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EFFECT OF VARIOUS SURFACE TREATMENT PROTOCOLS OF POLYETHERKETONEKETONE ON SURFACE ROUGHNESS, WETTABILITY AND BONDING TO DIFFERENT VENEERING MATERIALS: AN IN-VITRO STUDY

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ABSTRACT

Aim: To investigate how different surface treatments affected surface roughness, wettabilty and bonding of polyetherketoneketone (PEKK) to various veneering materials.

Material and Methods: Three pretreatment groups of 120 disc-shaped PEKK specimens (10 x 4 mm) were assembled. Group A (control) : No treatment, Group B: Air abrasion, and Group C: Sulfuric acid etching. Then specimens were further divided into three subgroups according to type of veneering materials. Subgroup I: PEKK veneered with hybrid ceramics (Vita Enamic), subgroup II: PEKK veneered with lithium disilicate (IPS E.max CAD), and subgroup III: PEKK veneered with zirconia (Prettau anterior). A 3D non-contact optical profilometer was used to measure surface roughness (Ra), and SEM was used to analyze surface morphology. For contact angle measurements, wettability was assessed using static sessile drop method. Additionally, two classes before and after thermocycling were developed for each subgroup. Using a universal testing system, shear bond strength (SBS) was measured immediately and after thermocycling, and a stereomicroscope was used to investigate the failure modes.

Results: Surface roughness was dramatically increased ($P<0.001$) by air abrasion. According to the wettability results, sulfuric acid produced better contact angles than air abrasion. Regardless the veneering material, sulfuric acid etched group had the highest shear bond strength. Regardless surface treatment, Prettau zirconia had the highest shear bond strength values, followed by Vita Enamic and IPS E.max CAD with significance. All examined groups showed a significant decrease in SBS following thermocycling.

Conclusions: Durable bond can be achieved with PEKK etched for one minute with sulfuric acid.

KEYWORDS: Surface treatment, Surface Roughness, Polyetherketoneketone, Veneering materials, Shear bond strength.

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INTRODUCTION

Polyaryletherketones (PAEKs) belong to a group of high-performance thermoplastic polymers characterized by their semi-crystalline nature and their unique composition of keto- and ether groups. This composition grants them impressive chemical stability and mechanical strength. (1).

These properties render PAEKs especially attractive for use in various sectors, including the manufacturing of orthopedic implants and prosthetics, since their introduction in 1987 (2).

The polymers commonly used in the medical sector include Polyetheretherketone (PEEK) and Polyetherketoneketone (PEKK) Bonner first synthesized Polyetherketoneketone (PEKK) in 1962 , while Rose and Staniland obtained a patent for Polyetheretherketone (PEEK) in 1982 (3,4).

PEEK, a prominent member of the PAEKs family, is extensively utilized in orthopedic surgeries as a substitute for titanium. This is due to its exceptional chemical and mechanical properties, including excellent biocompatibility, high strength, low water absorption, and resistance to heat. (5).

In dentistry, it mainly acts as a framework structure in the making of metal-free removable and fixed partial dentures, implant abutments, healing caps (6).

In recent times PEKK (Cendres'M_etaux SA, Biel/Bienne, Switzerland) has been introduced, demonstrating a capability to attain a potential increase in compressive strength up to 80% higher than that of unreinforced PEEK. The enhanced properties of PEKK and PEEK polymers are attracting attention for use in dental applications.

(PEKKs) are high-performance, biocompatible polymers that are lightweight, extremely rigid, stable in dimensions at elevated temperatures, and can be fabricated from milling or pressing techniques. High performance polymers are being introduced as a substitute for glass ceramics and metal in dental applications due to their excellent shock-absorbing capabilities, good fracture resistance, and improved stress distribution. (7, 8).

Although PEKK offers numerous advantages, its limited translucency and grayish color restrict its application as a monolithic dental restoration. Consequently, light-curing resin composites, prefabricated veneers and ceramic crowns are typically used to veneer PEKK material that has been machine-milled or heat-pressed to achieve high esthetic demand. (9).

Achieving a strong bond with veneer materials is still difficult due to PEKKs' low surface energy and inert structure. It is therefore necessary to perform additional pretreatments on the PEKK surface to enhance the adhesive qualities between veneering materials and PEKK. (10)

PEKKs have been subjected to a variety of micromechanical and chemical surface treatment techniques to modify the surface properties for a more robust and improved bonding. These methods include tribochemical silica coating (Tbc) using silica (SiOx) modified Al_2O_3, plasma application, laser applications, and etching with sulfuric acid (Sa) or its mixture with hydrogen peroxide (Piranha solution) (8,11).

Among these, the most effective surface treatment for PEKK polymers was found to be etching with a 98 percent Sa solution. Additionally, Sb and Tbc methods have demonstrated favorable bonding results on PEKK polymers (12).

Various surface treatment methods that modify the surface topography can change both the surface area and the wetting behavior of the polymer substrate. Consequently, this can affect the polymer's surface energy and its adhesive potential for different veneering materials. (13).

Wettability is the ability of a liquid to spread over the surface of a solid and is usually estimated by the contact angle of a dispersion liquid on a substrate which is employed as an indicator of the substrate's total surface energy. (14)

To form a strong and lasting chemical bond between PEEK and veneering materials, it's crucial to utilize appropriate adhesive systems. (10) Recent research has demonstrated that methyl methacrylate (MMA) dental adhesives can effectively bond with PEKK. Additionally, ensuring a durable bond is essential for achieving long-term durability and satisfactory functional results. (11)

Eating, drinking, and breathing can cause temperature changes in the oral cavity throughout the day, which can lead to functional thermal stresses that eventually compromise the stability of the bonded interface. Due to its ability to generate consistent thermal stresses at the interface, thermocycling is one helpful method for mimicking in-vitro aging of specimens (12,15) .

Shear bond strength testing is commonly utilized methods in restorative dentistry and dental materials research to compare products and techniques (16). It is believed that shear forces are the main cause of restorative material bonding failures in vivo (17).

The recently introduced PEKK polymer is still restricted by limited information concerning the bonding performance. Additionally, it is necessary to eliminate the lack of knowledge regarding the bonding performance of zirconia, lithium disilicate, and hybrid ceramics to PEKK.

Therefore, this in-vitro study was performed to explore the impacts of various surface treatment methods. (Such as 98% sulfuric acid etching or sandblasting with 110 µm Al_2O_3) on surface roughness, wettability, and bonding of polyetherketonketon to various veneering materials (hybrid ceramics, lithium disilicate, and zirconia).

The null hypothesis states that there are no significant differences in surface roughness and wettability or SBS among surface pretreatment techniques or the three types of veneering materials, whether or not the specimens are aged.

MATERIALS AND METHODS

Ethical approval

This study was approved by Research Ethics Committee of Faculty of Dentistry, Tanta University (R-BIO-9-23-3058, September, 2023). This study's design and methods were in accordance with recommendations issued by the Research Ethics Committee, Faculty of Dentistry, Tanta University

MATERIALS:

Table 1: Lists the materials utilized in this study.

TABLE (1) The materials utilized in the current study.

