COMPARATIVE EVALUATION OF SHEAR BOND STRENGTH AND SURFACE ROUGHNESS OF VARIOUS REINFORCED POLYETHERETHERKETONE MATERIALS - AN IN VITRO STUDY

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Abstract:
Comparative evaluation of shear bond strength and surface roughness of various reinforced polyetheretherketone materials - an in vitro study

Aim: This study aims to evaluate and compare the shear bond strength and surface roughness of various reinforced polyetheretherketone materials and to find if surface roughness has a positive effect on shear bond strength.

Materials and methods: A total of 144 PEEK discs were prepared for this study. PEEK specimens were divided into three groups based on reinforcements. It included unfilled PEEK, 30% carbon reinforced PEEK, and 10%carbon+10%graphite+10%PTFE reinforced PEEK. Each group included 48 specimens. From each group, specimens (n=36) were subjected to different surface treatments and were bonded with indirect composite discs. The shear bond strength between the veneering composite and PEEK specimens was measured. The remaining specimens (n=12) from each group were subjected to nanoindentation after which surface roughness was measured.

Result: The statistical analysis was done by one-way ANOVA and the mean values were compared using Post Hoc tests. The results showed that there was a significant difference ($p < 0.05$) in shear bond strength between veneering composite and different PEEK materials and the highest value was noted in 30% carbon-reinforced PEEK. A significant difference was also found in surface roughness and the highest value was seen in 30% carbon-reinforced PEEK.

Conclusion: Among the tested materials, 30% carbon-reinforced PEEK exhibited the highest shear bond strength and surface roughness concluding that surface roughness has the positive effect of improving the bond strength of the material.

Keywords: Bond strength, Polyetheretherketone, surface roughness, surface treatment, veneering, surface roughness

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INTRODUCTION:

Polyetheretherketone, also known as PEEK is a member of polyaryletherketone (PAEK), and has recently gained attention as a potential replacement material for fixed dental prostheses. In addition, PEEK generates few imaging artifacts, providing significantly better performance than zirconia and metal alloys. It is the ideal material for dental restorations as it has a close resemblance to natural teeth in color, radiolucency, rigidity, and lightweight but when compared to zirconia, it falls short in terms of aesthetics. Therefore, the veneering of PEEK with composite resin is important. But due to its inert surface, bonding PEEK and composite veneers is challenging [1]. Effective bonding to PEEK is a prerequisite for its use as a prosthetic material in dentistry. Among different testing methods, shear bond tests are appropriate methods for evaluating the bonding quality of dental materials [2].

Adhesion is a crucial attribute that is influenced by the surface area of the adherent on which the adhesive spreads. The mechanical anchoring of the adhesive is improved because the surface contact area is more on the rougher surface than the smoother surface [3]. The evaluation of surface roughness at the very first surface molecular layers has always been a challenge. Nanoindentation is a nano-length scale mechanical characterization technique for measuring near-surface mechanical properties. Over the past two decades, indentation at the nanoscale has become a practical technique for examining the mechanical characteristics of materials at shallow penetration depths [4]. Literature on the influence of surface roughness on bond strength is limited. Thus, in the current study, the shear bond strength (SBS) and surface roughness (SR) of various reinforced PEEK materials was evaluated and the relationship between the two properties was assessed.

MATERIALS AND METHODS:

A total of 144 PEEK specimens (Shree Krishna Polymers, Chennai) with a diameter of 10mm and height of 10mm were included in this study. They were mounted on acrylic jigs after polishing and rinsing thoroughly with distilled water for 10 minutes. The samples were grouped into three groups based on the reinforcement fibers added to the unfilled PEEK [Figure 1] (Group A - unfilled PEEK, Group B -30%Carbon Reinforced PEEK, Group C- 10%Carbon + 10%Graphite + 10%Polytetrafluoroethylene (PTFE) reinforced PEEK). Each group included 48 discs(n=48). Samples were subgrouped according to different surface treatments - without treatment (Test 1), sandblasting with 110um alumina particles (Kramer industries pvt ltd) (Test 2), acid etching with 98%sulphuric acid (Nice Chemicals Pvt Ltd) (Test 3). 36 specimens from each group are bonded with indirect composite for evaluating shear bond strength. Surface roughness was measured for the remaining 12 specimens from each group after nanoindentation using a continuous stiffness measurement (CSM) testing module.

