

**“COMPARATIVE EVALUATION OF SHEAR BOND STRENGTH
OF COMPOSITE RESIN WITH POLYETHERETHERKETONE (PEEK)
FABRICATED BY CAD CAM AND 3D PRINTING
TECHNIQUES : AN *IN-VITRO* STUDY AND SEM ANALYSIS.”**

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IN

**PROSTHODONTICS INCLUDING REMOVABLE,
FIXED, MAXILLOFACIAL AND IMPLANTOLOGY**

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LIST OF ABBREVIATIONS USED

Sr. No.	Abbreviations	Full form
1.	PEEK	polyetheretherketone
2.	PEAK	polyaryletherketone
3.	3D printing	3 dimensional printing
4.	AM	Additive manufacturing
5.	MMA	Methylmethacrylate
6.	SBS	Shear bond strength
7.	UTM	Universal testing machine
8.	SEM	Scanning electron microscope
9.	FFL	filament fabrication layer
10.	ANOVA	Analysis of Variance
11.	CAD CAM	Computer aided designing and computer aided machining
12.	Co-Cr alloy	Cobalt chromium alloy
13.	Co-Cr-Mo alloy	Cobalt chromium molybdenum alloy
14.	°C	Degrees Celsius
15.	3D	3-Dimensional object
16.	<i>et al.</i>	And others
17.	FDP	Fixed Denture Prosthesis
18.	RDP	Removable dental prosthesis
19.	Fig.	Figure
20.	gm	Gram
21.	i.e.	That is
22.	min	Minutes
23.	µm	Micrometre
24.	No.	Number
25.	N	Newton
26.	Ni-Cr alloy	Nickel chromium alloy

27.	PFM	Porcelain Fused to Metal
28.	p	Probability value
29.	SD	Standard Deviation
30.	SLM	Selective Laser Melting
31.	S. No.	Serial Number
32.	sec	Second
33.	sig	Significance
34.	STL	Standard Tessellation Language
35.	FFF	Fused filament fabrication
36.	%	Percent

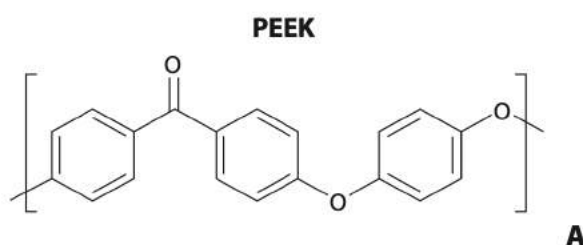
INTRODUCTION

Fixed dental prostheses (FDP) and Removable dental prostheses (RDP) are commonly used in dentistry. Usually, the frameworks of FDP and RDP are made up of metal alloys. For various types of prosthetic framework, nickel-chromium, cobalt-chromium-molybdenum alloy, and titanium are used ^{1,2}. Ceramic layering or resin veneer layering is possible in all the above metals to give a natural tooth appearance ³. Even though metal alloys are widely used for prosthetic frameworks, it is seen that some patients are allergic to this alloy, so, there is a need to use alternative materials for such patients ^{4,5}. In recent times PEEK is a material widely used in place of metal and can be used in such allergic patients ⁶.

The biocompatibility and chemically stable nature of PEEK make it very popular among dental practitioners ^{7,8}. PEEK is a polyaromatic semi-crystalline thermoplastic polymer originally introduced by Victrex PLC then imperial chemical industries used this material in the early 1980s for

engineering applications. It was first commercialised for industrial applications in the manufacturing of aircraft, turbine blades, piston parts, cable insulation, bearings and compressor plate valves ⁹. Later in 1998, it was proposed for biomedical applications by Invibio Ltd. In the same year, Victrex PEEK business launched PEEK-OPTIMA for long-term implantable applications ¹⁰.

PEEK is a high-performance semi-crystalline thermoplastic material related to the polyaryletherketone (PAEK) group, made up of a repeating unit of three aromatic rings linked by two ether groups and one carbonyl group ¹¹. It is a member of high-performance engineering thermoplastics known as amorphous groups. PEEK comes in three viscosity classes (high, medium, and low), all of which are derived from the same fundamental formula $(-C_6H_4-O-C_6H_4-C_6H_4)_n$. PEEK is resistant to mechanical forces, thermal and oxidative reactions, as well as high temperatures, due to its aromatic rings ¹². PEEK's ability to be sterilised by radiation and heat without causing structural damage made it an appealing biomaterial for medical usage ^{11,13,14}.



Molecular structure of PEEK

PEEK can be machined using CAD CAM techniques (Subtractive manufacturing) and can be produced using 3D printing (Additive Manufacturing) ¹⁵.

The production of polymer-based blanks for the CAD CAM fabrication of dental prostheses is a logical extension of the therapeutic spectrum in modern dentistry ². PEEK fabricated by CAD CAM process shows increased fracture strength, more uniform stress distribution, and reduced wear of opposing teeth ¹⁶. CAD CAM milling systems can achieve extremely high fit accuracy hence prostheses made using CAD CAM technology is becoming increasingly popular amongst prosthodontists ¹⁷⁻¹⁹.

3D printing technique, often known as fast prototyping, is the process of creating new material classes via 3D printing. It allows for more efficient and material-saving production techniques ²⁰. There are numerous benefits of 3D printing in dentistry that improves a dentist's or dental technician's daily work as well as the quality of patient care ²¹. One of the most significant benefits is that patient-specific parts may be developed and manufactured with the least amount of time, material, and expense ²².

In comparison to CAD CAM manufacturing technology, 3D printing technology allows for unlimited design changes during prosthesis development and manufacturing. The main benefit of a PEEK 3D printed prostheses is its material-saving technology. As for disadvantages, the most required postprocessing such as support structure removal, surface polishing and anisotropic behaviour such as mechanical characteristics vary depending on printing direction must be mentioned ²².

Creep resistance, low water absorption, and good fracture resistance are just a few of the mechanical features of PEEK^{11,23-25}. It has been proposed as a metal-free material for implants, temporary abutments, orthodontic wires, detachable prostheses, fixed prostheses etc.²⁶⁻³¹. Its mechanical qualities, as well as its biocompatibility and stability with all organic and inorganic substances, make it a popular dental material^{7,11,14}. Even for fixed dental prostheses PEEK can be used as an implant-supported bar and clamp material^{28,30,32,33}.

A three-unit fixed partial denture made of PEEK can withstand a load of 1383N on average, which is ideal for clinical use given the maximum documented masticatory force of 600N^{7,34}. The low translucency and a greyish or snow-white colour component of PEEK limit its clinical usage as a full coverage monolithic prosthesis^{7,35}. To simulate the natural tooth appearance, veneering resins are indicated to conceal the bottom greyish and opaque colour of PEEK-based restorations³⁶. The bonding of PEEK to other dental materials, in contrast to the favourable features, is an issue. It does not appear that a direct chemical link between PEEK and composite is achievable^{37,38}. The issue is that the PEEK is inert, making it difficult to connect with another polymer. However, PEEK and resin composite materials have poor adhesion qualities due to their inert hydrophobic surface and low surface free energy³⁹.

Several recent research looked at the bonding capabilities of PEEK and resin composites and discovered that without further surface treatment of the PEEK surface, no or just insufficient adhesion may be obtained therefore surface pre-treatments of PEEK before adhesive bonding have

been examined, and bond strength between PEEK and resin composites has been demonstrated ^{7,35,40-42}.

