.1.9.4 test.

b. Samples preparation:

A cylinder of 18 mm length and 10 mm diameter was designed using 3D Builder software and saved as STL file which was then transferred to exocad DentalCAD software. Three cylinders were dry milled from Bredent BioHPP blank using 5-Axis Milling Machine (Redon GTR, Turkey). Each cylinder was then sectioned into 7 discs of 2 mm thickness using a bench lathe machine (BV20L, Xi'an Industrial Machinery, China) using stainless-steel cutting disc (Bosch, Germany). 20 discs were produced. 45 seconds hand polishing of front surface of each disc was performed by 600-grit abrasive paper (silicon carbide) under tap water (Shabib et al., 2022). Samples were randomly divided into 2 equal groups (n=10): Group H_2SO_4 (acid etching) and Group Al_2O_3 (air abrasion).

c. Surface treatment for PEEK:

For acid etching, discs were placed on a laboratory watch glass. a glass pipette was used to apply few drops of 98% sulfuric acid to evenly cover the entire front surface for 60 seconds. Then, the discs were held with a tweezer, rinsed under tap water for 60 seconds then dried with oil-free dry air for 20 seconds (Sproesser et al., 2014; Chaijareenont et al., 2018).

For air abrasion, a customized wooden disc holder was used to hold the discs at a fixed distance of 10 mm and at 90 degrees to the air blaster nozzle. Discs were air blasted using 110 μm aluminum oxide for 10 seconds with 2.5 bar pressure using air-blasting machine (Bego air blaster, Germany). Finally, they were cleaned with oil-free dry air for 10 seconds (Keul, et al., 2014; Rosentritt et al., 2015).

d. Resin bonding:

Visio.link primer (VL) composed of methylmethacrylate (MMA) and pentaerythritol triacrylate (PETIA) was applied on each sample and light polymerized for 90 seconds. MMA containing adhesives improve the bonding of PEEK. Additionally, it has been observed that PETIA has a great potential for altering the PEEK surface (Keul et al., 2014; Uhrenbacher et al., 2014).

Crea.lign veneering composite was placed on the bonded surfaces using a customized split mold (5mm diameter - 2mm height) and light polymerized for 180 seconds.

e. Topographic Analysis:

Surface images were recorded using scanning electron microscope (FEI Company, Hillsboro, Oregon-USA) for un-treated sample and samples after surface treatment and after shear bond strength test. Images were analyzed by Image J software version 1.53 (National Institute of Health, USA) for surface roughness measurement (Martelo et al., 2021). Then, analysis of the elemental compositions of samples was carried out using energy dispersive X-ray analysis (EDX) both after surface treatment and after shear bond strength test (Hallmann et al., 2012).

f. Shear bond strength measurement:

Each sample was fixed in an acrylic resin mold (Acrostone Manufacturing & Import Company, Egypt) which was attached to the lower immovable part of the universal testing machine (Instron model 3345 England). 0.5 mm width blade unibeveled chisel was secured to the upper mobile part of the universal testing machine. Up until sample failure, compression mode of force was delivered using the chisel blade at the PEEK/composite interface at a crosshead speed of 1.0 mm/min. SBS was recorded in MPa by dividing the force necessary for failure (Newton) by the surface area (mm^2) through BlueHill software (Instron England) (Aboushelib et al., 2011).

g. Failure Analysis:

A stereomicroscope (Nikon MA100, Japan) at 20X magnification was used to inspect the debonded area and classify the failure types as: 1) Failure at interface between PEEK and overlying composite such that the sample appeared under microscope as exposed PEEK surface without any composite remnants (adhesive failure), 2) Failure in PEEK only (Cohesive failure of PEEK), 3) Failure in overlying composite only (Cohesive failure of veneering material), 4) Combined failure in both PEEK and overlying composite such that the sample appeared under microscope with areas of exposed PEEK surface together with some composite remnants bonded to surface (Mixed failure). One experienced examiner, who was not aware of the grouping, evaluated all samples failure modes.

h. Statistical Analysis:

Microsoft Excel 2016, Graph Pad Prism®, and SPSS 20® were all used to perform the statistical analysis. Mean and standard deviation were used to represent the data. Shapiro Wilk and Kolmogorov-Smirnov normality tests were used to examine the data for normality which showed normal distribution. Comparison between groups were performed by ANOVA test followed by Tukey`s post hoc test for surface roughness multiple comparisons, and Independent t test for shear bond strength. The significance level was set at $P \leq 0.05$.

