Original Article

EVALUATION OF THE EFFECT OF DIFFERENT SURFACE TREATMENTS ON THE BONDING BETWEEN PEEK AND GINGIVAL COMPOSITE RESIN: AN IN VITRO STUDY

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DOI: 10.47750/pnr.2022.13.S06.537

Abstract

Context: Achieving adequate bond strength between polyetheretherketone (PEEK) surface and resin composite is challenging due to low surface energy of PEEK. There is insufficient data regarding the bonding of PEEK with composite. Therefore, there is a need to evaluate the bonding between the two and the effects of different surface treatments on this bonding.

Aim: To evaluate the effect of various surface treatment methods on the shear bond strength between PEEK and gingival composite resin.

Materials and method: Thirty two specimens of PEEK milled with dimensions of 5x5x2mm were divided into four groups (n=eight/group), surface treatment using: (A) sand blasting, (B) aluminium nitride nano-particles, (C) hydrofluoric acid, (D) sulfuric acid. The specimens were observed in scanning electron microscope (SEM) after different pre treatments. Composite resin was luted over each surface treated PEEK specimen after application of visio.link primer. The shear bond strength was tested using universal testing machine and failure mode analysed under stereomicroscope.

Statistical analysis used: One way analysis of variance (ANOVA) and multiple comparison Tukey's test.

Results: The mean shear bond strength found in sulfuric acid group (8.18 ± 1.42 MPa) was statistically significant ($p<0.05$) than those observed in hydrofluoric acid (5.27 ± 1.97 MPa), air abrasion (4.58 ± 1.32 MPa) and aluminium nitride nano-particles (2.93 ± 1.04 MPa) groups. Stereomicroscopic evaluation showed adhesive and mixed bond failures.

Conclusion: This study showed the highest values of shear bond strength in the sulfuric acid group. The group where aluminium nitride nano-particles were used did not show promising results.

Keywords: PEEK, composite resin, shear bond strength, surface treatments

Introduction:

The high-strength polymer, polyetheretherketone (PEEK) is now being studied extensively in the dental field. PEEK is a high-performance thermoplastic polymer with good chemical, thermal, and mechanical properties, as well as excellent biocompatibility[1]. A modified PEEK with 20% inorganic fillers has been used in dentistry for implants, temporary abutments for implant supported prosthesis, healing abutment, implant supported bars, clamp materials, or frameworks for removable and fixed partial prosthesis[2-7]. It has a Young's modulus that is similar to that of a human bone[4]. The thermoplastic material can be used unfilled because of its mechanical qualities (flexural strength 165 MPa, Young's modulus 3.5 GPa)[2]. The material has a low translucency, making it suitable for most dental uses. PEEK, on the other hand, must be veneered with composite for aesthetic reasons. Despite this, the chemical aromatic structure, which includes ketone and other components, creates an inert surface, resulting in inadequate bonding. As a result, surface conditioning processes such as etching or abrasive treatments must be used. Creating a micro retentive surface texture and applying a primer, according to the majority of research, are crucial[3].

Mechanical or chemical approaches can be used to create a micro retentive surface texture. Recent investigations have focused on two strategies for obtaining a high bonding performance between the resin cement and PEEK: altering the PEEK surface and conditioning with an adhesive system to facilitate chemical interaction. There are various surface treatment methods available, some of which have been previously used on PEEK[8-13] and the other surface treatment methods are yet to be evaluated[14]. Sandblasting improves the bond strength between resin and PEEK material, according to studies, and is recommended as one of the best initial pre-treatments for PEEK surfaces[2].

Materials and Method:

The details of the materials used in this study are mentioned in table 1. Thirty two PEEK specimens were milled from a PEEK blank. Four surface treatment methods were used, air abrasion, air abrasion combined with aluminium nitride nano particles, hydrofluoric acid etchant, and sulfuric acid. The adhesive system used was visio.link and composite resin crea.lign.