To increase bonding, most research suggested using 98 percent sulfuric acid to change the chemical and physical surface of PEEK ^{7,41,43-45}. Sulfonate groups were produced in the polymer chains of PEEK by sulfuric acid, which chemically cross-linked to methylmethacrylate (MMA) dental adhesives ^{43,46-50}. When sulfuric acid etching was utilised, shear bond strength was reported to be higher than hydrofluoric acid, argon plasma, air abrasion (50–110 micrometre) and silica coating ⁴³. Higher surface roughness and irregularity of PEEK were observed using a scanning electron microscope, which was linked to increased sulfuric acid etching concentrations ^{51,52}. Due to the addition of water to 98 percent sulfuric acid, the chemical balance in the diluted sulfuric acid changes, and the degree of sulfonation reaction decreases ⁴⁷. As a result, when compared to the larger concentration, the lower concentration of sulfuric acid did not cause severe surface corrosion of the PEEK surface ⁴⁸.

Due to the several advantages of PEEK as a framework material, its use in Prosthodontics is increased in recent times ⁵³. The cornerstone of prosthodontic treatments is veneered restorations with a core material. Successful prosthetic treatment has long been recognised as a robust core combined with an attractive veneering material. To benefit from the ideal qualities of the strong core as well as the aesthetic look of the veneering, a strong shear bond strength between the veneering and the core material is necessary ⁵⁴, hence the aim of this study is to compare and evaluate the shear

bond strength of composite resin with PEEK fabricated by CAD CAM and 3D printing techniques followed by SEM analysis at bond failure interface.

AIM AND OBJECTIVES

AIM:

‘Comparative evaluation of shear bond strength of composite resin with polyetheretherketone (PEEK) fabricated by CAD CAM and 3D printing techniques: An *In-vitro* study and SEM analysis.’

OBJECTIVES:

Primary objective

1. To evaluate and compare shear bond strength of composite resin with PEEK fabricated by CAD CAM and 3D printing techniques followed by SEM analysis at bond failure interface.

Other objectives

1. To evaluate the shear bond strength of composite resin with PEEK fabricated by CAD CAM.
2. To evaluate the shear bond strength of composite resin with PEEK fabricated 3D printing.
3. To compare the shear bond strength of composite resin with PEEK fabricated by CAD CAM and 3D printing.
4. To evaluate bond failure interface of composite resin with PEEK fabricated by CAD CAM and 3D printing technique by SEM analysis.
5. To compare bond failure interface of composite resin with PEEK fabricated by CAD CAM and 3D printing technique by SEM analysis.

REVIEW OF LITERATURE

Patrick R. Schmidlin, Bogna Stawarczyk, Marco Wieland, Thomas Attin, Christoph H.F. Hammerle and Jens Fischer (2010)⁴¹ Evaluated and compared the effect of different surface treatments on the shear bond strength of PEEK and luting cement. PEEK disc shape samples were made and split into surface treatment as no treatment, 98 percent sulfuric acid etching, sandblasting by 50-micrometre alumina, sandblasting by 110-micrometre alumina and silica coating. Acrylic hollow cylinder luted on all the samples. Shear bond strength is measured with a universal testing machine. The study found that only the sulfuric acid group showed a strong bond between cement and PEEK.

Matthias Kern and Frank Lehmann (2012)⁴⁰ evaluated and compare the tensile bond strength between resin and PEEK when treated with different

surface treatments. PEEK sample was divided into 6 groups. 5 groups were surface treated with Air-abrasion with Rocatec Pre at 0.28 MPa for 15 s and cleaned with compressed air for 15 s. and Luxatemp Fluorescence without adhesive promotor, Ecusit Composite repair with Luxatemp Fluorescence, glaze and bond with Luxatemp Fluorescence, Espe Sil with Luxatemp Fluorescence were applied on 5 groups respectively. Sixth group 2.8MPa were used instead of 0.28MPa with Clearfil ceramic primer with Luxatemp Fluorescence. Samples were divided and stored for 3 days without thermocycling and stored for 150 days with thermocycling. A universal testing machine is used to check the tensile bond strength. The study concluded that the sample treated with air abrasion and bonding with Luxatemp Glaze and Bond showed a higher tensile bond strength significantly compare to other samples.

Lauren Levi, Shomo Barak and Joseph Katz (2012)⁵⁵ conducted a systematic review on allergic reactions to metal alloys in porcelain fused to metal fixed prosthodontics devices. From 1970 to 2012, papers were searched in PubMed, Science Direct, and Google Scholar. Only English language articles were included. The study found that Allergies to metal alloys have been well reported in studies, but only a few articles have focused on the link between FPD and metal allergies. Different forms of allergy reactions are associated with different metals, and these reactions can be linked to the level of an alloy's corrosion, population exposure, and biologic environment. Because there are few studies that show allergic reactions to

metals in PFM crowns and partial dentures. To find out more about this topic, more research is needed.

Bogna Stawarczyk, Florian Beuer, Timea Wimmer, Dirk Jahn, Beatrice Sener and Malgorzata Roos (2013)⁷ evaluated the bond strength of PEEK with two veneering resins after different conditioning methods and also evaluated the fracture load of PEEK 3 unit FDP. PEEK samples were divided into surface treatment groups as etched with 98 percent sulfuric acid, air abrasion with 50-micrometre particles, air abrasion with 100-micrometre particles, silica coating with Rocatec system and no treatment as control. Each group was further divided and two resin veneering materials Gradia, Sinfony applied and cured. Three unit PEEK FDPs samples were made to check the fracture load. Shear bond strength and fracture load were checked with a universal testing machine. The study concluded that the acid-etched group shows the highest shear bond strength value and a Fractured load of 1383 N were seen.

Rui Ma and Tingting Tang (2014)³⁹ studied PEEK as an implant material and found that it would become a popular component of clinical orthopaedic and spinal applications. PEEK is radiolucent, biocompatible, chemically stable and it has an elastic modulus similar to the bone which makes it possible to use as implant material. PEEK is a highly inert material that prevents its integration with the surrounding bone. This problem can be solved by surface treatment of PEEK and adding bioactive material in PEEK.

Li Zhou, Yuetong Qian, Ye Zhu, Hong Liu, Kang Gan and Jing Guo (2014)⁴³ Investigated the effect of various surface treatments on the bonding strength of PEEK and composite material. PEEK samples were separated into four groups: no treatment, 98 percent sulfuric acid, 9.5 percent hydrofluoric acid, argon plasma treatment, and sandblasting with 50-micrometre Al₂O₃ particles. On the samples, two different types of cement were applied: Rely X Unicem and SE Bond/Clearfil AP-X. All samples were kept in distilled water for 24 hours at 37 degrees Celsius. A universal testing machine was used to determine bond strength. The study concluded that in both types of cement groups, surface etching and argon plasma treatment increased shear strength.

Martin Rosentritt, Verena Preis, Michael Behr, Nuno Sereno and Carola Kolbeck (2014)⁵⁶ compared shear bond strength between PEEK and composite when treated with different surface treatments. PEEK samples were etched with H₂SO₄ 98 percent for 1 min, H₂O₂/H₂SO₄ ratio 1:1 for 30 s, air abraded with Al₂O₃—50 µm/2 bar, Al₂O₃—120 µm/2.8 bar, Rocatec Pre/Plus and untreated PEEK as control. On all these PEEK groups composite resin is applied and light-cured. A universal testing machine is used to measure shear bond strength. Each group sample was divided into three subgroups before doing the shear bond strength test. In first subgroup test is performed after 24 hours of polymerization, the second subgroup test is performed after thermocycling and the third subgroup after storage in distilled water. The study concluded that nine of the investigated systems

showed higher shear bond strength after thermocycling and seven showed higher shear bond strength after water storage.

Shariq Najeeb, Muhammad S. Zafar, Zohaib Khurshid and Sfahad Siddiqui (2015)³¹ stated that PEEK is a polymer with numerous potential applications in dentistry. They claimed that PEEK dental implants had less stress shielding than titanium dental implants because the mechanical characteristics of PEEK and bone were more similar. They came to the conclusion that because PEEK has mechanical and physical qualities similar to bone, it might be used in a variety of dental applications. They also recommended that more tweaks and improvements to the material's characteristics would expand its clinical applications.