III. RESULTS

a. Surface Roughness:

The mean surface roughness average (Ra) values in un-treated samples, Group H_2SO_4, and Group Al_2O_3 were (15.1635_µm ± 2.223 µm), (22.9547 µm ± 2.002 µm), and (26.3157 µm ± 2.431 µm) respectively Figure (1).

Comparison between them revealed that group Al_2O_3 was significantly higher than both the un-treated samples and group H_2SO_4 ($P < 0.0001$).

SEM images of samples showed increase in surface roughness after surface treatments as compared to un-treated sample Figure (2).

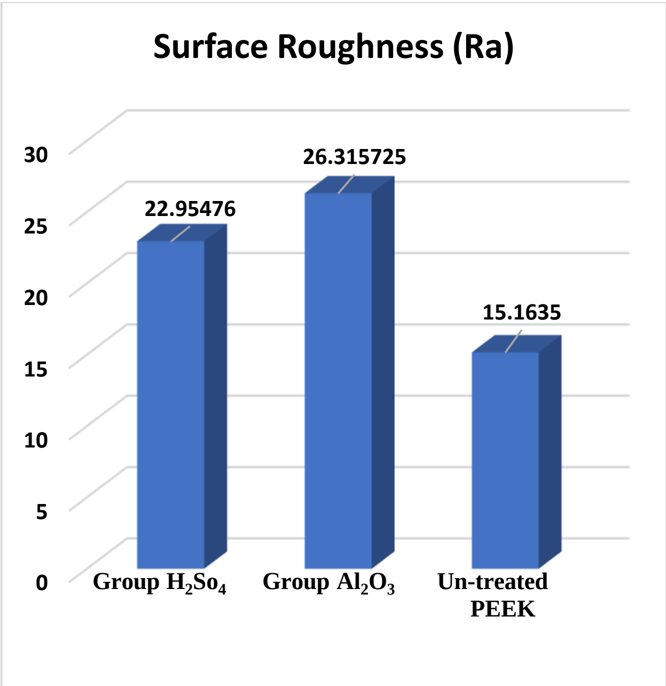

Figure (1): Bar chart of the mean of surface roughness values of all groups.