Brand name	Type	Composition	Manufacturer
(Pekkton® Ivory)	PEKK polymer	90% PEKK and 10% TiO_2 for coloring and optimization of mechanical properties	Cendres+Métaux SA, Biel, Switzerland
VITA Enamic	Hybrid ceramics	Polymer-infiltrated feldspathic ceramic (86% ceramic network and 14% acrylate polymer) Ceramics: SiO2 (58%–63%), Al_2O_3 (20%–23%), Na_2O (6%–11%), K_2O (4%–6%), B_2O_3 (0.5%–2%), CaO (<1%), TiO_2 (<1%). Polymers: (14% wt.): Bis-GMA, UDMA, Bis-EMA and TEGDMA.	VITA Zahnfabric, Bad Säckingen, Germany
IPS e.max CAD	Lithium disilicate glass ceramic	Lithium disilicate ($Li_2Si_2O_5$)-based ceramic containing 70% $Li_2Si_2O_5$ crystals: SiO_2 (57.0%–80.0%), Li_2O (11.0%–19.0%), K_2O (0.0%–13.0%), P_2O_5 (0.0%–11.0%), ZrO_2 (0.0%–8.0%), ZnO (0.0%–8.0%), Al_2O_3 (0.0%–5.0%), MgO (0.0%–5.0%), Coloring oxides: 0.0%–8.0%.	Ivoclar Vivadent, Schaan, Liechtenstein

Brand name	Type	Composition	Manufacturer
(Prettau® Anterior)	Translucent zirconia ceramics	ZrO_2 (92.27), Y_2O_3 (5.2 mol %), Al_2O_3 (<1%), SiO_2 (0.02%), Fe_2O_3 (0.01%), and Na_2O (0.04%)	Zirkonzahn, Worldwide, Gais, Italy
Sulfuric Acid	Sulfuric Acid	98% sulfuric acid (H_2SO_4), water	Sigma–Aldrich; St. Louis, MO, USA.
Hydrofluoric acid etch	Porcelain Etchant gel	Buffered 9.5% hydrofluoric acid	BISCO Inc. Schaumburg, Illinois, U.S.A
Hydrofluoric acid etch	Ceramic Etching Gel	5 % hydrofluoric acid gel	Vita Ceramics Etch, Vita Zahnfabrik, Bad Sackingen, Germany
Porcelain primer	Silane coupling agent	30–50% Ethanol, 30–50% Acetone, Silane 1–5%	BISCO Inc. Schaumburg, Illinois, U.S.A
Z- PRIME plus	Zirconia primer	75–85% Ethanol, 5–10% Bisphenol A Diglycidylmethacrylate, 5–10% Hydroxyethyl Methacrylate, 1–5% MDP	BISCO Inc. Schaumburg, Illinois, U.S.A
Visio.link	Primer for PEKK	MMA, pentaerythritol—triacrylate (PETIA), photoinitiators	Bredent GmbH & Co., Senden, Germany
TheraCem ™	Universal dual cure self- adhesive resin cement	Base: Calcium base filler, glass filler, dimethacrylates, ytterbium fluoride, initiator, amorphous silica Catalyst: Glass filler, MDP, amorphous silica	BISCO Inc. Schaumburg, Illinois, U.S.A

METHODS:

PEKK discs preparation

120 disk-shaped PEKK specimens were fabricated for this investigation using PEKK blank (Pekkton Ivory, Cendres+Métaux, Biel/Bienne, Switzerland). (Figure. 1) (with each PEKK disc measuring 10 × 4 mm). Using the CAD/CAM technique, specimens were prepared by cutting and milling a PEKK blank into the shape of a bar while being heavily cooled by water (Arum x5 400, Doowon Co., Ltd. Daejeon, South Korea).

A low speed diamond saw (Isomet 4000 precision cut, Buehler, USA) with a 0.6 mm thick blade was used to cut a bar of PEKK perpendicularly under copious amount of water (running at 2500 rpm) to achieve a uniform thickness of each PEKK disc (final thickness 4 mm).

Each PEKK disc was embedded and secured in auto-polymerizing acrylic resin (Acrostone, Egypt) using a cylindrical mold that measuring (25 mm diameter) and (10 mm in height) with (2 mm of its thickness protruding outside the acrylic resin. (figure.2)

To attain a standardized surface, The bonding surface of each prepared disk was polished using microcut Silicon Carbide grinding papers with grit numbers 400 and 600 (BuehlerMet II 400,600, Buehler Inc) under water for 40 second. Following a 30-minute cleaning process with an ultrasonic water bath (Baioden Ultrasonic Cleaner, China) filled with distilled water, the polished specimens were left to air dry. (18).

Grouping of samples

In accordance with surface treatment methods, 120 PEKK specimens were used and alienated into 3 equal groups (n = 40 per group): 10 specimens were used to study surface roughness, wettability, and surface morphology, and 30 specimens were used to evaluate shear bond strength in the manner described below;

Group A: No treatment was administered (control)

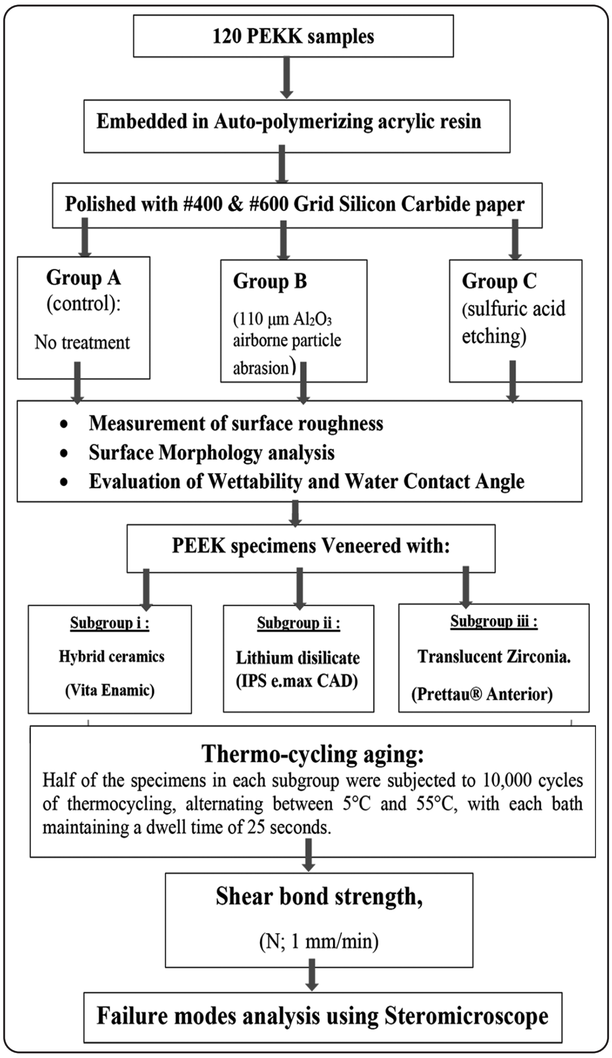

Fig. (1). An experiment design flowchart.

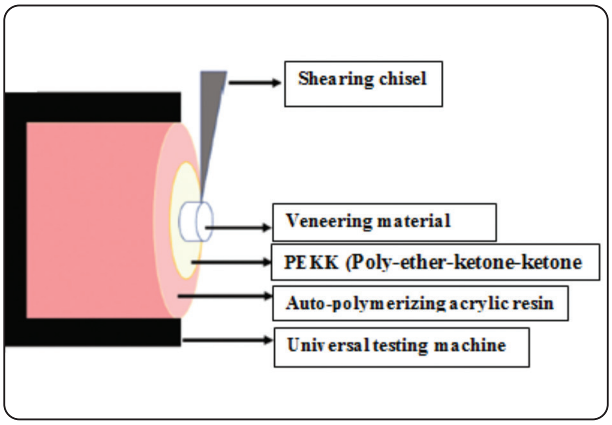

Fig. (2) Schematic illustration of the specimen that is mounted on the Universal Testing Machine.

Group B: (110 µm Al_2O_3 airborne particle abrasion) surfaces air abraded with 110 µm Al_2O_3 (JNBP-2, Jianian Futong Medical Equipment Co. Ltd., Tianjin, China) for 10 seconds at a distance of 10 mm at 2 bar of pressure, and then air dried for 20 seconds.

