Effect of Piranha Solution on PEKK Bonding to Veneering Composite Resin

[1]Sadiq Ameen Hakim, BSc. and [2]Amaal Khadim Mohammed, MSc.
Department of Prosthetic Dental Technology, College of Health and Medical Technology, Middle Technical University, Iraq.
Corresponding author: Sadiq Ameen Hakim
E-mail: Sadiqalmayali2@gmail.com

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Abstract

Background Polyetherketoneketone (PEKK) has been recently introduced for dental uses due to its superior mechanical, physical properties, and high biocompatibility. PEKK has a hydrophobic inert surface, making it highly insoluble in almost all organic and inorganic solutions, except for extremely concentrated strong acids such as piranha solution. Moreover, no previous researches have investigated the utilization of piranha etching in dentistry as a surface treatment agent for PEKK before bonding. **Objectives** to assess the effect of piranha acid etching on the Shear Bond Strength (SBS) between PEKK and veneering composite. **Materials and Methods** Twenty-one square-shaped PEKK specimens of (7×7×2) mm dimensions were designed and milled with CAD/CAM system and assigned randomly to three groups for surface treatment (n=7). (1): The control (sandblasting with 110μm of Al2O3); (2): Etching with piranha solution; and (3): Both sandblasting with 110μm of Al2O3 and etching with piranha solution. After surface pretreatments, a qualitative assessment of surface roughness was achieved by using scanning electron microscopy (SEM). Composite resin veneer was applied on each specimen with the help of a bonding jig using light-polymerization before being subjected to the SBS test. Then the SBS test was performed and the mode of failure was analyzed. Statistical analyses were carried out with one-way ANOVA followed by a post-hoc LSD test. **Results** Sandblasting+Piranha acid etching group showed the highest SBS value among all groups ($p<0.01$). All groups showed a clinically acceptable SBS value according to ISO standardization (10477). **Conclusions** Piranha acid treatment of the PEKK specimen surface may be a viable alternative to sandblasting for better bonding with veneering composite resin. The highest SBS was achieved in the combination group of Sandblasting+piranha.

Keywords: Composite resin; piranha acid; PEEK; surface treatment; SBS.

Introduction

Studies in the field of polymer dental materials are now mainly focusing on materials with excellent esthetics, acceptable biocompatibility, and good mechanical and chemical characteristics (Stawarczyk et al, 2017). Polyaryletherketones (PAEK) is a group of high-performance polymers (HPP) that have been studied for their outstanding chemical and mechanical characteristics, abrasion resistance, and biocompatibility (Hong et al, 2020). PAEK has gradually become the most popular polymer material in the medical field for orthopedic and trauma purposes because of its excellent mechanical and physical properties (Hu et al, 2021; Ates et al, 2018). Also, PAEK has emerged as a promising dental material to replace metal and glass ceramics due to its shock-absorbing properties, efficient stress distribution, outstanding fracture resistance, and radiolucency (Yuan et al, 2018; Choi et al, 2017; Younis et al, 2020). PEKK (polyether ketone) and PEEK (polyetheretherketone) are predominant members of the PAEK family in the dental field that consist of an aromatic backbone chemical chain linked by functional ketone and ether groups (Gouveia et al, 2021; Batak et al, 2021). However, because of the superior properties and the two ketone functional groups between the aryl rings, PEKK overlaps all other PAEK polymers with up to 80% greater compressive strength and many processing methods than PEEK (Shetty, 2018; Roland et al, 2021; Dawson et al, 2018). Above mentioned characteristics, as well as the high biocompatibility of PEKK material, it is considered a suitable material for prosthodontics restorations such as single crowns, fixed partial dentures (FPDs), removable partial dentures (RPDs), and implant-supported frameworks (Alqurashi et al, 2020; Labriaga et al, 2018). Due to the low translucency and white/grayish color of PEKK, it is not suitable to be used as a monolithic dental restoration, requiring additional veneering composite with a sufficient binding to PEKK to obtain satisfactory aesthetics (Gama et al, 2020). Furthermore, PEKK's low surface energy, inertness, and resistance to surface conditioning have made it challenging to establish a durable bond with a veneering composite (Fokas et al, 2019; Gama et al, 2020). Therefore, various surface pretreatments have been proposed to overcome the mentioned limitations (Jun et al, 2020; Çulhaoğlu et al, 2020). The effect of chemical etching solutions such as sulfuric and vinyl sulfonic acids on the bonding strength of PEKK to composite resin has been studied (Lee et al, 2017; Sakihara et al, 2019). However, the use of piranha etching solution is limited to PEEK material (Silthampitag et al, 2016; Uhrenbacher et al, 2014; Stawarczyk et al, 2014; Keul et al, 2014; Hallmann et al, 2012). But, since PEKK has similar chemical properties to PEEK, a comparable method of surface treatment is assumed to obtain adequate bonding. Therefore, the present study aims to evaluate the effect of piranha etching on the bond strength between PEKK and veneering composite resin.