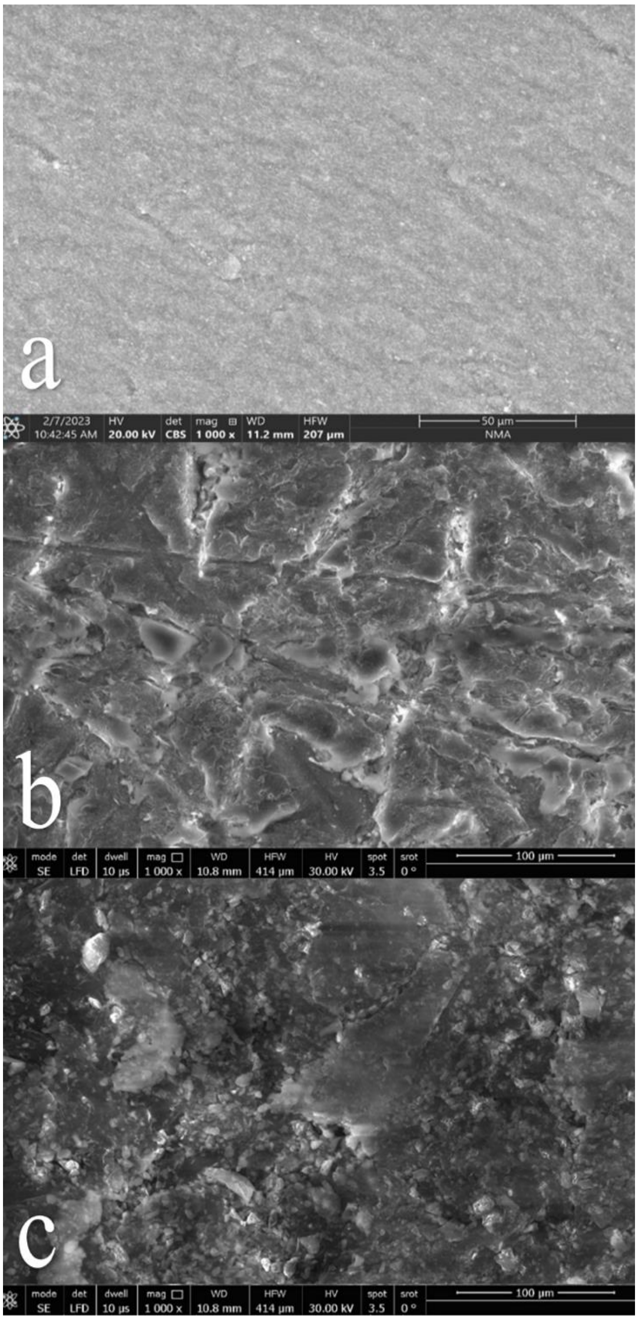

Figure (2): SEM images under 1000X magnification for samples: a) un-treated, b) subjected to 98% sulfuric acid, c) subjected to 110 μm aluminum oxide.

b. Shear bond strength:

The mean shear bond strength (SBS) in group H_2SO_4 was (11.72 MPa ± 2.93 MPa) while it was (9.07 MPa ± 1.63 MPa) in group Al_2O_3, Figure (3).

Comparison between the groups revealed that group H_2SO_4 was significantly higher than group Al_2O_3 (P = 0.02).

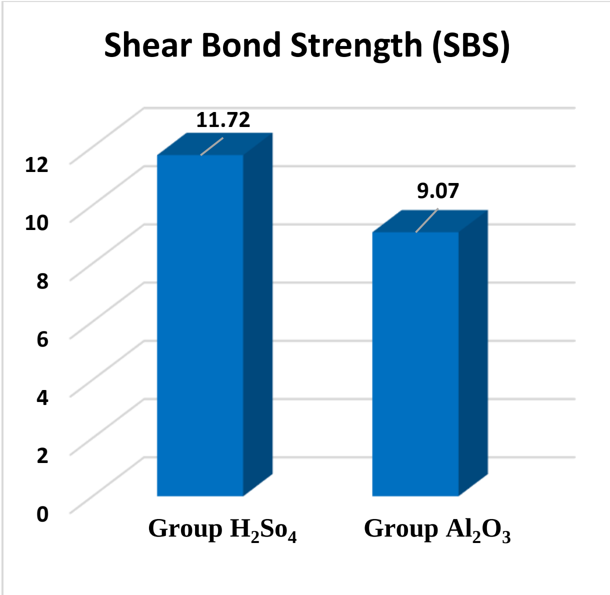

Figure (3): Bar chart of the mean of shear bond strength values of group H_2SO_4 and group Al_2O_3.

c. Failure Analysis:

Failures that occurred in group H_2SO_4 were 80% mixed and 20% adhesive. While in group Al_2O_3, they were 40% mixed and 60% adhesive.

d. Elemental Analysis:

There was an obvious increase of sulfur and oxygen in group H_2SO_4 after SBS test when compared to etched surface before bonding as shown in Table (1). In addition, SEM images for group H_2SO_4 samples after SBS showed multiple remnants of composite material on PEEK surface, Figure (4).

Table (1): EDX analysis comparing the weight percentages of elements C, O, Al, Si and S before bonding and after SBS test for group H_2SO_4.

	Group H_2SO_4 before bonding (wt%)	**Group H_2SO_4 after SBS (wt%)**
Carbon (C)	42.02-46.09	41.2-46.09
Oxygen (O)	22.61-23.81	36.55-42.83
Aluminum (Al)	0.68-0.72	0.57-0.6
Silica (Si)	0.47-0.63	0.66-2.1
Sulfur (S)	2.1-3.62	5.26-9.98