Group C: (etching with sulfuric acid) The surfaces were etched with 98% sulfuric acid (Sigma-Aldrich; St.Louis, MO,USA) for one minute and then carefully rinsed with distilled water for one minute.

Each pretreatment group was subsequently divided into one of three subgroups (n=10), according to the type of veneering materials applied:

Subgroup I: consisted of PEKK discs veneered with hybrid ceramics (Vita Enamic).

Subgroup II: consisted of PEKK discs veneered with lithium disilicate ceramic (IPS e . max CAD)

Subgroup III: consisted of PEKK discs veneered with translucent zirconia. (Prettau® Anterior).

Each sub-group was then randomly divided into two sets of five specimens each, with the specimens either being stored in distilled water at 37°C for 24 hours or subjected to thermocycling.

Surface roughness measurements after surface treatment

To measure surface roughness, 15 PEKK specimens were used, five from each surface treatment group. With optical profilometry, quantitative surface topography characterization can be accomplished without contact (19).

A USB digital microscope (ScopeCapture Digital Microscope, Guangdong, China) with an integrated camera that was linked to an IBM compatible PC took 120X pictures of the samples. Images were taken with Microsoft Office Picture Manager at 1280 x 1024 pixels, cropped to 350 x 400 pixels, and then examined with WSxM software (20).

Limitations, sizes, frames, and quantifiable metrics are all represented by pixels in WSxM. Therefore, pixels were converted into absolute real-world units through system calibration. The calibration procedure computed the average height (Ra) in µm, a good measure of surface roughness, by comparing a ruler to a software-generated scale [(21)].

Surface Morphology analysis after surface treatment

Nine PEKK specimens, three from each surface treatment group, were reserved exclusively for morphological examination and were not included in the final study. The surface topography of each treated group was analyzed using a Scanning Electron Microscope. (JEOL JSM-5200LV scanning microscope, Tokyo, Japan). Specimens were air dried after being ultrasonically cleaned for two minutes for this purpose. The specimens were then attached to metallic stubs, coated with gold sputter (SPIMODULETM, SPI Supplies, USA), and examined using a Scanning Electron Microscope (SEM) to ascertain the treated surfaces' topography (X 1,000). [(22)]

Evaluation of Wettability and Water Contact Angle

The wettability test was performed on six PEKK specimens, two from each surface treatment group. Using a camera-based goniometer and the sessile drop technique, the contact angle (θ) was determined. (OCA 15EC, Germany) connected to a computer with a special software. A micro syringe adapted to the goniometer deposited a droplet of distilled water of volume 1 µ onto the PEKK surface. After 5 seconds, images were taken with a camera coupled at a fixed distance of 30 cm. Then, the contact angle was recorded using a software program (figure 3). For each specimen five contact angle measurements were recorded at different areas of the specimen. The reduced contact angle values were thought to be a sign of the specimen's improved wettability. [(23)]

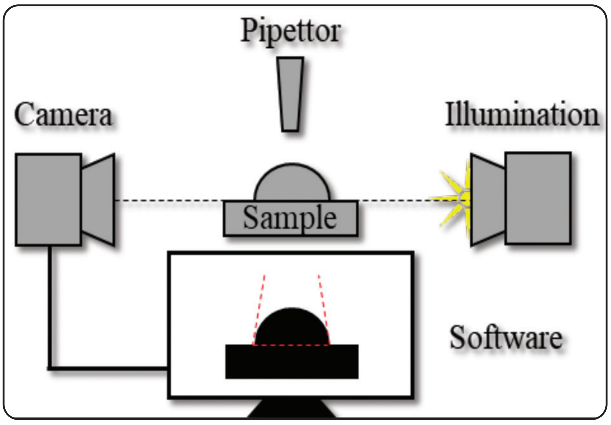

Fig. (3) Diagrammatic representation of the sessile drop technique.

Preparation of the veneering materials

A cylinder was designed using suitable digital software (3D Builder, Microsoft, WA, USA) with intended dimension (Ø = 3mm, and height = 10mm). A total of thirty cylindrical specimens were prepared using a low-speed diamond saw with an ample amount of water.

(n=10 for each veneering material) were obtained from cutting of the designed cylinders. Each ceramic specimen was uniformly cut using a slicing machine equipped with a low-speed diamond blade (Isomet 4000 precision cut, Buehler, USA) (final thickness 10.0 mm).

Vita Enamic: no sintering or firing needed for this type of the specimens.

IPS E-max CAD specimen was crystallized at a temperature (840°C to 850°C) in a ceramic furnace (Programat P 310 ceramic furnace, Ivoclar Vivadent, AG, schaan/Liechtenstein) using a pre-programmed setting limited to the polished ceramic. While, for approximately eight hours**, Prettau® Anterior Zirconia** specimens were sintered in a sintering furnace at a temperature of 1580°C (TABEO-1/5 ZIRKON-1000-Germany) following the recommended sintering temperature chart. [(24)]

Following that, the treated PEKK surfaces were then coated with visio.link primer (bredent,senden,Germany), and light polymerized using a laboratory-use light polymerization device(bre.lux Power Unit 2W/LED 370-500NM, bredent, Senden, Germany) for 90 seconds(25). Using 5% hydrofluoric acid gel (Vita Ceramics Etch, Vita Zahnfabrik, Bad Sackingen, Germany), **Vita Enamic** specimens were etched for 60 seconds, rinsed for another 60 seconds, and allowed to air dry**.** Coat of Silane for 60 seconds was then applied to the bonding surface of the specimens(26). Hydrofluoric acid 9.5% (BISCO Inc. Schaumburg, U.S.A.) was applied to **IPS.Emax CAD** specimens for 40 seconds, and then a silane coupling agent was applied(Porcelain primer, BISCO Inc) (27). **Prettau® Anterior zirconia** were exposed to air particle abrasion (Al_2O_3 50µm at a distance of 10mm at pressure 2 Bar for 20 second), and Z- PRIME plus (BISCO Inc. Schaumburg, Illinois, U.S.A) was then applied on the surface of samples.(28)

Bonding of the veneering materials to PEKK specimens

The bonding surface of the PEKK specimens was coated with universal dual cure self-adhesive resin cement (TheraCem TM, BISCO Inc.). The veneering materials' discs were then seated and cemented to their corresponding PEKK substrate under a standardized static load (constant seating load of 10 N).(29) The specimens were then light polymerized for 40 sec using a wireless LED light curing device (Woodpecker Med. Instrument, Guilin, China) (with wavelength 420-480 nm and light intensity 1000-1200 m W/cm^2).

Thermo-cycling

Half of the specimens (n=5) in each subgroup were thermocycled for 10,000 cycles between 5°C and 55°C using a thermocycler equipment (Thermocycler, Robota automatic thermal cycle; BILGE, Turkey) (12). Each cycle lasted 60 seconds and included 25 seconds of immersion at 5°C, 10 seconds at intervals, and 25 seconds at 55°C. (15)

Testing of shear bond strength (SBS)

A universal test device (Model 3345; Instron Instruments Ltd.) was used to conduct the SBS tests. USA). With the specimen-embedded acrylic blocks secured to the device's holder, a knife-edged load tip was applied to the bonding interface at a crosshead speed of 1 mm/min until failure ensued (Figure 2).

Then, in accordance with ISO 10477 standards, The loads in Newtons at the point of failure were recorded, and the shear bond strength (SBS) values in megapascals (MPa) were calculated using the formula $\sigma = F/A$. In this formula, σ represents the SBS, F is the load at failure (in N), and A is the adhesive area (mm^2). (30)

After the SBS test, an optical stereomicroscope (Olympus model no. SZ11, Japan) was used to examine failure modes at a magnification of × 40. After the specimens fractured, three sets of failure types—adhesive, cohesive, and mixed—were analyzed and determined.