Xin Zhang, Li-Cheng Wei, Bin Wu, Li-Ying Yu, Xiao-Ping Wang and Yue Liu (2016)⁵⁷ evaluated and compared metal allergies linked with dental alloy prostheses and HLA-DR expression in gingival tissue was conducted. The prosthetic materials gold, cobalt-chromium, nickel-chromium, and titanium were compared. Individuals' sensitivity to alloys used in recommended metal-containing prostheses were compared using patch tests, as well as a correlation study between metal allergy and associated clinical symptoms in sensitised patients. The study concluded that nickel allergy was shown to be more common than in other groups, and HLA-DR levels in nickel-chromium were likewise high. Palladium and Nickel-chromium allergies were shown to be more common in women than in men.

Patcharawan Silthampitag, Pisaisit Chaijareenont, Kittipong Tattakorn. Chaiyasit Banjongprasert, Hidekazu Takahashi and Mansuang Arksornnukit (2016)⁴⁵ studied the effect of surface pre-treatment on PEEK and composite shear bond strength. PEEK Specimens were split into four categories based on their surface treatment. They were etched with 98 percent sulfuric acid, etched with piranha solution, etched with a 10:3 mixture of 98 percent sulfuric acid and 30 percent hydrogen peroxide, and sandblasted with 50-micrometre aluminium oxide particles at 0.2 MPa at a 10 mm distance for 10 seconds. Surface roughness is measured using a profilometer. All samples had composite attached to them. A universal testing machine was used to conduct the shear bond strength test. When compared to the piranha solution, the roughness values in sandblasting groups and 98 percent sulfuric acid were much higher. SEM revealed porosities and pitting caused by chemical etching, indicating that chemical etching had a major impact on the adhesion of PEEK and resin materials.

Ivan Vladislavov Panayotov, Valerie Orti, Frederic Cuisinier and Jacques Yachouh (2016)¹⁰ did a study on clinical uses of PEEK material in the medical field and found that mechanical properties of a polyaromatic semi-crystalline thermoplastic polymer were suitable for biomedical applications. PEEK has already been applied in different surgical fields: spine surgery, orthopaedic surgery, maxillo-facial surgery etc. Studies have shown that the properties of PEEK can be developed by the manufacturing of PEEK composite. To improve their surface area and acceptance by bone many surface treatments are proposed. PEEK materials are becoming an

important group of biomaterials as one of the best materials for bone replacement. 3D printing technology in PEEK polymers will increase the role of this material in dentistry.

Patricia R. Monich, Fernanda V. Berti, Luismar M. Porto, Bruno Henriques, Antonio P. Novaes de Oliveira and Marcio C. Fredel et. al. (2017)⁵⁸ assessed physicochemical and biological properties of a PEEK composite containing 30 percent silica fibres by weight (NASF). The introduction of fibres enhanced the elastic modulus of the resultant PEEK composite by 56 percent, while its microhardness increased by 26.7 percent, according to the mechanical assays. PEEK and NASF have good interfacial adhesion, according to chemical and microscopic analysis. The scientists found that PEEK composites containing natural amorphous silica fibres have a great potential for replacing numerous polymeric and composite materials in medicine and dentistry.

Pisaisit Chaijareenont, Sasiprapha Prakhamsai, Patcharawan Silthampitag, Hidekazu Takahashi and Mansuang Arksornnukit (2018)⁵² evaluated and compared the shear bond strength between PEEK and composite. PEEK samples were surface treated with 70 percent H₂SO₄, 80 percent H₂SO₄, 85 percent H₂SO₄, 90 percent H₂SO₄, 98 percent H₂SO₄ and no surface treatment as a control group. Unfilled resin material was applied to the pre-treatment group with a single micro brush application. Shear bond strength was measured with a universal testing machine. They

concluded that 90 percent H₂SO₄ and 98 percent H₂SO₄ surface treatment showed the highest shear bond strength.

Reshma Premkumar, Vinni T K, Pramod Kumar A V, Gilza K Vasunni and Sampath K (2018)⁵⁹ assessed shear bond strength of composite veneer with PEEK implant prosthesis by two different bonding systems. Prefabricated composite veneers cemented on PEEK framework with two different bonding systems. The group one bonding system was visio.link primer-combo.lign luting composite resin and the second groups were GC Composite Primer and LuxaCore Z bonding resin. Samples were stored at room temperature for 24 hours after aging. Shear bond strength is measured with a universal testing machine. The study found that group one bonding system showed more shear bond strength compare to others. SEM analysis showed the mixed type of bonding failure.

Sabit Melih Ates, Ipek Caglar and Zeynep Yesil Duymus (2018)⁶⁰ investigated bond strength between PEEK and composite when treated with different surface treatments. PEEK samples were made and divided into subgroups as the untreated control group (C), airborne- particle abrasion (B), silica coating (S), etching with Er:YAG laser (L), etching with Er:YAG laser and airborne-particle abrasion (LB), etching with Er:YAG laser and silica coating (LS). Adhesive and veneering resin applied and cured. The universal testing machine is used to test shear bond strength. The study concluded that LB and LS show higher shear bond strength.

Friederike Botel, Tycho Zimmermann, Mona Sutel, Wolf-Dieter Muller, Andreas and Dominik Schwitalla (2018)⁶¹ examined shear bond strength between PEEK and composite when treated with oxygen or argon low-pressure plasma as a surface treatment. Samples were made up of unfilled PEEK Juvora, PEEK compound DC4420, PEEK compound DC4450. The sample was sandblasted and divided randomly for surface treatment. O₂ plasma for 3 minutes, O₂ plasma for 35 minutes, Ar/O₂ plasma for 3 minutes, Ar/O₂ plasma was used for 35 minutes, and no plasma surface treatment was used as control. On all samples, an adhesive visio.link was applied and cured. Vita, Gradia, Gradia flo composite were applied on all samples and cured. After incubating samples in distilled water at 37 degrees Celcius for 24 hours shear bond strength was measured with a universal testing machine. The study concluded that DC4420 AND DC4450 show the highest shear bond strength.

Mahinour A. Yousry, Sanaa A. Hussein and Fayza H. Al Abbassy (2018)⁶² evaluated shear bond strength of PEEK with veneering composite using two different adhesives. In group one PEEK samples were made and sub grouped by two different type of adhesive system DTK adhesive and combo.lign applied. For group two PEEK samples made and sub grouped as two different type of cement RelyX Unicem resin cement, Fuji Plus GI cement all the samples were subjected to thermocycling. Shear bond strength measured with a universal testing machine. The study concluded that shear bond strength were more with DTK adhesive system compared to other groups.

Lakshmana Bathala, Vaishnavi Majeti, Narendra Rachuri, Nibha Singh and Sirisha Gedela (2019)⁶³ done a review on PEEK and found that due to its high-quality mechanical qualities, the peek material can be considered promising in the future as a replacement for metals like Titanium and Zirconium. Surface treated PEEK has better properties than not treated. PEEK's can be used as implant materials because of their elastic modulus, strength, rigidity, and lightweight and also be used in a variety of clinical circumstances in dentistry. PEEK polymer material is already being utilised as a pioneering material in spinal, orthopaedic, and sports medicine, but it has yet to acquire traction in dentistry practice. This could be due to the fact that there are so few long-term clinical trials on the use of PEEK in clinical dental practice.