Materials and Methods

Specimen's preparation

PEKK specimens with a dimension of 7×7×2mm were designed by CAD software (ExoCAD GmbH), and the design was exported as STL formatted file and sent to the milling machine to mill PEKK CAD/CAM blocks (Pekkton ivory, Cendres+Métaux, Biel-Bienne, Switzerland). The PEKK specimens were embedded in auto-polymerizing acrylic (Spofa Dental Product, Czech Republic) with a dimension of 15×15×5mm (length, width, and thickness respectively) to allow the specimens to fit into the universal testing machine jaws as shown in figure (1). The surface of each specimen was polished using rotating silica carbide paper (P180, P320, P600, P1200 respectively), (Struers, Denmark) for 60sec at 150rpm under constant water cooling. After polishing, the specimens› surfaces were ultrasonically cleaned for 10 min in an ultrasonic cleaner unit (TECNO-GAZ, Italy) with deionized distilled water. The specimens were then randomly categorized into three different surface pre-treatment groups (n=7), figure (2). In the control group, the sandblasting was performed for 10sec using 110μm aluminum oxide particles (Al2O3), (Shera Werkstoff Technologie, Germany) at a pressure of 2-bar and a distance of 10mm the nozzle away from the specimen (Pekkton company recommendation), then cleaned for 10min in an ultrasonic cleaner with deionized distilled water to remove any remaining particles. With the 1st experimental Piranha acid etching group (H2SO4+H2O2), a combination of 98% sulfuric acid and 30% hydrogen peroxide at a ratio of 3:1 applied on the specimen surface using micro-pipette for 60sec, then rinsed with water spray for 5sec in an even motion to prevent the surface topography from any further directional changes with the final step of air drying. While the second experimental group of sandblasting (110μm of Al2O3)+Piranha acid etching, the specimens were first sandblasted with 110μm of Al2O3 as in the control group, then pretreated with Piranha etching solution as in the 1st experimental group.

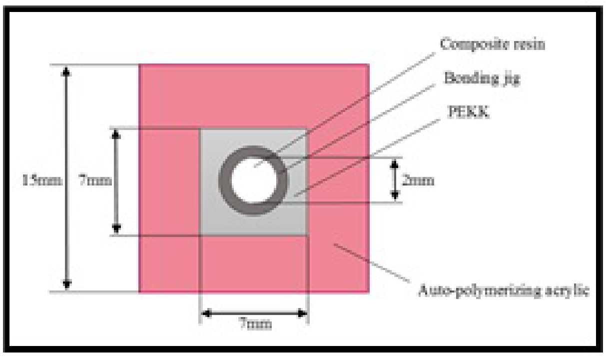

Figure (1): Schematic drawing of specimen preparation.

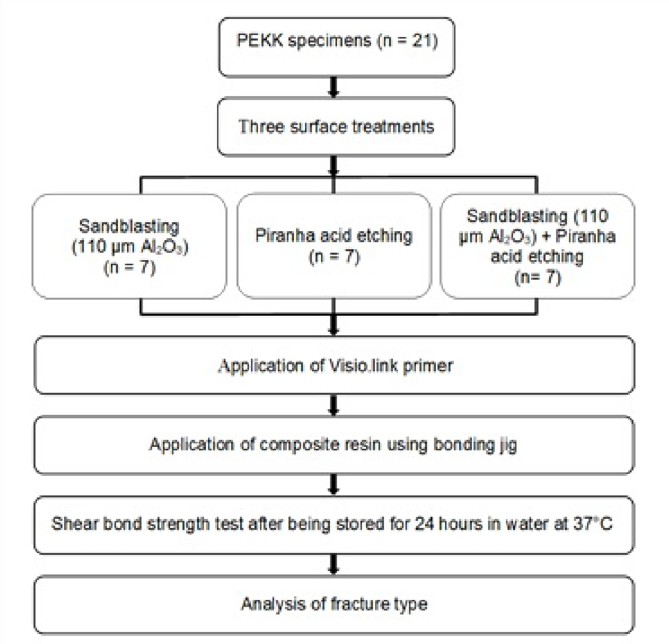

Figure (2): Experimental procedures for the present study.