Table 1

S.no	Material	Brand name	Manufacturer	Lot no.	Expiry date
1V1 1.	PEEK blank	BioHPP	Bredent GmbH & Co.KG, Germany	487916	
2.	Gum shade composite	Crea.lign paste	Bredent GmbH & Co.KG, Germany	200602	28/02/2023
3.	Primer	Visio.link	Bredent GmbH & Co.KG, Germany	192004	31/05/2023
4.	110 µm aluminium oxide particles	Alminox-110	Delta labs, Chennai, India	0816	
5.	Aluminium Nitride Nanoparticles	Aluminium Nitride	PlasmaChem GmBH, Berlin	R/36/37/38 S26	

6.	Hydrofluoric acid etchant	Hydrofluoric acid etchant 9.5 %	Revive	0321	22/03/2023
7.	Sulfuric acid	Sulfuric acid	Fisher Scientific	0447840315	03/2015
8.	Auto-polymerizing acrylic resin	DPI-RR Cold Cure Acrylic Repair Material	Dental Products of India, Mumbai	P-2198 L-3191	03/2024
9.	Distilled water	Distilled water	Agrawal Pharmaceuticals, Delhi	CP- 2223	

Specimen preparation:

First, the designing of the PEEK samples was done using exocad (GmbH, Germany) dental CAD software, then milling was done in the desired dimension of 5x5x2 mm. The CAM software used was hyperDENT (Zfx GmbH, Germany). A total number of 32 milled PEEK square sample were fabricated for this study. These samples were made by using CAD/CAM from PEEK. blank of 98.5 mm diameter and 20 mm thickness.

Grouping of samples were done and customized jig was used for the fixation of PEEK sample in self cure acrylic resin.

Surface pre treatments

The specimens were divided into four groups. In group B surface treatment was carried out before fixation of PEEK sample in acrylic resin whereas in group A, C and D it was carried out after fixation.

Group A:-Sand blasting

The specimens were air abraded with 110 micron aluminium oxide particles at 0.5 MPa for 5 seconds.

Group B: - Aluminium nitride nano-particles

The milled PEEK sample of specific dimensions were air abraded with 110 micron aluminium oxide at 0.5 MPa for 5 seconds. The aluminium nitride powder for the adhesive coating was aluminium nitride with median particle size of 20nm, a surface area of 80±7 m^2/gm and purity was >99%. A dilute aqueous suspension containing 3 wt% of aluminium nitride nano-particles was prepared by dispensing 3gm of aluminium nitride powder in 100ml of deionized water, preheated at 75 degrees Celsius. Immediately after that milled air abraded PEEK samples were immersed in the suspension for 15 minutes. Once exposed to hot water, the dispersed aluminium nitride powder starts decomposing resulting in the formation of a nanostructured boehmite coating onto the surface of immersed substrates. The coated substrates were subsequently air dried in an oven for 2 hours at 110 degrees Celsius. Following that, the specimens were ultrasonically cleansed in distilled water for 10 minutes and then air dried.

Group C: Hydrofluoric acid

The milled PEEK specimens which were embedded in self cure acrylic resin were air abraded with 110 microns aluminium oxide at 0.5MPa for 5 seconds. The specimens were air dried for 10 minutes after cleaning with water. Subsequently, 3.5 % hydrofluoric acid etchant was applied on it for 30 seconds and then the specimens were rinsed with deionized water and air dried.

Group D: Sulfuric acid

The milled PEEK specimens which were embedded in self cure acrylic resin were air abraded with 110 microns aluminium oxide at 0.5MPa for 5 seconds. The specimens were cleaned with water and air dried for 10 minutes. Sulfuric acid was then applied in 5x5 mm^2 of each specimen for 60 seconds and then specimens were thoroughly rinsed with distilled water for 10 minutes and dried at room temperature.

Luting of composite over PEEK:

After surface treatment, cleaning and air drying of all the specimens of PEEK, a clean brush was used to apply visio.link primer in a thin coat over the PEEK specimens. This was then light cured for 90 seconds so as to obtain a semi matte finish of PEEK samples.

To apply the gum shade composite, PEEK specimens embedded in self cure acrylic resin were placed in the metal jig with components C1 and C2 of the jig placed over it so that only the PEEK remained visible. Crea.Lign veneering gum shade composite (packable consistency) of 2mm uniform thickness was applied over the PEEK specimen .

A glass slab of 1.5 mm thickness was placed over the metal jig so that a uniform curing distance was maintained for the composite applied over all specimens. The composite was light cured for 90 seconds from the top while in the jig and for 45 seconds on each side after it was removed from the jig.