Statistical analysis

The Shapiro-Wilk and Kolmogorov-Smirnov tests were employed to assess the normality of the data distribution, which was confirmed to be normal. Wettability and surface roughness (µm) data were then analyzed using one-way analysis of variance (ANOVA).To identify the interaction between the independent variables, SBS (MPa) data were statistically analyzed using a three-way ANOVA, considering three factors: the type of veneering material, the type of surface treatment, and the thermal treatment. The Tukey HSD test was then employed to determine any significant differences between the groups. The Pearson Chi-Square test was employed to analyze failure modes, and Pearson correlation analysis was utilized to examine the relationship between SBS and failure modes. The relative frequencies (percentages) of failure types for each group were calculated with a significant level of $\alpha = 0.05$. Statistical analysis was conducted using version 21 of the Statistical Package for the Social Sciences (SPSS).

RESULTS

Surface roughness measurements

Analysis of surface roughness (µm) values using one-way ANOVA showed that the surface treatment procedure significantly influenced surface roughness ($p < 0.001$), as presented in Table 2. Table 3 presents the average surface roughness values (µm), along with their means and standard deviations, highlighting any notable variations.

TABLE (2) One-way ANOVA findings for surface roughness (Ra) for each group

Source	*df*	Sum of Squares	Mean Square	*F*	P
Between Groups	3	42.8738	13.7079	5.53	<0.001*
Within Groups	9	5.384	0.177		
Total	12	48.2578			

Statistically significant difference at P < 0.05

***df* Degree of freedom, *F* F-ratio**

TABLE (3) Surface roughness (Ra) averages ± standard deviation in µm for each group, along with Tukey analysis.

Groups	Mean ±SD	p-value
Group A: Control (No treatment)	**0.2881±0.0014^{a}**	
Group B: 110 µm sandblasting	**0.2921±0.0013^{b}**	< 0.001*
Group C: Sulfuric acid etching	**0.2901±0.0011^{c}**	

; significant ($p \leq 0.05$).

Mean with the different superscript letter are significantly different

In comparison to the other groups, Group B, which was subjected to 110 µm Al_2O_3 sandblasting, had the highest mean surface roughness (0.2921±0.0013). Group C was subjected to etching with sulfuric acid came in second (0.2901±0.0011). The lowest value, however, was displayed by the control group (0.2881±0.0014).

Results of the profilometry assessment

3D digital profilometry images showing surface roughness (Ra) of PEKK specimens are presented in Figure (4).The obtained 3D images of PEKK specimens revealed that the surface roughness pattern at baseline (before surface pretreatment, Group A) consisted of broader peaks and shallow valleys as presented in Figure (4) a. 3D images of PEKK specimens after 110 µm Al_2O_3 airborne particle abrasion (Group B) showed uniform pattern of micro irregularities with crater like appearance and deep valleys as presented in Figure (4) b . 3D images of PEKK specimens after sulfuric acid etching (Group C) showed uniform pattern of micro irregularities characterized by high peaks and deep valleys as presented in Figure (4) c .

Surface Morphology analysis (Scanning electron microscopy (SEM) observations):

Figure (5) shows Scanning Electron (SE) photomicrographs of control and treated PEKK specimens at magnification of X1000. Figure 5(a) shows SE photomicrograph of a representative control specimen (Group A); showed a plain and homogeneous surface. Whereas Figure 5(b) shows SE photomicrograph of a representative specimen treated with airborne particles abrasion (110 µm Al_2O_3) (group B); the surface topography exhibited irregular, fissured surfaces with polygonal-shaped alumina oxide embedded in them. Figure 5(c) shows SE photomicrograph of a representative sulfuric acid etched specimen (Group C); the surface topography is extensively different from the control displaying round cavities on the PEKK surface showing a complex network were characterized by a sponge-like porous fiber network and sub-surface corrosion

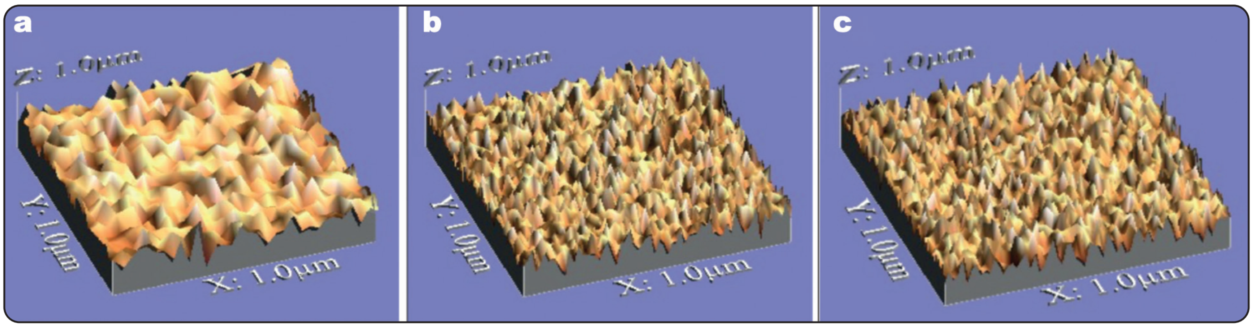

Fig. (4) 3D digital profilometry images showing surface roughness (Ra) of PEKK specimens under Scope Capture Digital Microscope: a) Microscopic image of PEKK specimens at baseline (before surface pretreatment, Group A) b) Microscopic image of PEKK specimens after 110 µm Al_2O_3 airborne particle abrasion (Group B) c) Microscopic image of PEKK specimens after sulfuric acid etching (Group C)

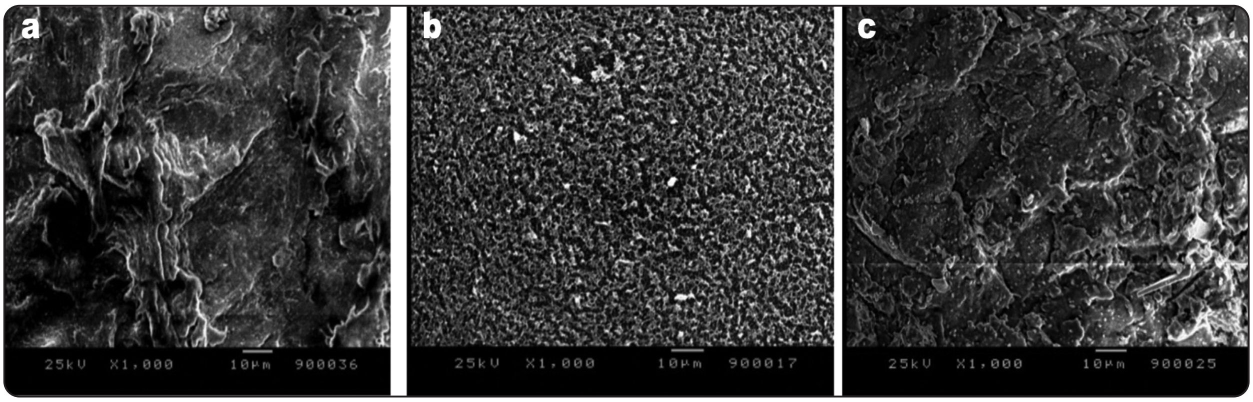

Fig. (5) PEEK specimen Scanning Electron (SE) photomicrographs at X1000 magnification. In (a), a representative control specimen (Group A) is shown with a SE photomicrograph without any treatment; in (b), A SE photomicrograph of a typical specimen (group B) that was subjected to airborne particle abrasion (110 µm Al2O3); and in (c), a SE photomicrograph of a representative sulfuric acid-etched specimen (group C).