Abid Haleem and Mohd Javaid (2019)⁸ perform a review on the usage and progress of PEEK in dentistry when manufactured with 3D printing, and they came to the conclusion that dental implants, tools, and devices made with 3D printers had greater design and development success. It aids in the reduction of product development cycle time, cost, and weight. It also improves prosthesis quality and assists in the resolution of numerous dental difficulties. This cutting-edge technology serves as a concept generator and makes it simple to make a required adjustment to a dental prosthesis. As a result, this technique may be used to make personalised PEEK-based orthodontics parts and crowns and implants.

Mohamed Younis, Alexey Unkovskiy, Ashraf ElAyouti, Jurgen Geis-Gerstorfer and Sebastian Spintzyk (2019)⁶⁴ studied the effect of different plasma gases on shear bond strength of PEEK and composite resin. Milled PEEK samples were divided equally for surface treatment as a reference, adhesive, argon, nitrogen, oxygen, and air plasma treatment. Veneering composite bonded on PEEK. Shear bond strength was measured with a universal testing machine. The study found that the nitrogen surface treatment group has maximum shear bond strength compared to other groups.

Seham E. Mohamed and Hashem Rasha G. (2019)⁶⁵ compared patient satisfaction with a removable partial denture framework made up of conventional metal and milled PEEK. Patient with class one partially edentulous arches was selected as samples. Each type of prosthesis is given to the patient for 3 months. Patient satisfaction is checked with the questionnaire. The questionnaires were statistically analyzed, resulting in more patients' satisfaction with the digital PEEK framework RPD than with the conventional metallic RPD framework.

Ahmet Kursat Culhaoglu, Serhat Emre Ozkır, Volkan Sahin, Burak Yilmaz and Mehmet Ali Kılıcarslan (2020)⁶⁶ studies PEEK and composite surface roughness, wettability, and shear bond strength. Surface treatments included silicoating, acetone treatment, etching with sulfuric acid, abrasion with aluminium oxide particle, Yb:PL laser irradiation, and a no surface treatment as a control. A profilometer was used to determine the roughness

of the surface. A composite resin was used to veneer PEEK surfaces. The specimens were then subjected to 10,000 cycles of thermocycling at temperatures ranging from 5 to 55°C. Shear bond strength is measured by a universal testing machine. The study concluded that the sulfuric acid etching group showed the maximum shear bond strength.

Alexander Prechtel, Bogna Stawarczyk, Reinhard Hickel, Daniel Edelhoff and Marcel Reymus (2020)⁶⁷ investigated and compared fracture load, fracture types, and the impact of chewing simulation of inlay restorations made with 3D printed PEEK, milled PEEK, composite filled in inlay cavities, and a sound tooth as a control group. class one cavities were prepared in maxillary and mandibular molars. Essentium PEEK, KetaSpire PEEK MS-NT1, VESTAKEEP i4 VES G PEEK, VICTREX VIC PEEK 450G 3D printing material and JUVORATM milled PEEK material inlay restoration made from the scan cavity. Inlay restoration adapted to cavities. All samples were subjected to masticatory cycles in a chewing simulator. After this simulation, the fracture load was calculated. Fracture load is measured in a universal testing machine. Then with a hemispherical stamp, an increasing force was applied perpendicularly to the central fossa until failure occurred. According to the findings, Essentium PEEK and Tetric EvoCeram had the lowest fracture loads, while sound molars had the highest values. 3D Printed PEEK inlays, milled indirect PEEK inlays and composite filling fracture load tolerance were more than normal chewing force.

Rady EL-BAZ, Mostafa Fayad, Mohamed Abas, Ahmad Shoeib, Mohammed Moustafa Gad and Mohamed Ahmed Helal (2020)⁶⁸ evaluated and compare the cobalt-chromium and PEEK clasp for its mechanical properties in the removable partial denture. Cobalt chromium Aker clasps were cast in a conventional manner. PEEK Aker clasp was fabricated with injection molding process. The lower 1st molar was embedded in a customised mold. Each testing model and its clasps were mounted inside a universal testing machine, the retention was measured by applying withdrawal force 5 mm/min. ROBOTIC chewing stimulator used to perform fatigue test. Fatigue resistance tests were stimulated by removal and insertion cycling of clasps. Digital micrometre was used to measure the deformation before and after each cycle. The deformity was measured before and after each cycling using a digital micrometre. The study concluded that PEEK clasps retention were similar to chromium cobalt clasps.

Hasan Sarfaraz, Mohammed Rasheed N, Sanath K. Shetty, Uma M. Prabhu, Kevin Fernandes and Smrithi Mohandas (2020)⁶⁹ Assessed and compare the shear bond strength of composites bonded to zirconia and composites bonded to PEEK. Samples of zirconia and PEEK were milled. All the samples were surface treated with 110-µm aluminium oxide air abrasion and further divided as Group 1A sample of composite bonded to zirconia block before thermocycling, Group 1B sample of composite bonded to zirconia block after thermocycling, Group 2A sample of composite bonded to PEEK block before thermocycling, Group 2B sample of composite bonded to PEEK block after thermocycling. The shear bond

strength was measured by a universal testing machine. The study concluded no significant difference in shear bond strength was seen between the groups, while the PEEK sample showed higher shear bond strength.

Felicitas Mayinger, Danka Micovic, Andreas Schleich, Malgorzata Roos, Marlis Eichberger and Bogna Stawarczyk (2021)⁷⁰ investigated and compared the retention force of cobalt-chromium and PEEK removable dental prosthesis clasp. Models prepared to incorporate 2nd premolars and 1st molars. The clasp was made of Cobalt chromium molybdenum, Dentokeep PEEK milled, breCAM BioHPP Blank – PEEK milled, BioHPP Granulat for 2 press – PEEK milled. All samples were surface treated with AL203 air particle abrasion with 105 micrometers. For per aging fifty retention force measurement were performed for each specimen. The study concluded that initially BioHPP Granulat for 2 press-PEEK milled and Dentokeep PEEK milled showed the highest retention values. After artificial aging Cobalt chromium molybdenum showed a higher retention force value.

Oskar Bunz, Carla I. Benz, Wolfgang H. Arnold and Andree Piwowarczyk (2021)² assessed the shear bond strength of veneering composites including PEEK and fiber reinforced composites were compared. All samples are abraded with 50-micrometre Aluminium Oxide particles. For the application of the bonding agent, each group sample is separated into four groups. The bonding compounds utilised were Luxatemp Glaze, SR Nexco Connect, Scotchbond universal, and iBond universal. The veneering compound Nexco Paste (Ivoclar Vivadent) was manually applied

and polymerized in plexiglass tubes with an inner diameter of 5 mm. Short-term, long-term, and no artificial ageing specimens were separated into three subgroups, and shear bond strength was measured using a universal testing machine. The study concluded that the highest shear bond strength values from PEEK to composite were achieved with Scotchbond universal and Luxatemp Glaze & Bond.

Diogo Do Nascimento Machado Gouveia, Michael E. Razzoog, Marianella Sierralta and Maria Fernanda Alfaro (2021)⁷¹ compared shear bond strength between composite with PEEK and PEKK material when treated with different surface treatments. PEEK milled samples surface treated with air particle abraded 110-micrometre aluminium oxide particles and no surface treatment as control. PEKK 3D printed particles surface-treated with abraded 110-micrometre aluminium oxide particles and no surface treatment as control. PEKK milled samples etched with airborne particle abraded 110-micrometre aluminium oxide particles. PEKK milled samples surface treated with airborne particle abraded 110-micrometre aluminium oxide particles and no surface treatment as control. After the surface treatment resin primer is applied and cured. Composite resin is applied and cured. A universal testing machine was used to check shear bond strength and the study concluded that groups treated with 110-micrometre aluminium oxide show more shear bond strength compared to other groups. No significant difference was seen among groups.