Scanning electron microscopy (SEM)

To examine and investigate the surface topography, an extra specimen for each surface treatment group was constructed and visually displayed by an SEM device (Inspect S50) at ×10.000 magnification.

Bonding PEKK to veneering composite

Before bonding, a square-shaped bonding jig was designed by SolidWorks premium 2014 with the same dimension of the specimen in which bonding steps were performed through a 3mm hole in the center of each specimen. On the surface of the specimen, a thin coating of Visio.link primer adhesive (Bredent, Germany) was applied and light-cured for 90 sec using a dental laboratory light-curing device (Labolight, DUO). Subsequently, the bonding jig was positioned on the specimen and filled with composite resin (GRADIA PLUS GUM Heavy Body, GC Corporation, Japan). After that, the bonding jigs were gently removed and the specimen placed in a light-curing device for 180sec. For full polymerization, all bonded specimens were kept in water at 37°C for 24h.

Shear bond strength (SBS) test

The SBS of each specimen was measured using a universal testing machine (Laryee technology co. LTD, China). A load of knife edge-shaped piston applied with a cross-head speed of 1mm/min, figure (4). The SBS is calculated by dividing the fracture load on the bonding area (N/mm² =MPa).

Fracture mode Analysis

Following deboning, each specimen was examined under a microscope (OXION, China) at a magnification of ×25 to identify and assess the model and type of fracture. The mode of fracture is identified as:

1. Adhesive fracture, meaning that no composite residues were left on the PEKK surface.
2. Cohesive fracture, which occurs in the composite›s bulk layer.
3. Mixed fracture, where composite residues are partially visible on the PEKK surface.

Statistical methods

The data of the present study was analyzed using One-way ANOVA (post-hoc, LSD) at a significant P-value of ($p \leq 0.05$).

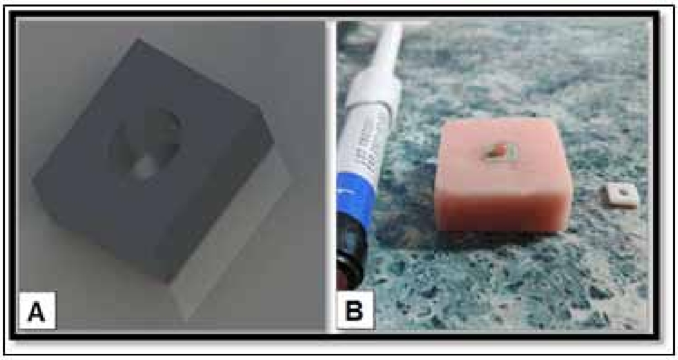

Figure (3): A: The design of bonding jig, B: Finished specimen ready for SBS test.

Figure (4): Specimen under SBS test.

Results

Shear bond strength (SBS) test

Table (1) shows the descriptive statistics and ANOVA test for the studied groups. The sandblasting piranha group showed the highest mean bond strength value 23.635(±1.405) MPa in comparison to the control group of 15.048 (±1.398) MPa, followed by piranha 17.070 (±1.350 MPa) as in figure (5). It was confirmed that there was a significant difference between the groups ($p \leq 0.05$). To verify the differences in shear bond strength between each experimental group, the post-hoc (LSD) were performed as in Table (2).

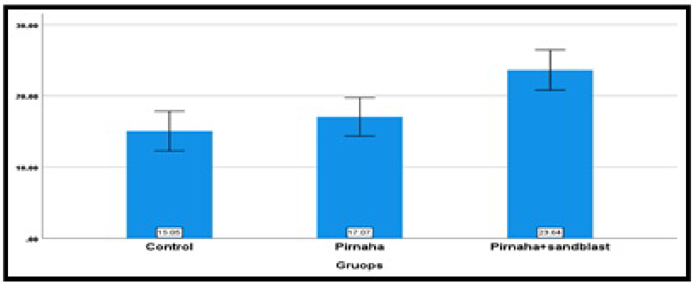

Figure (5): Bar-chart represents the SBS mean values of the studied groups.

Fracture mode analysis

Fracture mode analysis revealed that all groups showed mixed and adhesive fracture. While, no cohesive fracture was appeared in the present study results, figure (6).