Wettability and Water Contact Angle measurement

Means and SD for contact angle of tested groups are presented in table (4). The results showed that the PEKK samples treated with Sulfuric acid (Group C) showed The lowest water contact angles (better wettability) (54.92±0.69) followed by the samples air abraded with 110 µm Al_2O_3 (Group B) (67.39±1.13).The largest water contact angles (lesser wettability) was observed in Group A (Control group:No treatment) (87.69±2.02). According to the statistical analysis, there was a significant difference in the contact angles between the three groups (p≤0.001).

TABLE (4) The mean contact angle and SD (in°) of PEKK specimens after two different surface treatment protocols.

Groups	Mean (±SD)	p-value
Group A: Control (No treatment)	87.692.02±^{a}	≤0.000*
Group B: 110 µm sandblasting	67.391.13±^{b}	
Group C: Sulfuric acid etching	54.92±0.69^{c}	

; significant (p ≤ 0.05). Mean with the different superscript letter are significantly different

Shear bond strength results

The type of treatment, veneering, and thermocycling significantly impacted the SBS, as shown by a three-way ANOVA of the bond strength data in MPa (P< 0.001) (Table 5). Table (5) also highlights

TABLE (5) SBS (MPa) results for all tested groups as determined by three-way ANOVA.

Source of Variation	Sum of Squares	df	Mean Square	F	P
Surface treatment (A)	1083.976	6	180.663	62.971	< 0.001*
Veneering material (B)	1451.424	1	1451.424	505.903	< 0.001*
Thermocycling (C)	335.36	1	335.36	73.72	< 0.001*
A x B	64.937	1	64.937	14.32	.000*
A x C	31.00	2	15.50	3.41	0.043*
B x C	36.557	1	36.557	3.07	0.008*
A x B x C	72.64	3	72.64	15.97	< 0.001*

df = degree of freedom, F: F-ratio, p: p-value, *Statistically significant difference at P < 0.05,

TABLE (6) Tukey analysis and the means ±standard deviations of shear bond strength (SBS) in MPa for each group.

Surface Treatment	Immediate (0 TC)			Thermocycling (10000 TC)		
	Vita Enamic	IPS E.max CAD	Prettau anterior	Vita Enamic	IPS E.max CAD	Prettau anterior
Control (No treatment)	7.37±1.369^{a}	5.68±3.58^{ad}	9.29±2.94^{b}	4.34±1.48^{ad}	2.16±0.98	7.52±2.43^{a}
110 µm sandblasting	9.16±4.69^{b}	7.26±3.84^{a}	13.28±3.89^{ab}	6.58±4.31^{a}	4.23±2.68^{ad}	9.76±4.93^{b}
Sulfuric acid etching	11.78±5.25^{c}	9.76±4.92^{b}	15.24±5.78^{cd}	8.58±5.52^{b}	6.35±2.91^{a}	11.68±2.84^{c}

Mean with the same superscript letter are not significantly different.

a significant interaction between veneering material type, treatment type, and thermocycling (P <0.001). The standard deviations and mean SBS values (MPa) are presented in Table (6).

When compared to the control groups, it was demonstrated that both surface treatment applications considerably increased the SBS. It was demonstrated that, in comparison to the control groups, both surface treatment applications considerably increased the SBS values for all veneer materials (p<0.01).

Comparing the means of immediate SBS among the various surface treatment groups revealed that group C (sulfuric acid etched group) had the highest value across all veneering material types. (Vita Enamic: 11.78±5.25, IPS E.max CAD: 9.76±4.92 and Prettau anterior: 15.24±5.78), while group A (control group) had the lowest value (Vita Enamic: 7.37±1.369, IPS E.max CAD: 5.68±3.58 and Prettau anterior: 9.29±2.94).

Based on the kind of veneering materials used, SBS values (MPa) generally decreased in the following groups, as shown in Table (6): sulfuric acid etching group, 110 µm sandblasting group, and control group. Based on the kind of veneering materials used, Prettau® Anterior Zirconia had the highest shear bond strength values (Control group: 9.29±2.94, sandblasting group: 13.28±3.89 and Sulfuric acid etching group: 15.24±5.78), followed by Vita Enamic (Control group: **7**.37±1.369, sandblasting group: 9.16±4.69 and Sulfuric acid etching group: 11.78±5.25), then IPS E.max CAD (Control group: 5.68±3.58, sandblasting group: 7.26±3.84 and Sulfuric acid etching group: 9.76±4.92). Table 6 indicates that there was a statistically significant difference between the three categories, with a P value <0.001. All groups under study showed a substantial decrease in SBS following thermocycling (P<0.001).

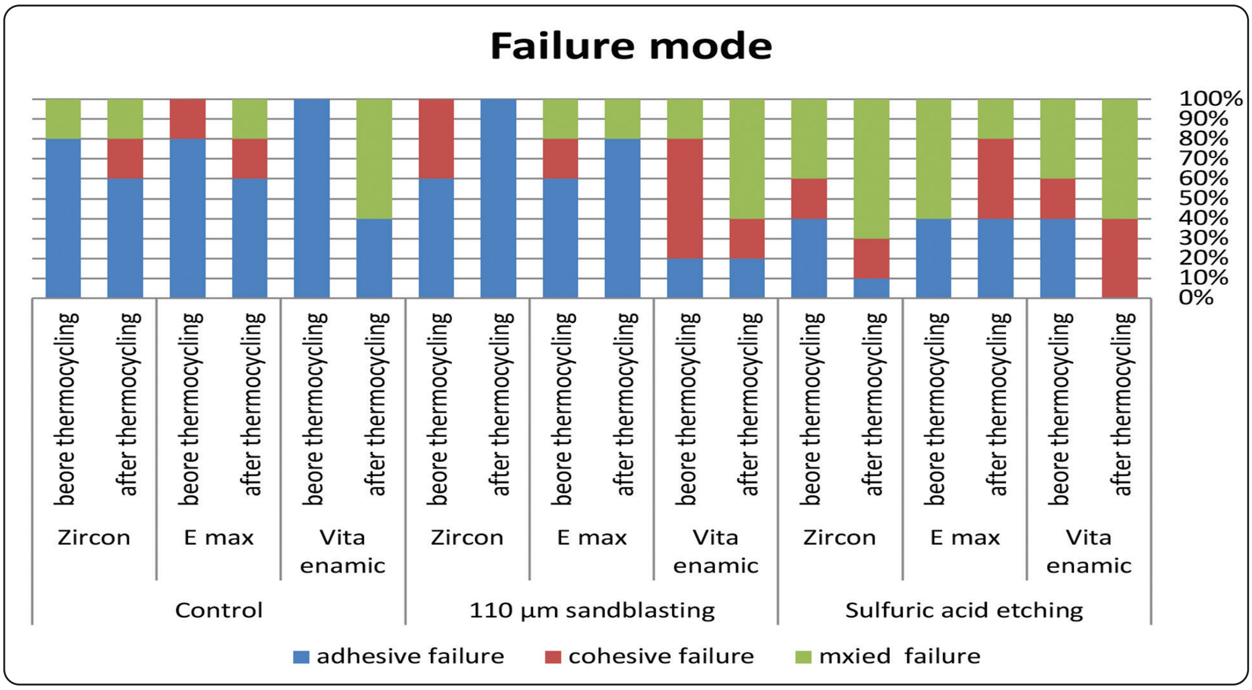

Fig. (5). PEEK specimen Scanning Electron (SE) photomicrographs at X1000 magnification. In (a), a representative control specimen (Group A) is shown with a SE photomicrograph without any treatment; in (b), A SE photomicrograph of a typical specimen (group B) that was subjected to airborne particle abrasion (110 µm Al2O3); and in (c), a SE photomicrograph of a representative sulfuric acid-etched specimen (group C).

The Pearson chisquare test revealed no statistically significant difference between the test groups' failure mode results ($p = 0.298$).