Fatih Demirci and Samet Tekin (2021)⁷² compared the shear bond strength of PEEK with composite when 2 types of adhesive systems are used. PEEK specimens were divided as Unfilled PEEK, carbon-fiber-reinforced PEEK, glass-fiber-reinforced PEEK and ceramic-reinforced PEEK. Each group was further divided into two subgroups Visio.link, Bredent adhesive system and Single Bond Universal, 3M ESPE adhesive system based on adhesive application. All specimens were subjected to airborne-particle abrasion with 50- μm Al₂O₃. Composite resin was applied and cured on all samples. After polymerization, thermocycling with 5000 cycles is done. The compressive load was measured using the universal testing machine. Shear bond strength (SBS) values for carbon fibre reinforced PEEK and unfilled PEEK were highest.

Jiaqi Zhang, Yingjie Yi, Chenwei Wang, Ling Ding, Ruijin Wang and Guofeng Wu et. al. (2021)⁷³ Evaluated and compared the effect of acid etching duration on the bond strength of PEEK and composite resin. PEEK samples were made with CAD CAM and 3D printing techniques. Each group sample was divided into seven subgroups for sulfuric acid etching based on the duration of the etching as 0, 5, 10, 30, 60, 120, 300 seconds. Two subgroups in each group were analysed in SEM for surface evaluation. Primer is applied to all the samples. Composite resin is applied on all the samples and shear bond strength and failure mode analysis are done. The study concluded that based on SEM analysis the appropriate time for etching the milled sample is less than 120 seconds as above that time surface damage is seen and for 3D printed PEEK etching time is 30 seconds. Milled PEEK

shows higher shear bond strength compared to 3D printed PEEK, although 3D printed PEEK shows slight less SBS compare to milled PEEK still the values are sufficient to use 3D printed PEEK clinically.

Umair Parkar, Ramandeep Dugal, Pallavi Madanshetty, Trupti Devadiga, Abid Sharifullah Khan and Aamir Godil (2021)⁷⁴ Evaluated surface roughness and shear bond strength of PEEK after different surface treatments. CAD CAM milled PEEK samples were made. Samples were surface treated as air abrasion with alumina particles 110 micrometres, etched with 98 percent sulfuric acid, air abrasion with synthetic diamond particles 10–20 micrometre and no surface treatment as the control group. The surface roughness was measured using a surface profilometer. Composite resin discs cured on PEEK discs. Shear bond strength is measured with a universal testing machine. The study concluded the highest shear bond strength and surface roughness value were noted with the 98 percent sulfuric acid group.

MATERIAL AND METHODS

This study was carried out in the department of prosthodontics. All attempts were made to standardize the procedures throughout the study to minimize the effects of variable factors on the observations and the final results.

Material and method are divided into the following heads.

- I. Materials.
- II. Armamentarium and equipment.
- III. Methodology.

I. Materials

Sr. no.	Material	Manufacture	Batch number
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1	CAD CAM PEEK Disk of 96mm x 12mm dimension (Fig.1)	Bredent breCAM.BioHPP	497897
2	3D Printing PEEK Filaments (Fig.2)	Vestakeep PEEK	19082902
3	98 percent sulfuric acid (Fig.3)	Thomas Baker	149656
4	Deionised water (Fig.4)	Anand sales	1021
5	Primer Z (Fig.5)	GC	1708041

6	Composite resin (Fig.6)	SHOFU	112033
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II. Armamentarium and equipment

- A. CAD CAM machine.(Sirona inLab MC X5) (Fig.7)
- B. 3D printing machine.(Apium M220) (Fig.8)
- C. Scanning electron microscope.(Zigma) (Fig.9)
- D. Ultrasonic cleaning machine.(Gepufte Sicherheit) (Fig.10)
- E. Beaker.(BFC) (Fig.11)
- F. Glass tube dropper.(Starlabs) (Fig.12)
- G. 800 grit abrasive sandpaper.(3M) (Fig.13)
- H. Cotton.(Kapfinex Solitaire) (Fig.14)
- I. Tweezer.(Waldent) (Fig.15)
- J. Applicator tip.(GC) (Fig.16)
- K. Laboratory curing unit.(Solidilite V) (Fig.17)
- L. Composite instrument.(GDC) (Fig.18)
- M. Vernier caliper.(Safeseed) (Fig.19)
- N. Universal testing machine.(Instron) (Fig.20)

III. Methodology

The basic methodology consisted of-

- a. Preparation of CAD CAM milled PEEK sample (Group -A).

- b. Preparation of 3D printed PEEK sample (Group -B).
- c. Surface treatment of all samples.
- d. Composite application.
- e. Determination and comparison of shear bond strength between CAD CAM milled PEEK samples and 3D printed PEEK samples.
- f. Determination of the type of failure and Comparison of type of failure between CAD CAM milled PEEK samples and 3D printed PEEK samples.

(a) Preparation of CAD CAM milled PEEK sample (Group -A).

ISO 10477 guidelines for polymer-based crown and bridge materials were followed in this study.

Fifteen disc-shaped samples of 15 mm diameter and 2 mm thickness (Fig. 30) were milled with the help of a CAD CAM device (Sirona inLab MC X5) (Fig. 7), from commercially available PEEK blanks (breCAM.BioHPP) (Fig.21). 800 grit sandpaper (Fig. 13) was used to polish samples and cleaned with distilled water (Fig 4) for 10 min in an ultrasonic cleaner (Fig. 10).

Group 1	CAD CAM Milled PEEK samples	15
Group 2	3D printed PEEK samples	15
Total		30

(b) Preparation of 3D printed PEEK sample (Group -B).

Fifteen disc-shaped samples of 15 mm diameter and 2 mm thickness were 3D printed with the help of fused filaments fabrication (FFF) 3D

printing device (Fig. 8), from commercially available PEEK filaments (Fig.22). 800 grit sandpaper was used to polish samples and cleaned with distilled water for 10 min in an ultrasonic cleaner.

(c) Surface treatment.

Concentrated 98 percent sulphuric acid was dispensed into a beaker with the help of a glass tube dropper. Following this, a cotton pellet held with a tweezer was dipped in concentrated 98 percent sulphuric acid and applied over the surface of PEEK samples for 60 seconds. After this, all samples were ultrasonically cleaned in a water bath (Fig. 10) and air-dried. In this manner, the surface of 30 PEEK samples from both groups was chemically treated with concentrated 98 percent sulphuric acid (Fig. 3).

(d) Composite application.

Uniformly one layer primer (Fig. 5) is applied on all the samples with an applicator tip and cured for 30 seconds in a laboratory light-curing unit (Fig. 17). after that composite (Fig 6) is applied on PEEK samples layer by layer and cured in laboratory light-curing unit for 3 min and 2 mm thickness of composite is checked with a vernier caliper device (safeseed). CAD CAM milled sample with composite application (Fig. 23), 3D printing sample with the composite application (Fig. 24).

(e) Determination of shear bond strength.

Composite bonded PEEK samples stabilized in universal Testing Machine (Fig. 20). A shear bond strength test was performed to evaluate the

bond strength between PEEK and the composite in both groups. For each group

The samples were secured in a horizontal position with the assistance of a metal fixture. A metal blade with an edge thickness of 0.5 mm was moved vertically at 90 Degrees, at a crosshead speed of 0.5 mm/min until the sample fractured(Fig.25).

The load was applied at the PEEK-composite interface. All tests were performed under uniform atmospheric conditions of $23.0 \pm 1^{\circ}\text{C}$ and $50\% \pm 1\%$ relative humidity. The values for shear bond strength were derived with the use of the following formula: Shear bond strength (MPa) = Force (N) / Area (mm²).

(f) Determination of the type of failure.