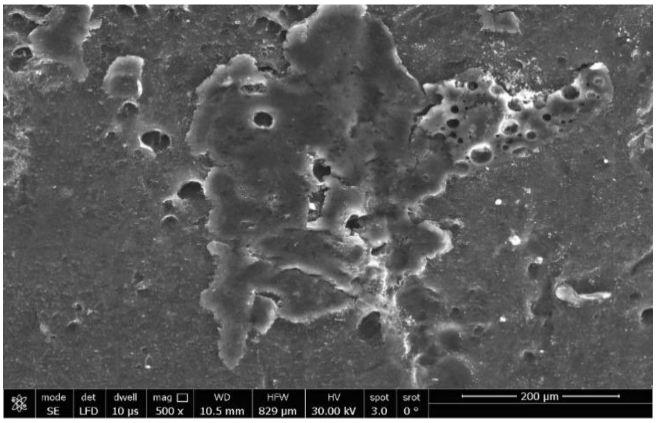

Figure (4): SEM image of group H_2SO_4 sample under 250X magnification.

On the other hand, there was an obvious increase of carbon and silica in group Al_2O_3 (air abrasion) after SBS test compared to abraded surface before bonding as shown in Table (2). In addition, SEM images for group Al_2O_3 samples after SBS showed mostly few or no composite remnants on PEEK surface, Figure (5).

Table (2): EDX analysis comparing the weight percentages of elements C, O, Al and Si before and after the SBS test for group Al_2O_3.

	Group Al_2O_3 before bonding (wt%)	**Group Al_2O_3 after SBS (wt%)**
Carbon (C)	35.61-36.45	43.42-46.93
Oxygen (O)	30.37-31.64	26.04-29.04
Aluminum (Al)	10.96-11.62	2.82-6.16
Silica (Si)	0.94-1.04	3.09-14.71

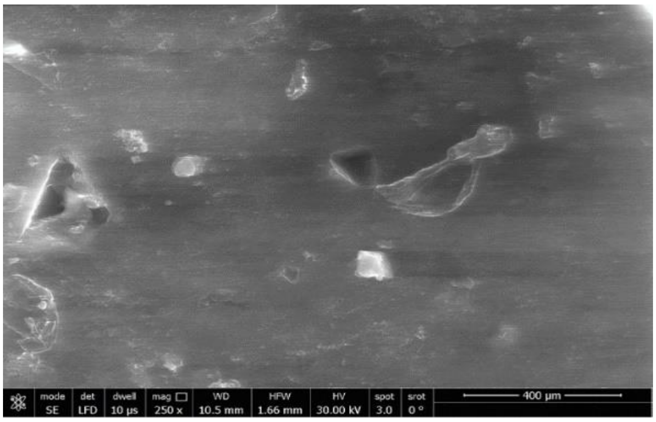

Figure (5): SEM image of group Al_2O_3 sample under 250X magnification

IV. DISCUSSION

BioHPP PEEK is a ceramic filler reinforced PEEK material with high mechanical properties and polishability (Aboelnagga et al., 2022). Bonding of PEEK to veneering composite is considered critical.

In the current study two surface treatment protocols were tested (acid etching vs. air abrasion). Sulfuric acid is the most common chemical surface treatment method of BioHPP. We used 98% concentrated sulfuric acid specifically as it was reported that this concentration enhances the adhesion of composite veneering material to PEEK (Chaijareenont et al., 2018).

Air blasting was also used in the present study as it is considered a successful technique in attaining proper SBS values with the advantage of being a safer method (Shehab-Eldin et al., 2020). The aluminum oxide particle size used was 110 µm as this size was stated to cause high roughness of the treated surface and enhance its bond strength to resin (Rosentritt et al., 2015).

The first null hypothesis was rejected as there was a significant difference between two tested groups regarding PEEK samples's surface roughness. Higher Ra was noticed in air blasting group than acid etching group.

The findings of the present study are in agreement with EL-Wassefy et al., (2019) and Çulhaoğlu et al., (2020). They found that the mean values of Ra for PEEK surface were higher in air abrasion group than sulfuric acid etching group.

This could be owed to the high kinetic energy of alumina particles at the tested pressure. Their impact causes the surface to become microporous (Parkar et al., 2021). This is confirmed in the current study by the surface topography that showed that air abrasion group had abraded textures with multiple porosities, deep grooves and cracks and some superficial particles.