Three modes of failure were revealed by stereomicroscopic analysis at the debonding sites: **cohesive failure** within veneering materials, **mixed failure** when remnants of veneering materials were partially left on the PEEK surface, and **adhesive** failure when no remnants of veneering materials were left on the PEEK surface. As seen in Figure (6), these failure modes differed between the investigated groups. The sulfuric acid etching group displayed more cohesive and mixed failure modes, whereas the control and 110 µm sandblasting groups displayed more adhesive ones. Additionally, following thermocyling, all groups under study displayed less adhesive failure. The findings of the Pearson correlation test showed a moderate correlation between SBS and failure modes and a statistically significant correlation between the two variables ($p < 0.001$, $r^2 = 0.335$).

DISCUSSION

The difficulty in establishing effective bonding between PEKK and various veneering materials remains an unresolved issue and has garnered growing interest from the scientific community. Achieving strong and reliable bonding to PEKK is essential for its use as a dental prosthetic material. Therefore, the primary objective of this study was to examine the impact of various surface pretreatment methods on the surface roughness, wettability, and bonding of (PEKK) to different veneering materials.

The current findings disproved the hypothesis that was first put forth in this study, which states that there are no appreciable variations in surface roughness, wettability, or SBS among the three types of veneering materials or surface pretreatment techniques, whether or not the specimens are aged. We found that surface roughness, wettability, and bonding to various veneering materials were all significantly impacted by the different polyetherketoneketone surface treatment protocols

Restorative dentistry has progressively evolved to incorporate polymers with outstanding physical, mechanical, and biological properties. Introduced in the late 1990s, (PEKK) emerged as a semi-crystalline material. Meanwhile, (PEEK), known for being inert and highly biocompatible, was deemed an ideal alternative for patients allergic to titanium and other metals. PEEK's first application in dentistry dates back to 1992. (31)

PEKK, a linear aromatic polyether ketone represented by ultrahigh molecular weight polyethylene (PE), also attracted interest because of PEEK's overwhelming response.

With an additional ketone group, PEKK exhibits superior mechanical and physical prroperties, including compressive strength, in contrast to PEEK. A PEKK product called Pekkton_ivory (Cendres + Métaux, SA, Switzerland) has an 80% greater compressive strength than unreinforced PEEK. Because of PEKK's superior soft tissue response, the Food and Drug Administration has authorized it for use in oromaxillofacial surgery. (32). PEKK has many applications in dentistry because of its excellent wear and abrasion resistance, stress distribution, fatigue and tensile strength, fracture resistance, and shock absorption. (31,32)

Its low density, low elastic modulus, high compressive strength, and excellent wear resistance make it an ideal material for crowns, posts and cores, fixed partial dentures, and frameworks for implant-supported prostheses. The presence of an extra ketone group provides more SO_3H groups, varied surface microporous structures, and a greater surface area, all of which support long-term osseointegration. Additionally, it induces a lesser inflammatory response compared to PEEK. (32)

Although hot pressing or milling can be used to process PEKK polymers, the samples used in this study were milled using CAD/CAM technology because there hasn't been any discernible difference between the two processes. (33)

PEKK's usage as a monolithic material is limited due to its low translucency and unsightly grayish color. PEKK is used in two layers with a ceramic veneer or indirect composite. (31).

Dental ceramic materials have been upgrading greatly. Advances in their composition and CAD/CAM technology have contributed to the production of a wide variety of materials with the aim of achieving the optimum esthetic, mechanical and biological properties of restorations. (34)

In our study we selected three different ceramic veneering materials belonging to different families. The first selected veneering material was hybrid ceramics (Vita Enamic). which belongs to the resin-matrix ceramic family. This material combines the advantageous qualities of both ceramics and composites. It has enamel and dentine like mechanical properties with proper resilience. Its fracture toughness and ease of machining allowed for the promising results of delivering restorations with thin margins. (35)

Lithium disilicate glass ceramics (IPS e.max CAD), a member of the glass ceramic family, was the second veneering material chosen. Lithium disilicate glass ceramics are low-glass-content, particle-filled glass ceramics. The material contains 70% lithium disilicate crystals that enhance the mechanical properties and resistance to crack propagation. The CAD/CAM blocks (e.g., IPS e.max CAD) are supplied in a pre-crystallized (blue) state and exhibit a low flexural strength ranging between 30 and 130 MPa. Firing after milling is necessary to achieve final crystallization, which will achieve the final superior properties of the material, both mechanically and esthetically (36).

The third selected veneering material was translucent zirconia material (Prettau® Anterior) which belongs to the polycrystalline ceramic family and has proven its reliability in fixed prosthodontics owing to its biocompatibility and high mechanical properties. Furthermore, the aesthetic qualities have been markedly improved by the translucent zirconia types. Zirconia's high flexural strength made it possible to create strong crowns with thin radial and occlusal thickness. (37)

Improved adhesive properties of the resin cement to PEKK are essential to reduce micro leakage, enhance retention, and increase prosthesis stability. Achieving the maximum binding strength between the veneering material and PEKK is thought to be significantly influenced by appropriate surface treatment. The PEKK material's surface needs to be sufficiently rough during the adhesion process to achieve the right amount of mechanical retention. However, PEKK's high strength and hardness, complex chemical structure, low surface energy, and veneering material properties make bonding to it challenging. Adequate bond strength can be obtained through mechanical adhesion, chemical adhesion, or a combination of both methods. (38).

The current study used a variety of pretreatment methods to increase the bonding strength of the PEKK material. Drawing from earlier research that identified airborne particle abrasion as one of the most effective initial pretreatment methods developed for PEKK surfaces, this technique was selected as the mechanical surface treatment. The chemical surface treatment for PEKK was selected to be sulfuric acid etching, which involved etching PEKK surfaces for one minute using 98 percent sulfuric acid. (39)

In comparison to the surface roughness an etched PEKK surface(0.31µm), the study's findings revealed that the surface roughness of airborne particle abrasion on Al_2O_3 (0.67µm) was higher, being significantly different. The higher surface roughness values for the sandblasted PEKK specimens were also demonstrated in the pictures of SEM, revealing an irregular and fissured rough surface for sandblasted specimens, with some surface-embedded alumina particles originating from sandblasting .The result is consistent with earlier research which recorded that 50µm air abrasion produced more roughness than acid etching ***Gorab et al. (2021)*** (40) and also, ***Çulhaoğlu et al.(2020)***(41) who reported increased mean surface roughness values for airborne particle abrasion with Al_2O_3.

Also, the results of this study recorded a smaller contact angle of acid etched specimens (54.92±0.69°) compared to sandblasted specimens (67.39±1.13°), being significantly different. The production of polar groups, including hydroxyl, carboxyl, and peroxide groups, can be used to explain why acid etching-treated objects have greater wettability. This method proved to be more suitable for biological applications because the surface of treated samples is depleted of debris, thus increasing its hydrophilicity. Also, the wettability of sandblasted specimens showed a decrease rather than an increase as expected. This controversy may be linked to the wettability property's qualities, which is influenced by both the surface chemical and the contact angle. This result agrees with ***Culhaoglu et al.'s (2020)*** findings (41) who demonstrated a lower contact angle of an acid-etched PEEK (76.0°) than that of a sandblasted PEEK (84.83°).

The veneering materials were also surface treated to enhance and achieve the highest bonding of the materials to PEKK. In hybrid ceramics, Micromechanical interlocking and chemical bonding are considered the two most crucial techniques for creating a reliable connection between cement and ceramics.

Micromechanical method is achieved by HF acid application, while chemical bonding is achieved by silane coupling agent. Several studies reported that HF acid enhance bonding to resin content by dissolving the silica containing glassy matrix portion. ***Bayındır et al (2020)***(42) and ***Schwenter et al (2016)***(43) claimed that, HF acid etching and silane coupling agent exhibited a favorable increase in shear bond strength values within Vita Enamic.