Shear bond strength test:

Shear stress tends to resist the sliding or twisting of one portion of a body over another. The specimens were subjected to shearing forces until bond failure occurred using a Universal Testing Machine with a cross head speed of 1mm per minute. The shear bond strength between PEEK and composite resin for each sample was measured, calculated and tabulated, following which, statistical analysis was performed. Qualitative assessment was done using scanning electron microscope and stereomicroscope.

Statistical Analysis:

Statistical analysis of evaluation of the effect of shear bond strength between composite resin and PEEK after different surface treatments of PEEK was carried out to find out the significant difference between those values. The software used to perform statistical analysis was IBM statistics (SPSS version 18). The statistical tests used for the analysis of the result were, one way ANOVA and multiple Comparison : Tukey test.

Results:

SEM evaluation:

The surfaces after different surface pretreatments are shown by scanning electron microscope (SEM). Untreated PEEK surface (Figure 1) showed surface scratches, irregularities and certain abrasive tracts that were created due to grinding, while the rest of the structure appeared regular, group A (Figure 2) in which aluminium oxide particles were used, demonstrated more flaws, and irregularities in it when compared to untreated PEEK surface. They showed a more rugged and fissured surface with polygonal shaped aluminium oxide particles embedded in it. No pits and porous pattern was observed, group B (Figure 3) the aluminium nitride nano-particles treated group had only a slight effect on surface topography, they showed a relatively smooth surface with slightly reduced traces of sanding and with less irregularities, this group was almost similar to the untreated group, group C (Figure 4) Hydrofluoric acid treated specimens showed increased irregularities and a rough when compared to the untreated group, and was similar to the air abrasion group, a few abrasive tracts that were created by grinding with particles of sand were still evident and some pits were also observed over the surface, group D (Figure 5). Specimens which were treated with sulfuric acid led to a distinct blister like dissolution of PEEK surface. They showed sponge like porous complex fibre networks, large pits and micro retentive areas. Irregularities with corrosion over most of its surface were evident.

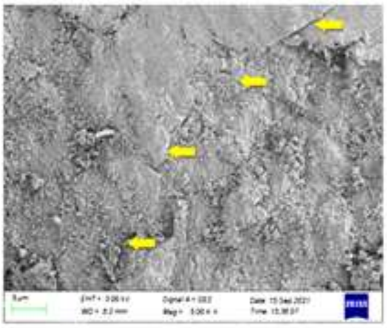

Figure 1: Scanning electron micrograph of PEEK surface with no surface treatment showing abrasive tract (yellow arrow) produced due to grinding (Original magnification X 5000)

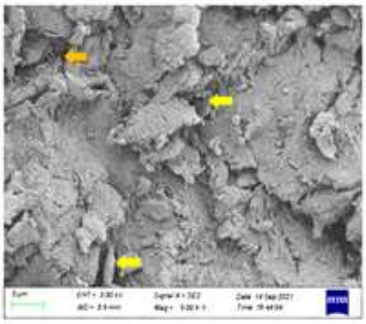

Figure 2: Scanning electron micrograph of PEEK surface with air abrasion surface treatment showing small pits (orange arrow) and abrasive tracts (yellow arrow) (Original magnification X 5000)

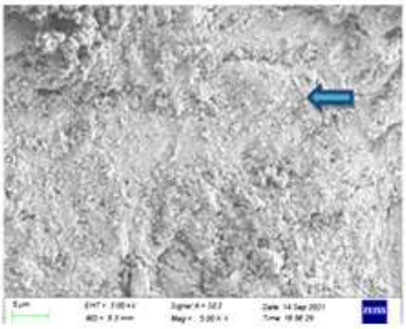

Figure 3: Scanning electron micrograph of PEEK surface with aluminium nitride nano-particles surface treatment showing a relatively smooth surface with less irregularity (blue arrow) (Original magnification X 5000)

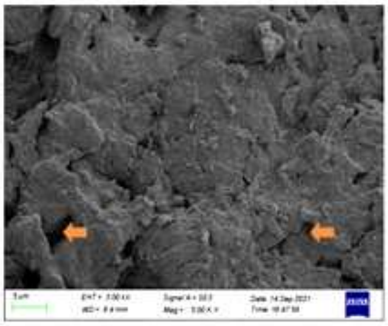

Figure 4: Scanning electron micrograph of PEEK surface with hydrofluoric acid surface treatment showing rough surface with pits (orange arrow) and increased irregularities (Original magnification X 5000)