The debonded surface of all samples was examined under a Scanning electron microscope (Fig 9) under a magnitude of 40x. This examination was done to determine whether the type of fracture was cohesive, adhesive or mixed.

- (a) Adhesive (no composite remnants left on the PEEK surface,
- (b) Mixed (composite remnants partially left on PEEK with PEEK surface exposed),
- (c) Cohesive failure in PEEK.

COLOUR PLATES

Colour plate – 1

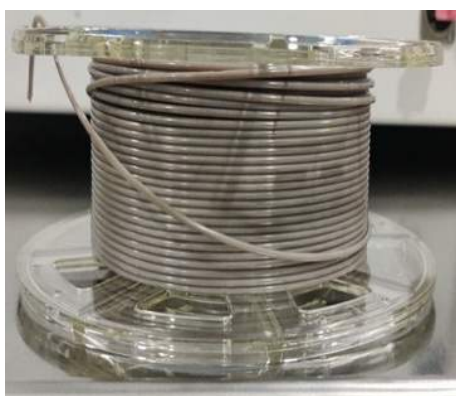
Fig. 1: CAD CAM milled Polyetheretherketone.



Manufacture – bredent breCAM.BioHPP

Batch number – 497897

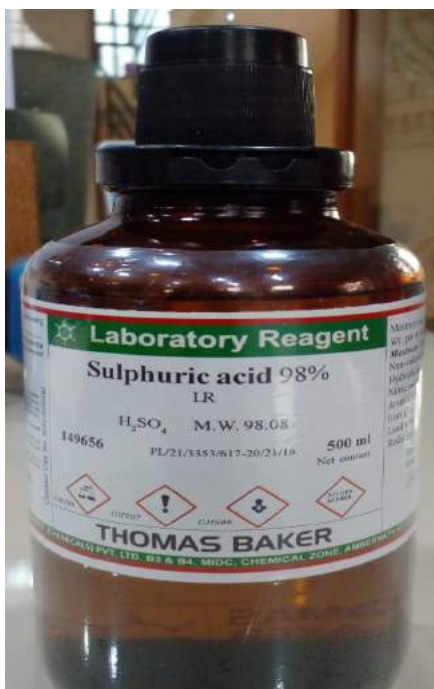
Fig. 2: 3D printed polyetheretherketone.



Manufacture – vestakeep PEEK

Batch number – 19082902

Fig. 3: 98 percent sulfuric acid.



Manufacture – Thomas Baker

Batch no- 149656

Fig. 4: Deionised water



Manufacture – Anand sales

Batch number – 1021

Fig. 5: Primer



Manufacture – GC metal primer Z

Batch number – 1708041

Fig. 6: Composite resin.



Manufacture – SHOFU ceramage

Batch number – 112033

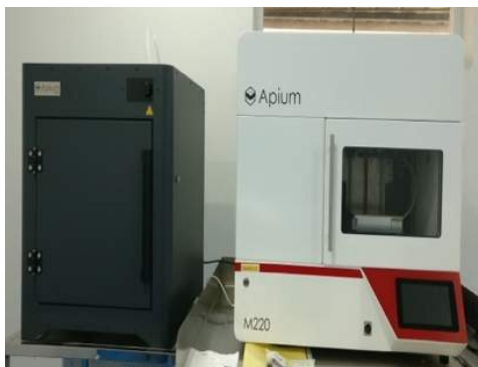
Colour plate 2

Fig. 7: CAD CAM unit.



Manufacture – Sirona inLab MC X5

Fig. 8: 3D Printing machine.



Manufacture – Apium M220

Fig. 9: Scanning electron microscope



Manufacture – Zigma

Fig. 10: Ultrasonic cleaning machine.



Manufacture – Geprüfte Sicherheit

Fig. 11: Beaker.



Manufacture – BFC

Fig. 12: Glass tube dropper.



Manufacture – Starlabs

Colour plate 3

Fig. 13: Sandpaper



Manufacture – 3M

Fig. 14: Cotton



Manufacture – Zephram

Fig. 15: Tweezer



Manufacture - waldent

Fig. 16: Applicator tip



Manufacture – GC

Fig. 17: Laboratory light-curing unit.



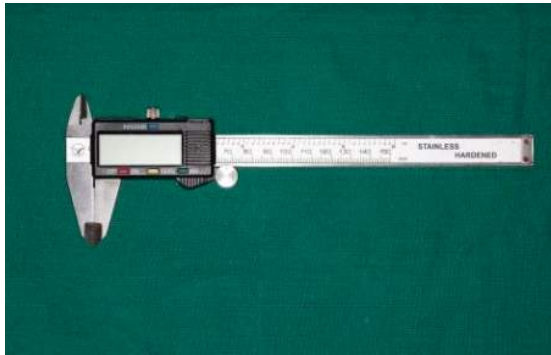
Manufacture- Solidlite V

Fig. 18: Composite instrument



Manufacture – GDC

Fig. 19: Vernier caliper



Manufacture – safeseed

Fig. 20: Universal testing machine.



Manufacture – Instron

Colour plate 4

Fig. 21: CAD CAM milled sample (Group 1)



Fig. 22: 3D printing sample (Group 2)

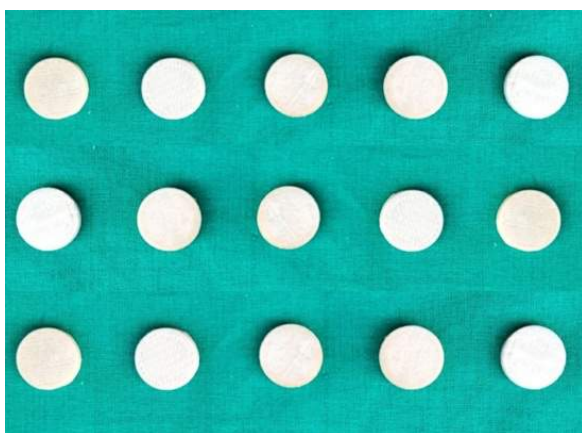


Fig. 23: CAD CAM milled sample with composite application

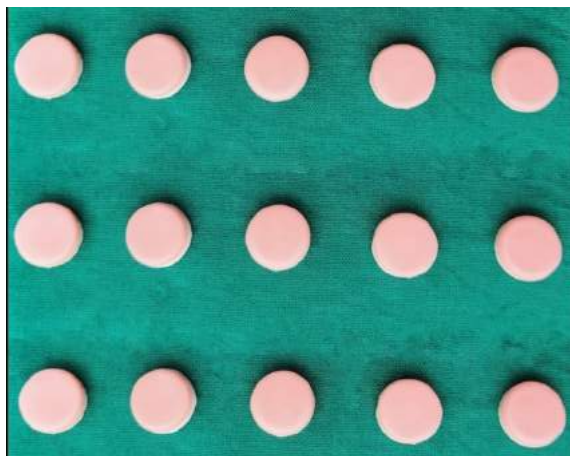


Fig. 24: 3D printing sample with composite application

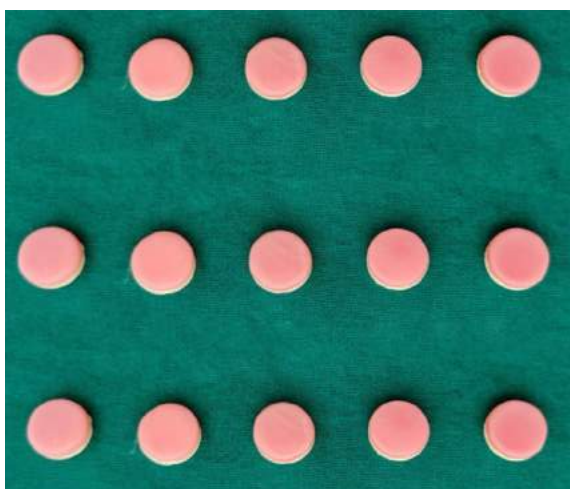


Fig. 25: Shear bond strength testing of the sample by universal testing machine

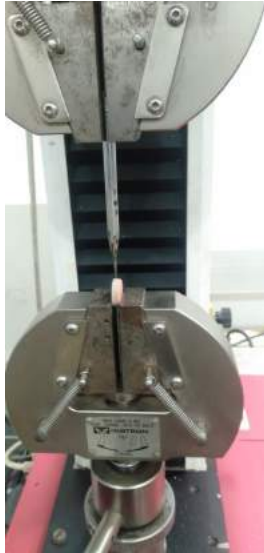


Fig. 26: SEM analysis of CAD CAM milled sample after etching with 98 percent sulfuric acid