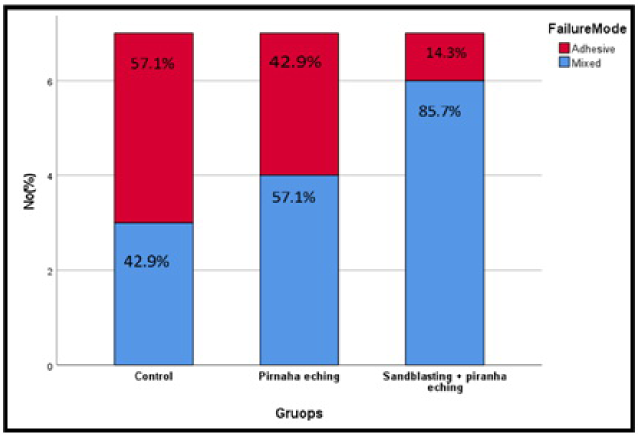

Figure (6): Fracture modes after SBS. test.

SEM observations

The characterization of the PEKK surface after different surface modifications was demonstrated by SEM at 10.000× magnification. In the control group, the sandblasted PEKK specimens show irregular surface topography with flaws and streaks distributed along the surface, figure (7: A). While in the Piranha etching group, the surfaces were covered with small pits and filler particles after PEKK specimens treated with piranha etching, figure (7: B). On the other hand, the sandblasting+piranha etching group shows a more irregular surface pattern with microporosity when compared to the control group, figure (7: C).

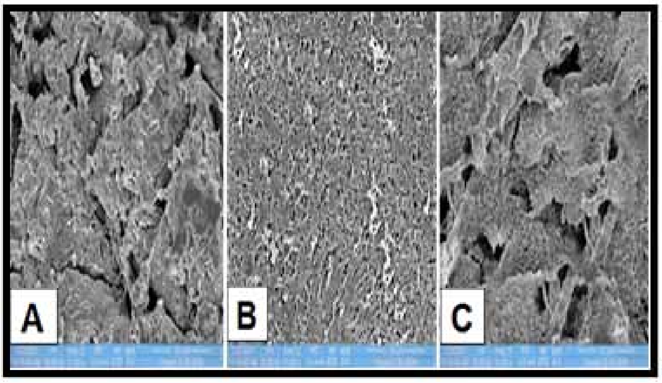

Figure (7): SEM images of the PEKK surface after surface treatments, A: Sandblasting, B: Piranha etching, C: Sandblasting+piranha etching.

Table (1): Descriptive statistics and ANOVA test for different surface treated groups.

Studied groups	No.	Mean	SD	SE	Min.	Max.	ANOVA test *P*-value (Sig)
Control	7	15.048	1.398	.528	13.43	17.68	000. (S) (*P*<0.01)
Piranha	7	17.070	1.350	.510	14.85	18.80	
Sandblasting +piranha	7	23.635	1.405	.531	21.21	25.45	
Total	21						

Table (2): Multiple pairwise comparisons using post-hoc (LSD) tests according to the surface treatments of PEKK.

Groups		Mean Difference	*P*-value	Sig.
Control	Piranha	-2.021*	.008	S
	Sandblasting+piranha	-8.587*	.000	S
Piranha	Control	2.021*	.008	S
	Sandblasting+piranha	-6.565*	.000	S
Sandblasting+piranha	Control	8.587*	.000	S
	Piranha	6.565*	.000	S