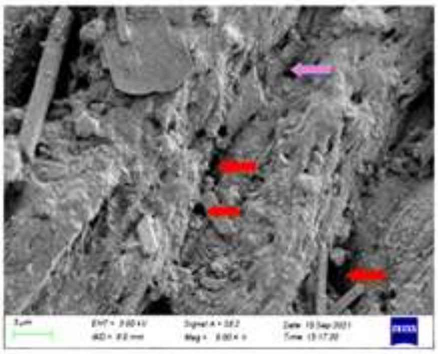

Figure 5: Scanning electron micrograph of PEEK surface with sulfuric acid surface treatment showing large pits (pink arrow), blister like dissolution (red arrows) (Original magnification X 5000)

Shear bond strength measurements:

The mean shear bond strength of all the groups are mentioned in table 2. The shear bond strength values of the specimens ranged from 8.18 ± 1.42 MPa (sulfuric acid etching) to 2.93 ± 1.04 MPa (aluminium nitride nano particles). Sandblasting and hydrofluoric acid etching showed no statistically significant difference with values of 4.58 ± 1.32 MPa and 5.277 ± 1.97 MPa respectively.

Table 2: Mean shear bond strength of specimens

Surface treatment	**Bond strength (MPa)**
Air abrasion	4.58[a]
Aluminium ntride nano-particles	2.93[b]
Hydrofluoric acid	5.28[a]
Sulfuric acid	8.18[c]

Note: the same superscripted letters indicate no significant difference

Stereomicroscopic evaluation

The most frequently experienced failure types were the presence of adhesive failure at the bonded composite resin and adhesion surface interface in which only PEEK is seen in the stereomicroscopic image as composite resin is separated from PEEK when the fracture occurs in the interface (table 3).

The other failure mode which was commonly seen was the mixed failure in which both cohesive failure and adhesive failure occurs, the bond failure is located at the composite PEEK interface as well as within the composite. In the stereomicroscopic image remnants of composite is found over the PEEK surface.

Table 3 Stereomicroscopic evaluation of fracture mode

Groups	**Fracture Mode**

Group A: Air abrasion	100 % mixed
Group B: Aluminium nitride nanoparticles	50% Adhesive, 50% mixed
Group C: Hydrofluoric acid etchant	100% Adhesive
Group D: Sulfuric acid	50% Adhesive, 50% mixed

Discussion:

PEEK is claimed to be an advantageous material for dental applications due to the material's improved mechanical properties and biocompatibility as well as resistance to nearly all organic and inorganic chemicals. PEEK's main drawbacks include its greyish colour (which makes it unsuitable for anterior replacement) and poor composite resin bonding. As a result, a number of experiments have been conducted to determine the bond strength between PEEK frameworks and resin composites based on various pre treatments[3-6]. PEEK's chemically inert behaviour indicates a possible coupling problem at the PEEK core/veneering resin interface as well as the PEEK core/resin luting cement interface.

So, in this study, an attempt was made to evaluate the shear bond strength between PEEK and composite resin after different surface treatments of PEEK.

Immediately after the surface treatment the conditioning was performed using an adhesive system. In a study by Stawarczyk et al.[7], where they compared the different adhesive visio.link and Signum PEEK Bond led to an increase in SBS values for different pre treatment groups but the visio.link adhesive system demonstrated statistically significant higher shear bond strength.

Air abrasion increases surface roughness while removing organic contaminants from the surface, creating a fresh, active surface layer. It also promotes micromechanical interlocking of polymer-based dental materials and enables the bonding agent to penetrate them better, resulting in a micro-mechanical retention and, presumably, an increased surface bonding capacity[8].

A study by Silthampitag P et al.[9] found that increasing the surface area by airborne-particle abrasion improves the bonding qualities of PEEK and that varying the surface roughness by sandblasting considerably increased bond strength, which was similar to the results of the current investigation. Hallmann L et al [4] in their study showed that air abrasion in combination with chemical etching acts synergistically to produce strong bonds between PEEK based polymers and dental adhesives.