Composite discs (GC GRADIA) of a diameter of 8mm and height of 6mm were prepared from indirect composite by light curing (Woodpecker Mini S Light Cure Unit) for 40 seconds in a Teflon mold. The specimens were retrieved from the mold and additional external curing of 40 seconds was done on the other side to ensure complete polymerization. A smooth surface was obtained by removing the excess material with a finishing bur. Similarly, 108 composite discs were prefabricated in this manner. A uniform thin layer of adhesive (3M Single Bond Universal Adhesive 5ml) was applied and light cured on the PEEK specimens. Luting cement (G-CEM one self-adhesive resin cement) was coated uniformly on PEEK specimens and the prefabricated composite disc was immediately seated on PEEK specimens with finger pressure and light cured for 40 seconds. The specimens were stored in distilled water for 24 hours before testing.

The embedded PEEK and composite [Figure 2] were aligned in the universal testing machine (Model 3382, Instron (CIPET) following the 2003 ISO technical specification #11405) [Figure 3] to measure shear bond strength. The shear force was applied at a crosshead speed of 1mm/min with chisel shaped rod from the occlusal side parallel to the bonded surface of the specimen until debonding. The load at failure was recorded in a computer in Newton and converted into mega-pascal (MPa) by the following formula.

Shear stress (MPa) = Load / (л× r2)

Where, л = 3.14, r = radius of the specimen in mm^2.

To evaluate surface roughness, 12 specimens from each group were subjected to nanoindentation. Indentations were made using a TI 900 triboindenter (Hysitron, Minneapolis, MN) with a conospherical diamond tip at a rate of 30 n/s [Figure 4]. To reduce creep effects, a trapezoidal loading-unloading function with a 10-s hold at each maximum load was adopted. Each material group was indented at the recommended maximum load of 1000N [5]. To acquire statistically acceptable values at the maximum contact load, hundreds of indentations were made at the same maximum load and constant loading rate. The continuous stiffness measurement (CSM) testing module was utilized with which roughness is measured. The study was triple-blinded where the operator, lab technician, and statistician were all blinded, and all the procedures were done by the same operator. The mean and standard deviation values for Group A, Group B, and Group C were obtained, tabulated and statistical analysis was done.

RESULTS:

IBM SPSS version 21.0 (IBM Corp. IBM SPSS Statistics for Windows, Version 21.0. Armonk, NY: IBM Corp) was used to analyze the descriptive and inferential statistics. A normality test was performed to find the distribution of data. A one-way ANOVA test was conducted to analyze the difference in shear bond strength and surface roughness of Group A, Group B, and Group C [Table 1]. Bonferroni Post hoc test [Table 2] was performed to ascertain the pairs of groups that differ significantly from one another. A p-value of < 0.05 was considered a statistically significant difference. On comparing reinforcement to PEEK irrespective of surface treatment, 30%carbon-reinforced PEEK showed the highest shear bond strength and on comparing surface treatment, the highest shear bond strength was seen in acid etching with 98% sulphuric acid (17.47±1.2MPa) irrespective of reinforcements to PEEK. On comparing surface roughness, 30%carbon-reinforced PEEK showed the highest value irrespective of surface treatments. PEEK specimens sandblasted with 110um alumina particles showed the highest surface roughness irrespective of reinforcements to PEEK.

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TABLE 1: COMPARATIVE EVALUATION OF SHEAR BOND STRENGTH AND SURFACE ROUGHNESS OF DIFFERENT REINFORCED PEEK AFTER VARIOUS SURFACE TREATMENTS

	Unfilled PEEK(MEAN±SD)		**30% Carbon Reinforced PEEK(MEAN±SD)**		**10%carbon+10% graphite+10% PTFE reinforced PEEK(MEAN±SD)**		**F VALUE**		**SIGNIFICANCE**	
	SBS(MPa)	SR(nm)	SBS(MPa)	SR(nm)	SBS(MPa)	SR(nm)	SBS	SR	SBS	SR
Without Treatment	12.20±1.56	353.947±10.85	14.10±1.31	365.677±6.60	12.64±1.59	358.860±9.81	5.310	3.632	0.010	0.040
Sandblasting With 110um Alumina	13.82±2.15	358.258±6.16	15.63±1.34	365.988±4.05	13.89±1.45	365.58±5.12	4.059	1.028	0.057	0.371
Acid Etching With 98% Sulphuric Acid	14.48±1.35	335.4251±3.96	17.47±1.2	359.73±2.87	14.01±0.93	333.79±4.37	25.504	5.388	0.000	0.011