On the other hand, Binhasan et al., (2022) disagreed with our results. They stated that 98% sulfuric acid caused more surface roughness of PEEK when compared to 110 µm Al_2O_3 air blasting. This difference may be attributed to their use of a lower air blasting pressure (1 bar) than that used in our study (2.5 bar).

The second null hypothesis Was also rejected as upon comparing the two tested surface treatments of PEEK, SBS results were significantly different. Higher SBS was presented in 98% sulfuric acid group.

The results of this study are in agreement with Stawarczyk et al., (2013) who reported that the highest SBS values were achieved via sulfuric acid etching compared to silica-coating and air blasting.

Also, Çulhaoğlu et al., (2020) found that sulfuric acid etched surfaces had the greatest mean SBS values when compared to Al_2O_3 airborne abrasion and Yb:PL laser irradiation.

Moreover, Binhasan et al., (2022) reported higher SBS values with sulfuric acid etching when compared to Al_2O_3 and Diamond particles air blasting.

These results could be attributed to the dissolution of PEEK surface particles by concentrated sulfuric acid at ambient temperature as it causes PEEK to swell, which results in surface porosities that could be more easily penetrated by the adhesives and serve as an anchorage for resin material (Schmidlin et al., 2010; Rocha et al., 2015). This is proven by the current study's surface topography, which revealed a fiber network of a complex pattern with multiple dispersed porosities and the underlying surface appeared as blisters in group H_2SO_4.

It could also be explained by the fact that sulfuric acid led to the production of sulfonate groups (SO_3) in the polymer chains of PEEK, which were then chemically cross-linked to methylmethacrylate based adhesives. This is confirmed by our elemental analysis (EDX) which showed a dramatical increase of sulfur and oxygen.

The reason behind the lower SBS of air abrasion group was the possibility that the coarse alumina particles used to create the rough surfaces and increased porosities have prevented adhesives from penetrating and caused some weak areas at the bond interfaces (Shehab-Eldin et al., 2020).

Another explanation is related to wettability, air abrasion resulted in surface wettability values lower than that of sulfuric acid (Çulhaoğlu et al., 2020).

In addition, air abrasion provided mechanically treated PEEK surfaces with increased surface areas, whereas acid etching modified the surface's chemical properties, which resulted in more functional groups forming on the PEEK surface. The oxygen in sulfuric acid interacted with and broke the PEEK benzene ring resulting in higher surface polarity when additional functional groups (sulfonates SO_3) with high bonding potential were formed (Hallmann et al., 2012; Uhrenbacher et al., 2014).

The failure analysis showed adhesive and mixed modes of failures which supported the SBS results in current study. Mixed failures dominantly occurred in the acid etching group which had the highest SBS values while adhesive failures dominantly occurred in the air abrasion group.

The composition analysis (EDX) showed increase in the percentage of sulfur and oxygen in group H_2SO_4 (acid etching) after the SBS test which means that these elements most probably share in the formation of a chemical bond between veneering composite and PEEK surface (sulfonation) (Schmidlin et al., 2010; Rocha et al., 2015). Also, carbon and silica increased remarkably in group Al_2O_3 (air abrasion) after SBS test. Carbon and silica are the main constituents of Visio-link and Crea.lign veneering composite so EDX gave a valid proof of the penetration of Visio-link adhesive and composite resin into the treated PEEK surface.

Since SBS values of in-vitro tests that are more than 5 MPa are considered acceptable, both groups' results lie within the acceptable range (Caglar et al., 2019).

Finally, from the findings of this study, both surface treatments could be applied for BioHPP PEEK material to produce acceptable bond strength to the veneering composite with greater influence of 98% sulfuric acid treatment.

V. CONCLUSION

Conclusions drawn from our research with consideration of study's limitations were:

1. 98% sulfuric acid surface treatment of PEEK significantly increased shear bond strength to veneering composite.
2. Shear bond strength of PEEK to veneering composite was not directly correlated to its surface roughness.
3. PEEK material treated by 98% sulfuric acid relied on the chemical bond formation with the veneering composite, while those treated with Al_2O_3 surface treatment relied on the micromechanical interlocking.

Conflict of interest: The authors declare that they have no conflict of interest regarding the publication of this paper.

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Ethics: The study was approved by research ethics committee at Faculty of Dentistry Cairo University with an approval number of 20-2-28.

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