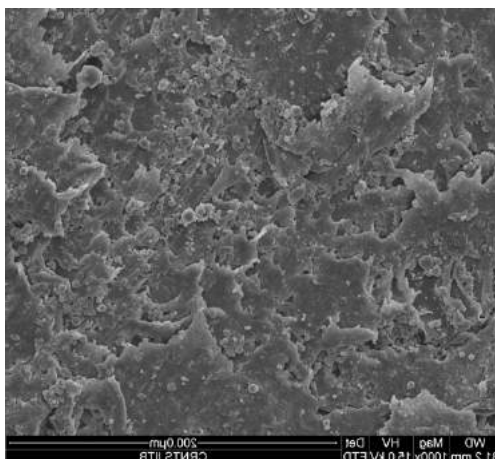


Fig. 27: SEM analysis of 3D printed sample after etching with 98 percent sulfuric acid

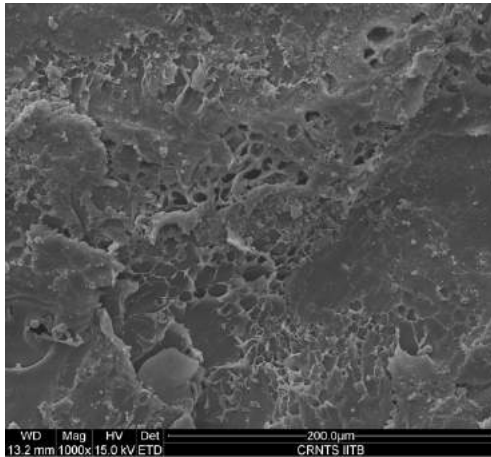


Fig. 28: SEM analysis of CAD CAM sample at bonding failure under 40X



Fig. 29: SEM analysis of 3D printed sample at bonding failure under 40X

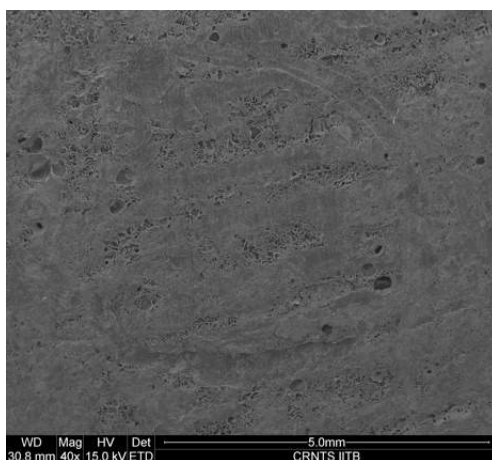
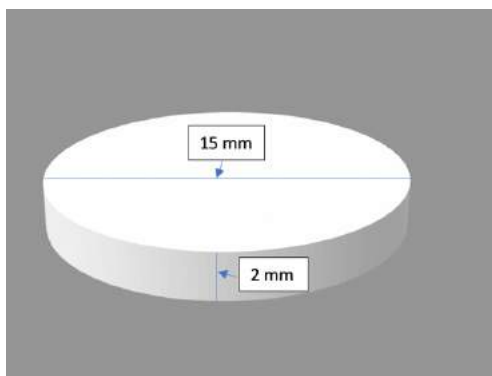


Fig. 30: sample dimension



RESULT

In this study, we have evaluated and compared shear bond strength of composite resin with PEEK fabricated by CAD CAM and 3D printing techniques.

Statistical Package for Social Software (SPSS) 22.0 (IBM Analytics, New York, U.S.A) was used to carry out the statistical analysis. The normality of the data was assessed using the Kolmogorov-Smirnov test. This Kolmogorov-Smirnov test allows you to make a determination as to whether a distribution - usually a sample distribution - matches the characteristics of a normal distribution. This is important to know if you intend to use a parametric statistical test to analyse data because these normally work on the assumption that data is normally distributed. The test statistic (D), provides a measurement of the divergence of your sample distribution from the normal distribution. The higher the value of D, the less probable it is that your data is normally distributed. The p-value quantifies this probability,

with a low probability indicating that your sample diverges from a normal distribution to an extent unlikely to arise merely by chance. Put simply, high D, low p, is evidence that your data is not normally distributed.

Statistical analysis was done by using tools of descriptive statistics such as Mean, and standard deviation (SD) for representing quantitative data. Probability $p < 0.05$, considered as significant as alpha error set at 5% with a confidence interval of 95% set in the study. The power of the study was set at 80% with a beta error set at 20%

Unpaired t-test was used to find significant intergroup differences between both groups i.e. shear bond strength of composite resin with PEEK fabricated by CAD CAM (Group A) and 3D printing techniques (Group B) respectively

1. Descriptive statistics of shear bond strength of composite resin with PEEK fabricated by CAD CAM (Group A) and 3D printing techniques (Group B) respectively.

Table 1 shows descriptive statistics of shear bond strength of composite resin with PEEK fabricated by CAD CAM (Group A) and 3D printing techniques (Group B) respectively. Mean shear bond strength of composite resin with PEEK fabricated by CAD CAM (Group A) was found to be 1.24 N. Standard deviation was found to be 0.14 N. Standard error was found to be 0.03 N. Minimum value of shear bond strength was found to be 0.93N and maximum shear bond strength was 1.46 N.

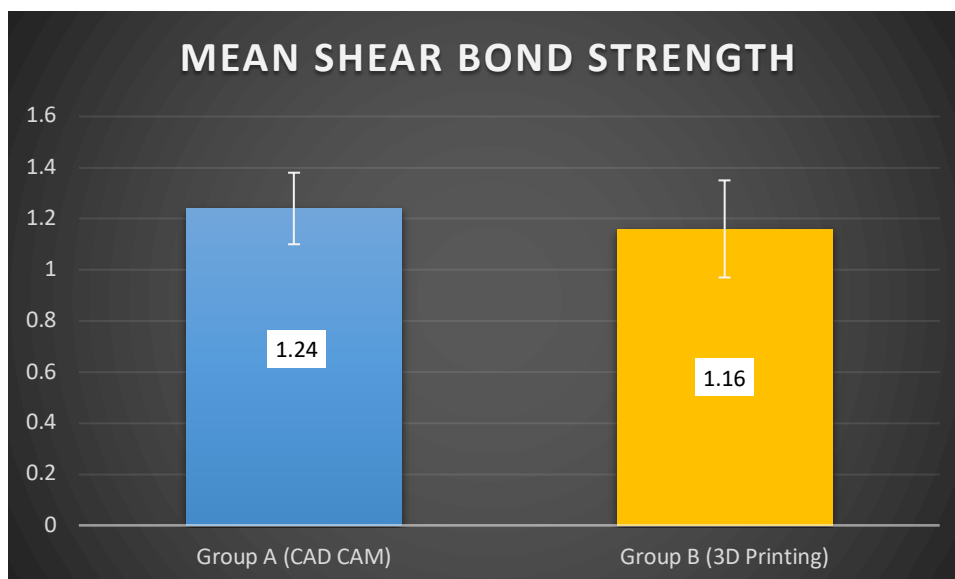
Mean shear bond strength of composite resin with PEEK fabricated by 3D printing (Group A) was found to be 1.16 N. Standard deviation was found to be 0.19N. The standard error was found to be 0.05N. The minimum value

of shear bond strength was found to be 0.79N and the maximum shear bond strength was 1.54 N.