The application of aluminium nitride nano-particles was based on the concept of rapid precipitation of aluminium hydroxides that originates from the hydrolysis of AlN powder in diluted aqueous solution. In a study by Jevnikar P et al.[14], hetrogenous nucleation of lamellar bohemite took place when zirconia substrates were submerged in this aqueous solution. Lamellas formed that grew perpendicular to the zirconia surface and formed a retentive surface for resin penetration as a result. The weakly crystalline bohemite makes up the interconnected nanoscale lamellas (AlOOH). The original coating morphology was conserved while the aluminium hydroxide lamellas were changed to a temporary alumina during a subsequent thermal treatment at 900 degrees Celsius. On the Y-TZP substrate, a sizable micro retentive region was therefore produced, with the potential to facilitate resin bonding. However, this approach could not produce the same findings because PEEK's receptive surfaces did not offer the same functional groups. Additionally, PEEK has a lower melting point than zirconia, thus the 900 degree Celsius heat treatment could not be used in this instance. As a result, the aluminium nitride nano-particles were unable to be incorporated into the microretentive regions. Compared to sand blasting, it created a smooth, uniform coating over the surface and reduced the shear bond strength. Hydrofluoric acid etching too had an effect on topography. Abrasive tracts created by grinding with particles of sand were evident along with the pits created by etching on the surfaces. Etching is often used as a surface treatment method. The adhesive can penetrate into the surface pores of the pre treatment PEEK to form an adhesion collateral that can perform micro mechanical retention. A study by Zhou Li et al.[10] suggested that the use of hydrofluoric acid alone, without sandblasting yielded less shear bond strength. This may be due to the fact that HF gel causes the total dissolution of exposed filler particles on the surface. The acid may also be absorbed into and cause the softening of the resin matrix. When used with sand blasting, the surface roughness increases with the use of this etchant as after the creation of surface roughness using sandblasting the etchant creates a larger contact surface which is responsible for better cross linking of polymers.

Sulfuric acid etching is the method aimed to achieve good surface properties of PEEK for bonding. The application of 98% sulfuric acid etching for 60 s in this study showed the best shear bond strength values. Acid etching provided a chemically modified PEEK surface by augmenting the functional features of the PEEK material. The micro-topographical changes seen in PEEK surface after sulfuric acid etching enhanced the penetration of the resin adhesive, which led to an increased SBS. This result implies that the 98% sulfuric acid etching is able to create fibre-liked network surface which resin can penetrate and create micromechanical interlocking. Similar results were obtained in previously conducted studies[11, 12, 13].

Silthampitag P et al. [6] evaluated the effect of surface pre treatments on resin composite bonding to polyetheretherketone and concluded that porosities and pitting results from chemical etching, which suggested a significant influence on the adhesion between PEEK and resin materials.

The bond strength is improved by chemical treatment following air abrasion. This improvement is due to two factors. Large contact surfaces result in more functional groups following chemical processing, which improves polymer cross-linking. Due to the adhesive's ability to penetrate the polymer, the surface structure created by air abrasion boosted the mechanical anchoring of the adhesive. 8In this study, the mean shear bond strength between PEEK and composite resin was the least when surface treatment was done using aluminium nitride nano particles, as they created a relatively smooth layer over the air abraded surface and the highest when sulfuric acid was used as a surface treatment method, as it resulted in dissolution of the PEEK surface producing a porous surface[11].

The present study was not a clinical one and was done in an in vitro condition and the effect of some surface treatments and materials can have a slight different effect in the oral environment and the size and shape of the PEEK specimen used in the study did not mimic the ones used for clinical implications. Further studies could be carried out in a clinical condition to verify the outcome of present study in clinical situations.

Conclusion

Within the scope and limitation of this study, following conclusion was drawn based on statistical analysis:

- This study showed the highest values of shear bond strength in the group where sulfuric acid was used as a surface treatment method. In the group, where hydrofluoric acid and air abrasion were used as surface treatment methods, almost similar results were found. The least value was shown by the aluminium nitride nano particles group.

- SEM analysis revealed that combination of 110µm alumina particles and sulfuric acid created more surface roughness than any other group.

- Use of aluminium nitride nano particles may not be a promising method to improve the bond strength between PEEK and composite as it creates a relatively homogenous surface as revealed by the SEM images.

- Failure analysis with stereomicroscope showed that adhesive bond failure was most common, followed by mixed bond failure. Cohesive bond failure was seen in none of the groups.

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