For lithium disilicate, ***Aboushelib et al (2014)*** (44) and ***El-Damanhoury et al (2018)*** (45) reported that hydrofluoric acid etching in conjunction with silane priming remains the most effective technique for producing a good bond reliability to lithium disilicate glass ceramics. According to ***Sudré et al. (2020)*** (46), exposure duration and acid concentration play a major role in the surface treatment of lithium disilicate. Thus, the most effective results with lithium disilicate were obtained with a concentration of 10% HF acid and an exposure duration of 20–40 seconds.

For zirconia specimens, ***de Lucena Pereira et al (2015)*** (47) and ***Joukhadar et al (2020)*** (48) concluded that a primer application after airborne particle abrasion demonstrated a positive improvement in the resin cement's bond strength to zirconia. Furthermore, air abrasions improve the primer's wettability on zirconia.

Several studies focused on the role of application of composite primer (visio.link). According to reports, the solvent pentaerythritol triacrylate in visio.link significantly improves bonding to PEKK. ***Stawarczyk et al (2014)*** (49) reported that, When veneering a PEEK restoration, an adhesive system (visio.link) needs to be applied to create a durable bond.

In this study, we used dual cure self-adhesive resin cement (Thera Cem) as it contains a hydrophilic monomer (methacryloxydecyl-dihydrogen-phosphate). It also had a feature that would help reduce or prevent secondary caries. In addition, it has many advantages such as bond strength and stability, antimicrobial activity, alkaline PH, as well as calcium release.(50)

Ensuring the stability of the bonded interface over time is crucial for maintaining long-term durability and achieving a satisfactory functional outcome. Functional thermal stress brought on by temperature change in the mouth cavity from regular eating, drinking, and breathing may have an effect on the bonding durability. The thermocycling test was selected to evaluate the durability of the restorations under in vitro conditions because it could replicate changes in oral temperature. Because it creates consistent thermal stresses at the interface, it is a useful technique that mimics in-vitro aging of specimens. (51).

The materials used in this investigation were subjected to 10,000 cycles. According to **Morresi AL et al. (2014)** (52) a 10,000 cycle is clinically equivalent to a year. There was a 10-second lag time and a 25-second dwell time for each water bath. 5°C was the low temperature. The highest temperature was 55°C. The ISO standard states that as this range was thought to be the most closely related to the physiology of the oral cavity, dental materials should be tested at temperatures between 5°C and 55°C. Galea MS et al. (1999) reported that the mean low temperature was 6°C (range 0–360°C, median 5.0°C). Between 40°C to 100°C, the median high temperature was 55°C. (15)

Numerous test procedures can be used to evaluate bond strength. These include, among other tests, the shear/micro-shear (SBS/μSBS) and tensile/micro-tensile (TBS/μTBS) bond strength tests (53). Because of its simplicity in specimen preparation, non-technique sensitivity, low pretest failure rate, ease of specimen alignment with the loading device, and uncomplicated testing methodology, the shear bond strength test was chosen for the current investigation. (54)

Airborne particle abrasion with 110 µm aluminum oxide and etching with 98 percent concentrated sulfuric acid were found to significantly increase the shear bond strength values of polyether ketone ketone to veneering materials. Airborne particle abrasions and sulfuric acid etching cause the PEKK surfaces to become rougher, which, when combined with the appropriate adhesive, increases the material's mechanical retention. According to ***Stawarczyk et al. (2013)***(55) and ***Gouveia et al. (2021)*** (51) airborne particle abrasion with 110µm aluminum oxide and sulfuric acid etching considerably improved the shear bond strength values of PEKK to the veneering material.

According to our study, the highest shear bond strength for all veneering material types was found when PEKK was etched using 98 percent concentrated sulfuric acid. This is explained by the fact that acid etching changes the PEKK construction's biochemical properties by removing organic residue, attacking aromatic structures, and dissolving the carbonyl and ether functional groups that are located between the benzene rings (13,22,23). Furthermore, sulfonate groups (– SO3) were created by sulfuric acid in the chains of PEKK polymers, which chemically cross-linked to methylmethacrylate-based adhesives. (56) Additionally, the diffusion of resin tags into the pits and pores on the PEKK surface resulted in micromechanical bonding. This result is related to the morphology of the treated surface, which after a one-minute treatment with 98 percent sulfuric acid became porous and permeable to adhesives, as shown in Figure (1b). Thus, the higher surface energy allowed the bonding agent to diffuse into PEKK surface porosities. This result is in agreement with previous studies that discovered the maximum shear bond strength values were reported in PEEK specimens that were etched with 98 percent sulfuric acid for one minute. (40, 57, 58)

The results indicated that while air abrasion with 110 µm alumina increased the (Ra) values, it did not significantly enhance the bonding strength to veneering materials compared to the other groups tested.

One potential explanation is that the rough surfaces and high porosities of the PEKK surface, created by the coarse alumina particles, may have impeded adhesive infiltration and led to the formation of weak spots at the bond interfaces. (59)

The current SEM analysis suggests that the cause may be the alumina particle agglomeration on the sandblasted PEKK specimens, which obstructed the pores. The overall shear bond strength decreased because of the bonding agent's limited ability to penetrate the pores. This outcome is linked to the topography of the treated surface, as Figure (1d) illustrated more pronounced architecture with distinct porosity and notably deeper grooves. This result aligns with the findings of ***Stawarczk B et al. (2013)*** (55), who observed that the acid-etched group exhibited the highest SBS, whereas the 110 µm air-abraded group had the highest surface roughness values.

The SBS results in all tested group were higher above the ISO 10477 minimum threshold level of 5MPa (60) and the ideal clinical service limits of 10MPa (limits between 10.47 and 22.55 MPa).

This experiment revealed a significant decrease in shear bond strength values during thermocycling. This result contradicted the results of previous investigations(49,61), which suggested that higher bond strength values after thermocycling might be achieved through post-polymerization in the interface region of the PEKK surface, the adhesive system, and the veneering resin. Thermocycling significantly decreased the cement's adhesive resistance according to ***Prochnow et al., (2018)***(62). The material's varying liner coefficient of thermal expansion, which naturally results in various degrees of expansion and shrinkage, may be related to the negative effects of thermal cycling on resin cement adherence. This process led to a fatigue phenomenon in the material, which in turn led to the bond and interface deteriorating (rupturing).

The type of surface treatment used to the studied specimens may have influenced the IPS E-max Cad and Vita Enamic findings, regardless of thermocycling. Hydrofluoric acid (HF) etching modifies the surfaces of Lithium Disilicate and Vita Enamic by partially dissolving the glassy and crystalline phases of the restorative material. The restorative material's surface developed micro porosities as a result of HF acid etching, increasing its surface area and improving its micro-mechanical interlocking with the luting resin cement. (63, 64).

Silane is bi-functional monomers that contain two essential groups: a) Silanol group reacting with surfaces of ceramic. b) metha-acrylate group that co-polymerizes with composite organic matrix. Silane play a significant role in facilitating the chemical interaction between restorative materials and resin cement. ***Cinar et al (2019)*** (64) reported that salinization after HF acid etching improved shear bond strength values of Vita Enamic and lithium disilicate.

On the other hand, Prettau® Anterior translucent zirconia showed a marked increase in shear bond strength values compared with other veneering material.