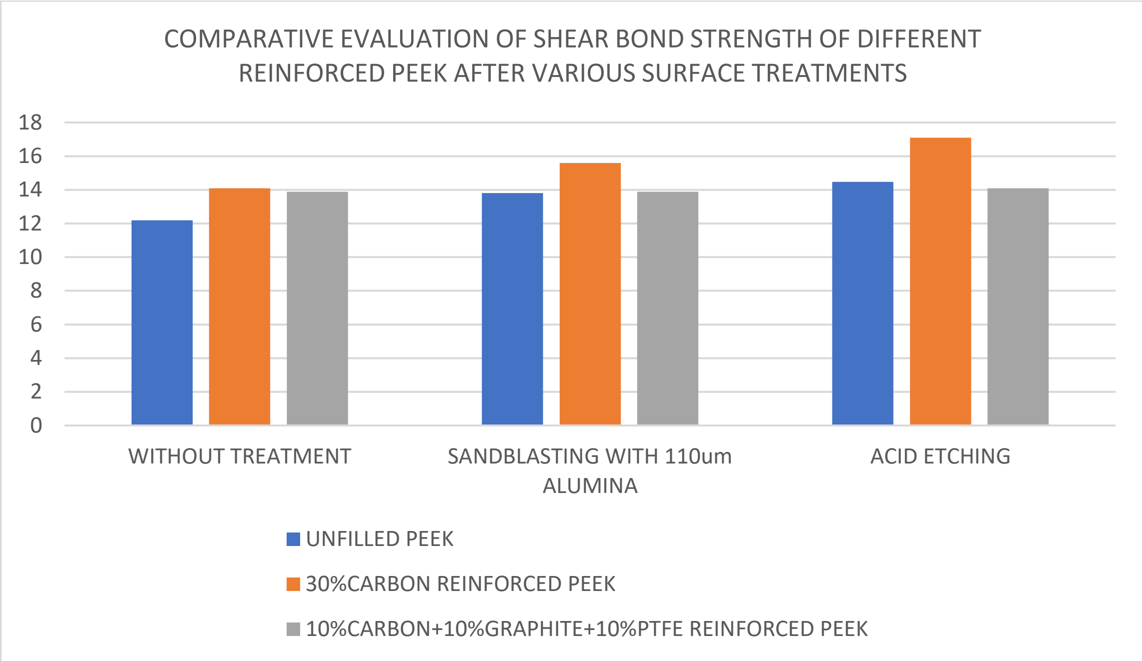
TABLE 2: POST HOC TESTS

TESTS	**GROUPS***	**P VALUE**	
		SBS	**SR**
Without treatment	Group A vs Group B	0.011	0.032
	Group A vs Group C	1.000	0.508
	Group B vs Group C	0.069	0.280
Sandblasting with 110um alumina	Group A vs Group B	0.051	0.383
	Group A vs Group	1.000	0.521
	Group B vs Group C	0.064	0.968
Acid etching with 98% sulphuric acid	Group A vs Group B	0.000	0.010
	Group A vs Group C	0.000	0.638
	Group B vs Group C	0.000	0.077

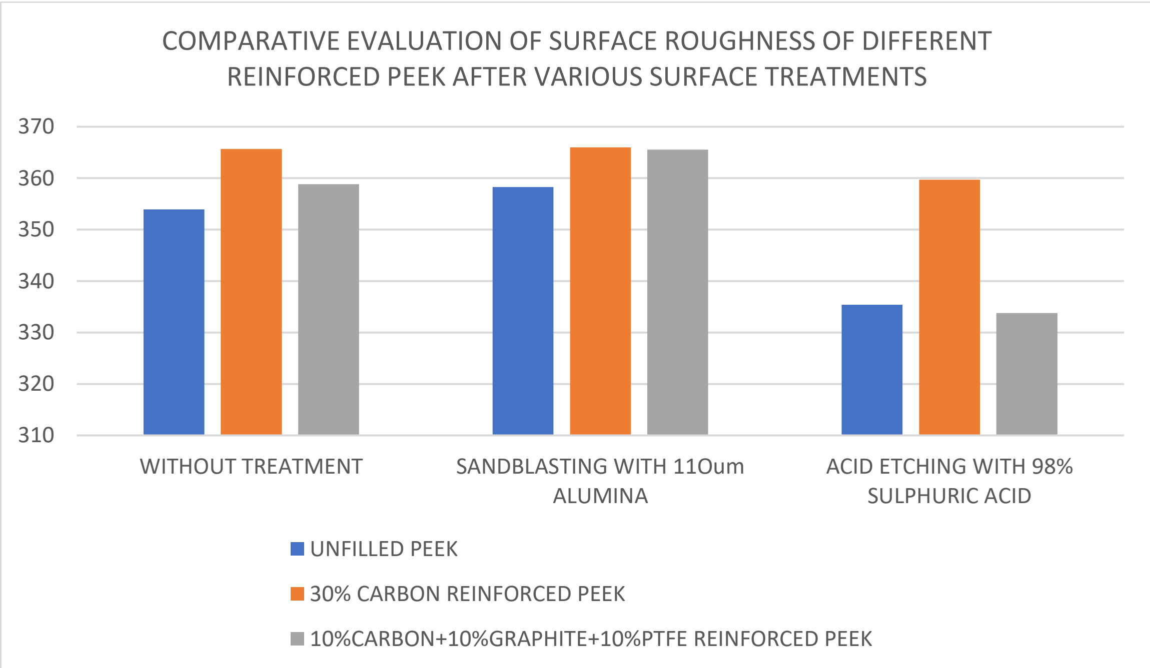
***Groups:** Group A – unfilled PEEK, Group B – 30% carbon reinforced PEEK, Group C - 10%Carbon+10%Graphite+10%PTFE Reinforced PEEK