Discussion

PEKK is the most recent PAEK material to be utilized in prosthodontics and has a great deal of potential in this field. As an overall trend is moving toward metal-free restorations, the bonding characteristics of PEKK with other polymer-based materials are of interest (Younis et al, 2020; Stawarczyk et al, 2017). In the present study, two surface treatment methods are proposed to enhance the binding strength between PEKK and veneering composite. Sandblasting roughens the surface, eliminates organic contaminants, and generates a fresh, active surface layer. It also aids in the promotion of micromechanical interlocking with the bonding agent, which results in enhanced binding capacity (Gama et al, 2020). According to recent researches conducted by the company lunched the Pekkton, it is recommended to use an MMA-based primer after surface roughening by sandblasting with 110µm of Al2O3. Previous researches have shown that Visio. link, which is a primer comprising MMA monomers, could produce high bond strength between composite resin and PEKK polymer (Stawarczyk et al, 2017; Lee et al, 2017; Hong et al, 2020). Additionally, the combination of sandblasting pretreatment with Visio. Link primer was the most effective in promoting adherence to PEKK (Stawarczyk et al, 2017; Gouveia et al, 2021). As a result, the surface treatment parameters of the control group were established in the present study in line with the manufacturer›s instructions. Latest studies showed that acid etching of the PEEK surface causes a chemical change in the surface, which increases the number of functional groups accessible for attaching to the adhesive components (Çulhaoğlu et al, 2020; Stawarczyk et al, 2014; Fokas et al, 2019). To the best of our knowledge, no research has been conducted into the effect of piranha solution as a chemical surface treatment on the bond strength of PEKK to veneering composite. Piranha solution, which is also known as peroxymonosulfuric acid, is a strong corrosive and oxidizing agent. It is a combination of concentrated sulfuric acid (H2SO4) and hydrogen peroxide (H2O2) (Silthampitag et al, 2016). According to earlier studies, when the surface of PEEK was only treated with sulfuric acid, the functional ether linkages (C-O-C) and carbonyl linkages (C=O) between benzene rings were attacked by the acid (Çulhaoğlu et al, 2020). While in piranha acid, the interaction of sulfuric acid with hydrogen peroxide resulted in the release of atomic oxygen, which interacts with and breaks the benzene ring. This leads to the oxidation of PEEK polymer, increasing surface polarity, aromatic ring opening, and formation of carbon-oxygen compounds. As a result, additional functional groups are available on the PEEK surface to bind to the adhesive›s components. The produced crosslinking improves the diffusion of adhesive components into PEEK polymer and, consequently, increases the binding strength (Stawarczyk et al, 2014; Keul et al, 2014; Uhrenbacher et al, 2014).The above-mentioned benefits can explain the considerable improvement in bond strength between PEKK and veneering composite after piranha etching with an increase in the SBS mean value of 17.070 (±1.350) MPa in comparison to the control group 15.048 (±1.398)MPa which is statistically significant ($p<0.01$). Also, SEM image (figure 7: B) of PEKK specimens following piranha acid etching has furtherly corroborated to these data by showing an irregular surface area, with pits and filler particles scattered over the surface, and this may agree with Hallmann et al, (2012) and Silthampitag et al. (2016) who also found that piranha etched PEEK showed small pits on its surface. However, piranha acid etching following sandblasting demonstrated the highest SBS mean value of 23.635(±1.405)MPa in comparison to the other groups with the significant difference among them. The reasons for this bonding enhancement could be that in addition to the increased ratio of functional groups caused by piranha etching which led to crosslinking between the two polymers, the roughened surface obtained from sandblasting allows for the penetration of adhesive inside the polymer, and this may improve the micromechanical interlocking to the veneering composite and thus resulting in bonding strength enhancement. Moreover, SEM evaluation (figure 7:C) could agree with Hallmann et al. (2012), who indicated that piranha acid etching following sandblasting might be exhibited a better-defined micro-roughness on the PEEK surface, contributing to a larger contact surface area accessible for mechanical interlocking with the adhesive material. According to ISO standardization (10477) guidelines, the minimum required SBS value between resin-based materials and the substrate is 5MPa. However, it has been proposed that under oral conditions, at least 10-12MPa is necessary to ensure long-term bonding (10477, 2004). In the present study, all the tested groups showed clinically acceptable SBS values. Also, the fracture pattern between PEKK substrate and veneering resin indicates the bond strength between them (Fokas et al, 2019). In this study, mixed and adhesive fractures were the most common with no cohesive fracture. The adhesive fracture was predominant in the control group, while mixed fracture was more common in experimental piranha and sandblasting+piranha groups. When the bonding strength is not sufficiently high, an adhesive fracture can take place. On the other hand, the mixed fracture may occur due to the irregular stress distribution at the interface (Labriaga et al, 2018). In general, the groups with high bonding strength values might have a high percentage of mixed fracture patterns. The fracture patterns confirm SBS data, as the bonding strength increases, the fracture patterns tend to shift from adhesive fracture to mixed fracture which seems to agree with a study by Ates et al, (2018). Regarding the outcomes of this study, piranha etching and sandblasting+piranha etching can be regarded as valuable surface treatment modalities for PEKK polymer bonded with veneering composite resin.

Conclusions

Piranha acid etching of the PEKK surface can be a viable alternative treatment method to sandblasting for better bonding with veneering composite resin. The highest SBS value was achieved in the combination group of sandblasting+piranha etching.

Conflict of interest

We are the author's (Sadiq Ameen Hakim and Assist. Prof. Amaal Khadim Mohammed) state that the manuscript for this paper is original, and it has not been published previously and it's part of MSc. dissertation and is not under consideration for publication elsewhere, and that the final version has been seen and approved by all authors.

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