In addition, the resin cement (Thera Cem) contains a hydrophilic monomer (methacryloxydecyl-dihydrogen-phosphate). The interaction between zirconia and MDP may be responsible for the high shear bond strength values that were achieved in zirconia. ***Nagoka et al (2017),*** and ***Mahrous et al (2020)*** outlined three different hypotheses for how MDP and zirconia interact: a) The 10-MDP monomer adsorbed on the surface as a result of hydrogen bonding between the Zr-OH group and the P=O (oxo group). b) Zirconia and the 10-MDP monomer forming an ionic connection. c) The adsorbed 10-MDP monomers engage with zirconia via P=O hydrogen-bonding interactions in addition to ionic bonding.(65,66)

Shear bond strength showed significant different before and after thermo-cycling with vita Enamic specimens. ***Campos et al (2016)*** (61) and ***Cekic-Nagas et al (2016)***(67) reported that resin bonding to hybrid ceramics significantly decreased following thermo-cycling. This may be due to water infiltrating tiny gaps between polymer chains or functional groups, ascribed to the high molar concentration of water and the tiny molecular size. As a result, the polymer's thermal stability decreased, resulting in its plasticization. It can be stated that the polymer in the material could not withstand variations in humidity and temperature.

The results of IPS E-max Cad specimens experienced a marked decrease in shear bond strength values compared with other two materials (vita enamic and Prettau® Anterior translucent zirconia). This could be attributed to hydrolytic cleavage of siloxane bonds in the siloxane interfacial layer that occur as result of exposure silanized interface to water. In addition there is a significant water sorption owing to exposure of the adhesive with water. As a result, these lead to plasticized polymers and lower their mechanical properties, resulting in lower bond durability. *(68)*

Several studies reported that, the interactions that occur between silane and MDP, which noticeably affect in the bond durability with E max. silane become unstable when combined with bis-GMA and MDP. In the acidic environment induced by MDP, self-condensation reaction may occur in the silane. *(69)*

Another possible explanation is that, the more HEMA presented in the resin, the more water absorbed. This action leads to hydrolysis of siloxane and weaken the adhesive bond at the adhesive interface. ***Takahashi et al (2011)*** *(70)* reported that HEMA presented in the adhesives significantly affected by increasing water sorption and decreasing ultimate tensile strength.

Another possible explanation could be related to the concentration of the 10 MDP presented in the resin cement. Higher concentration of 10 MDP experienced a noticeable increased in water sorption of the adhesive resin cement. ***Shibuya et al (2019)***(71) reported that water sorption in the experimental resin cements increased with increase concentration of 10-MDP, which in turn lead to impairment of bond durability.

The cause for bond deterioration between polyetherketoneketone and lithium disilicate might be due to the unreactive nature of the PEKK surfaces. This aligns with the findings of ***Sloan et al (2021)*** (72), who suggested that the difference in bonding between PEEK and lithium disilicate is due to the way these materials bond with the PEEK substrate. Adhesion to the PEEK substrate was believed to primarily rely on micromechanical interlocking.

As was previously mentioned, the usage of light-cured adhesives and dual-cured resin cements considerably decreased bond strength.

The incompatibility between the peroxide amine catalyst infiltrated in the dual-cured resin and the acidic resin monomer present in the adhesive was identified as the cause of this decrease in bonding strength *(73)*.

According to recently published research by ***Mustafa et al. (2023)***, the indirect laboratory composite showed a significant increase in SBS values in comparison to lithium disilicate. This could be attributed to MMA-PETIA content of the Visio.link. The chemical interaction between MMA-PETIA monomer and resin polymer provided a durable and better bonding with composite than other functional polymers.(74) Based on the aforementioned data, it was expected that, Vita Enamic specimens had the ability to withstand the thermal aging to the extent greater than IPS E-max cad specimens.

In this investigation, the zirconia specimens' shear bond strength dramatically dropped (15.3±2.2) after thermocycling. This aligns with the results of ***Aboushelib et al (2009)**(75)* and ***Oyagüe et al (2009)**(76)*, who observed a decrease in bond strength with aging owing to deterioration of zirconia resin bond. It was reported that tetragonal to monoclinic phase transformation was accompanied with a noticeable increase in crystal volume, which in turn leading to development of micro and macro-cracks. They claimed that low temperature degradation based on generation of hydroxyl ions that react with oxygen following adsorption of water on zirconia grain surface.

Multiple research investigations focused in the impact of water in the degradation of the MDP-induced bond between zirconia and resin. It was stated that water infiltration at the zirconia resin interface compromised the marginal seal. Their research confirmed that primers based on MDP were ineffective in preventing the infiltration of methylene blue dye. Additionally, it was demonstrated that the presence of leached phosphorous in a soaking solution indicated the release of at least a molecular fragment of MDP upon water sorption. Water has a detrimental effect on the resin bonding of Y-TZP that has been conditioned with MDP. (75)

Salem et al (2019) (77) reported that thermo-cycling significantly decrease SBS values of zirconia with all adhesive system used. This could be attributed to the degradation composite resin cement. Moisture absorption caused by thermo-cycling increased the coefficient of thermal expansion and lowered the glass transition temperature.

All adhesive test groups had cohesive, mixed, and adhesive failure modes identified by fracture analysis. It was found that the adhesive strength is usually reflected in the amount of substrate fracturing. Consequently, the bond strength findings from this investigation are consistent with the failure mode that was found. Furthermore, the unequal distribution of stress at the bonding interface during the loading process may be the cause of cohesive and mixed failures. (78)

In Vita Enamic group, predominantly mixed type of failure were observed at disc/cement interfaces, after they have been subjected to thermocycling. This was in accordance with finding of ***Moftah et (2018)***(79) and ***Beyabanaki (2022)***(80). However, various studies have recorded the interactions that took place between water and the epoxy network when exposing the resin-based material to thermocycling. The silica matrix's charge equilibrium is altered by hydrolytic degradation brought on by the reaction of positive ions in the filler particles and water. The disintegration of (Si-O-Si) linkages in the silica matrix caused by increased hydrogen ions filling empty spaces and surface deterioration as a result of thermal cycling had a negative impact on the SBS value of the Vita Enamic samples.

Moreover, adhesive mode of failure was observed in Ips-emax cad specimens. The reason for the negative impact of thermal cycling on adhesion may be due to the variation in liner coefficient of thermal expansion, which in turn led to varying degree of shrinkage and expansion. This phenomena generated a fatigue stresses on the material, leading to disparity of the bond and interface.(62)Another factor that might have attributed to the deterioration of the bond is the small dimension of the bonded area, which made the impact of thermocycling on its surface more noticeable. ***Shono et al (1999)*** (81) stated that, adhesive joint in samples with small areas experienced a deterioration of the bond strength after similar periods of storage and thermal aging. In Prettau® Anterior translucent zirconia. The involvement of water in the deterioration of MDP-mediated zirconia resin bond could be the exact reason for adhesive failure associated with thermal aging could be. (75, 76)

.The inability of in vitro research to accurately depict the real oral environment is one of the study's primary general limitations. Consequently, more in-vivo studies are required to record the long-term bond strength

CONCLUSIONS

The following conclusions could be drawn considering the research's limitations and findings:

1. PEKK could be treated by sandblasting and etching to development durable bond.
2. Despite having the maximum roughness, 110µm air abrasion did not considerably improve the veneering materials' ability to adhere to PEKK.
3. The type of veneering material, the method of treatment, and thermocycling all significantly influenced the shear bond strength values of the veneering material to (PEKK).
4. Increased surface roughness and wettability can be achieved through sulfuric acid etching, with the most optimal shear bond strength values obtained by etching for 1 min using 98% sulfuric acid.
5. Irrespective of surface treatment and thermocycling, zirconia specimens exhibited a significant increase in shear bond strength values compared to hybrid ceramics and lithium disilicate. All groups and subgroups experienced a notable reduction in shear bond strength after thermocycling.
6. Vita Enamic specimens were the least affected by thermocycling among the veneering materials. Conversely, the shear bond strength values for IPS-Emax Cad decreased significantly.

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