LIST OF GRAPHS

GRAPH 1:



GRAPH 2:



LIST OF FIGURES:

Fig.1 30% CARBON REINFORCED PEEK SPECIMENS

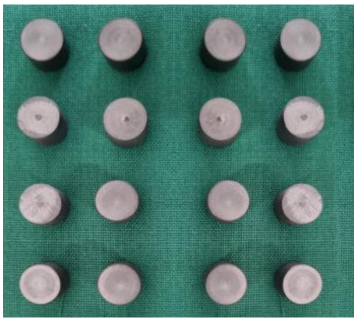


FIG.2 COMPOSITE EMBEDDED ON PEEK

Fig 3 EMBEDDED SPECIMEN PLACED IN UNIVERSAL TESTING MACHINE

Fig 4 TRIBOINTENDER

DISCUSSION:

PEEK exhibits low water solubility (0.5%), endures high-temperature thermal stress without substantial deterioration, and can reduce biocorrosion in bodily fluids. As a result, PEEK protects the abutment teeth and other tissue adjacent to extending the lifespan of a prosthesis [1]. Low translucency and a greyish color are two of PEEK's optical properties that limit its use as a full-coverage monolithic repair. A veneering layer made of extra resin composites is, therefore, necessary [6]. Research in the field of dentistry and reinforcement to PEEK is limited. To reinforce, the fibers are usually added into the PEEK matrix with a certain scale. PEEK reinforced with 30 wt% carbon fiber can provide greater rigidity and higher load-bearing capability according to the existing literature [7]. Polytetrafluoroethylene (PTFE) is a waxy and smooth synthetic polymer material with excellent thermal, electrical, and chemical stability with little friction. Graphite is composed of many layers of graphene and the graphene-reinforced PEEK material exhibited a 72% increase in lap shear strength in comparison to unfilled PEEK [8,9]. Although high-performance polymers (HPP) have good mechanical properties, their inert surfaces require surface conditioning due to poor adherence to veneering resin materials [10]. During the adhesion procedure, the surface of the PEEK material should be sufficiently rough to obtain appropriate mechanical retention [11]. There are two highly regarded surface treatment classes namely mechanical and chemical and this study approaches by sandblasting with 110um alumina (mechanical method) and acid etching with 98% sulphuric acid (chemical method).

PEEK has poor optical qualities, including low translucency and color which restrict its application as full-coverage monolithic restorations. Therefore, in order to achieve aesthetic standards, PEEK needs conventional or CAD-CAM milled composite veneers with extra aesthetic components, like composite resins. Indirect composite restorations have a reduced incidence of the aforementioned problems and produce less polymerization shrinkage stress when compared to the veneering of direct composites with PEEK. For assessing the adhesive properties, shear bond strength tests are more appropriate. The shear strength, which is linked to mechanical and chemical adhesion, may be impacted by any changes to the surface treatment of the material. Shear bond strength was highest in 30% carbon-reinforced PEEK because the carbon fibers caused roughness in the specimen and improved the adhesion between PEEK and indirect composite resulting in increasing the bond strength. Alumina sandblasting for PEEK has been documented in the literature with particle sizes between 50 and 110um. Alumina particles of 110 um demonstrated higher SR values and improved bond strength to resin cement [4]. Therefore, 110 um alumina particles used for sandblasting in this investigation would facilitate micromechanical interaction with dental adhesives improving the surface roughness [12, 13]. The alumina particles collide with the surface as they travel at a high rate, turning most of their kinetic energy into heat. This causes the surface to become microporous, increasing its wettability and giving it a larger, more "active" surface, both of which improve micro retention.

A statistically significant difference was found between group A and group B (p=0.011). Shear bond strength after sandblasting with 110um alumina particles was higher in all three groups (Group A=13.82±2.15MPa, Group B =15.63±1.34MPa, Group C = 13.89±1.45MPa) when compared with untreated specimens (Group A=12.20±1.56MPa, Group B =14.10±1.31MPa, Group C = 12.64±1.59MPa) irrespective of materials and a statistically significant difference was noted. This is because sandblasting with 110um alumina particles created roughness on the surface providing micromechanical interlocking to the indirect composites. Roughness also increases the wetting mechanism due to which the bonding mechanism was enhanced further. These results are controversial to Hallmann et and Ha et al where acid-etched polyetheretherketone surfaces reveal carbon-oxygen compounds, thereby providing adhesive systems with additional functional groups for bonding [14,15]. Furthermore, hydrolysis of the ether and ketone bonds that connect them occurs [14].

Shear bond strength after acid etching with 98% sulphuric acid was highest (Group A=14.48±1.35MPa, Group B =17.47±1.2MPa, Group C = 14.01±0.93 MPa) among surface treatments irrespective of the type of PEEK materials and it was statistically significant (p=0.000). This can be explained by the fact that sulfonate groups (-SO3) produced by sulfuric acid react chemically with adhesives to the PEEK polymer. Sulfuric acid changes the chemical makeup of the surface, increasing the number of functional groups on the PEEK surface [4]. In the present study, the application of an additional bonding system may also have improved the wetting of the micro retentive pores created after acid etching. This wetting might have played an especially important role in improving the bond strength of PEEK. On the other hand, as per various studies by Kern et al, Christine kuel et al, a strong resin bonding can be produced by employing primers on the material surface that include methacrylates [16, 17]. Additionally, micromechanical bonding was produced as a result of resin tags diffusing into the pits and pores of the PEEK surface. Prior to surface pretreatment with primers based on methyl methacrylate and layering, the etched PEEK surface can improve surface-free energy and surface roughness as well as the tensile bond strength [18]. Following sulfuric acid etching, the PEEK surface underwent micro topographical modifications that improved the resin adhesive's ability to penetrate, increasing the shear bond strength [12,19]. Additional research has demonstrated that treating PEEK's surface with abrasion by air or silica treatment improves the surface's microroughness and enhances the component's adhesion [14, 20, 21].

Indentation at the nanoscale has been established as a convenient method to investigate the mechanical properties of materials at reduced penetration depths. The appeal of nanoscale testing over macroscale testing is the ability to characterize and isolate constituent relationships in complex microstructures. Surface roughness was highest for

30%carbon-reinforced PEEK(Group 2) without surface treatment and it was statistically significant(p=.0.040). This is because of the influence of carbon fibers by which the surface was rougher when compared with unfilled PEEK. A rough surface for bonding often leads to stronger bonds for several reasons. On comparing surface treatments, sandblasted specimens (Test 2) showed the highest value irrespective of reinforcements to PEEK. Roughness imparts additional surface area with which the adhesive can make contact when forming a bond. It also provides additional mechanical interlocking at the interface and the irregularities on the surface may mitigate crack propagation, enabling stronger, more fatigue-resistant bonds. The lowest surface roughness was noted in 10%carbon+10%graphite+10%PTFE reinforced PEEK. The waxy substance PTFE created a smoother surface which reduced the bond strength also when compared with other groups. Therefore, it was proven that surface roughness increases wettability which increases the bond strength of the material. The limitations include the absence of thermocycling or long-term water storage to simulate artificial aging. Further investigations including brief exposure time in distilled water are necessary to determine the long-term durability of the veneering approach.

CONCLUSION:

Within the limitations of this study, it was concluded, on comparing various surface treatments on shear bond strength between veneering composite and different PEEK materials, the highest value was observed in the acid etched group irrespective of different types of PEEK specimens. Shear bond strength and surface roughness were highest in 30%carbon-reinforced PEEK irrespective of various surface treatments. It was also noted that shear bond strength increased when the surface roughness increased proving that surface roughness influences the substrate by improving the shear bond strength.

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