Table 1: Descriptive statistics of shear bond strength of composite resin with PEEK fabricated by CAD CAM (Group A) and 3D printing techniques (Group B) respectively.

Shear bond strength (in MPa)	Group A (CAD CAM)	Group B (3D Printing)
Mean	1.24	1.16
Standard deviation (SD)	0.14	0.19
Standard error (SE)	0.03	0.05
Minimum (Min)	0.93	0.79
Maximum (Max)	1.46	1.54

Graph – 1 Comparative evaluation of mean shear bond strength of composite resin with PEEK fabricated by CAD CAM (Group A) and 3D printing techniques (Group B) respectively.



2. Comparative statistics of shear bond strength of composite resin with PEEK fabricated by CAD CAM (Group A) and 3D printing techniques (Group B) respectively.

Table 2 shows comparative statistics of shear bond strength of composite resin with PEEK fabricated by CAD CAM (Group A) and 3D printing techniques (Group B) respectively.

Mean shear bond strength of composite resin with PEEK fabricated by CAD CAM (Group A) was found to be 1.24 (0.14) N. Mean shear bond strength of composite resin with PEEK fabricated by 3D printing (Group A) was found to be 1.16(0.19)N (Graph-1).

On comparison of shear bond strength between composite resin with PEEK fabricated by CAD CAM (Group A) and 3D printing techniques (Group B) using unpaired t-test, Group A (CAD CAM) showed higher shear bond strength as compared to Group B (3D Printing) but the difference is not statistically significant ($p < 0.05$).

Table 2: Comparative statistics of shear bond strength of composite resin with PEEK fabricated by CAD CAM (Group A) and 3D printing techniques (Group B) respectively

	Mean	SD	Mean Difference ± S. E	Unpaired t test	p value, Significance
Group A (CAD CAM) (n=15)	1.24	0.14	0.08 ± 0.06	t = 1.246	p = 0.223 (No Statistical significant difference)
Group B (3D Printing) (n=15)	1.16	0.19			

***p < 0.05 – statistical significant difference**

3. Determination of the type of failure.

All samples from both groups showed the adhesive type of failure between PEEK and composite resin.

SEM analysis of CAD CAM sample at bonding failure under 40X (Fig. 28)

SEM analysis of 3D printing sample at bonding failure under 40X (Fig. 29)

4. Comparison of type of failure between CAD CAM PEEK samples and 3D printed PEEK samples.

All the samples showed an adhesive failure from both groups. But adhesive failure in CAD CAM milled samples was achieved at higher force with no statistically significant difference between the two groups.

DISCUSSION

PEEK is an aromatic and semicrystalline linear thermoplastic polymer. Its high strength, stiffness, toughness, and fatigue quality, as well as its outstanding thermomechanical characteristics, chemical stability, biological inertness, and stability with practically all organic and inorganic substances, make it an appealing material for use in dentistry. The fact that PEEK may be manufactured without the use of any additives makes it ideal for medical and dental applications where biocompatibility is a concern ^{11,14}. PEEK has showed a good prospect as a restorative material for metal-free and ceramic-free crowns and bridges. It has enough strength to sustain masticatory stresses in the posterior region. It also has no difficulties when it comes to reshaping because it can be adjusted or trimmed with a regular dental burs ⁷⁵. When utilised as a posterior crown or bridge, it also has the benefit that it does not abrade opposite dentition ⁷⁶.

Despite its numerous benefits, PEEK's application is restricted due to challenges in developing a strong and long-lasting adhesion to composite

resin materials due to its low surface energy and resistance to surface modification by chemical treatments^{37,38}. When the adhesive is well attached into the substrate and dissipates majority of the energy, a strong connection can be formed⁷⁷. Numerous material qualities, such as adhesive bonding capabilities, wettability, reflectivity, and coefficient of friction, all of which are greatly impacted by surface treatment and processing, play a role in the creation of an effective bond^{41,78}. PEEK's surface has been recommended to be treated with a range of surface treatments in order to promote its bonding with resin composites. Several investigations have showed that etching the PEEK surface with 98 percent sulfuric acid increased the shear bond strength between the PEEK and the composite^{7,41,43-45}.

PEEK can be fabricated with 3D printing techniques and CAD CAM techniques¹⁵. However, there is no literature present comparing shear bond strength between composite resin with PEEK fabricated by 3D printing and CAD CAM technique, when treated with 98 percent sulfuric acid for one minute hence the aim of this study was to comparatively evaluate of shear bond strength of composite resin with PEEK fabricated by CAD CAM and 3D printing techniques and SEM analysis at bond failure interface.

GROUPING OF SAMPLES

The PEEK samples (N = 30) were divided into two groups (n=15)

In accordance with the fabrication method they were subjected to:

- i. Group 1 – CAD CAM milled PEEK samples.
- ii. Group 2 – 3D Printed PEEK samples.

Most reported PEEK prostheses were fabricated with the CAD CAM milling technique because of their accuracy¹⁷⁻¹⁹, While the cost of excess

material and the time required to fabricate the prosthesis make it a costly and time-consuming procedure^{79–83}.

3D printing has already proven to be effective in the dentistry⁸⁴. The manufacture of complicated individual geometries, on-demand production of small quantities, and great economic efficiency are all advantages of 3D printing. On the downside, there are high process and material costs, a complex workflow with pre-determined anisotropic behaviour, and time-consuming postprocessing of the 3D printed object to consider²².

For processing polymers such as polyamide, polycarbonate, and acrylonitrile butadiene styrene, several printing processes are available, including stereolithography, selective laser sintering, inkjet 3D printing and fused filament fabrication layer manufacture (FFM). Thermoplastic elastomers, such as current high-performance polymers from the PAEK group, are ideal for fused filament production^{85,86}.

SURFACE TREATMENT

Etched with 98 percent sulfuric acid for one minute.

The use of concentrated sulphuric acid for the surface treatment of PEEK has been effectively described in several investigations^{7,41,43–45}. The corrosive acid causes microporosities in the PEEK matrix due to the sulfonation reaction, which dissolves the PEEK matrix. As a result, the veneering substance and the veneering material form a micromechanical connection^{43,46–50}.

Chajjareenont P et al investigated the effect of concentrated sulphuric acid etching of PEEK at various concentrations (70, 80, 85, 90, 98 percent)

for 60 seconds on bond strength with resin cement and found that sulphuric acid concentrations of 90 and 98 percent were the best for improving adhesion between PEEK and resin-based materials ⁵². Furthermore, Culhaoglu AK and colleagues found that increasing the etching duration affects the PEEK material's strength, and that over-etching has negative impacts on SBS ⁶⁶.

Therefore, in this study, etching of PEEK samples was done with concentrated 98 percent sulphuric acid for 60 seconds.

EVALUATION OF SHEAR BOND STRENGTH

Oral restorations are subjected to occlusal forces that include shear, tensile, compressive, and flexural stresses and are exposed to complicated and hostile environments. Several laboratory studies have been conducted in an attempt to imitate oral circumstances and predict clinical adhesive performance. Shear and tensile bond tests are the most often utilised tests. A shear bond strength test was performed on PEEK and composite resin in the current investigation. Micro and macro shear bond tests are two types of shear bond testing ^{87,88}.

Because micro shear bond tests are technique-dependent, a macro shear bond test was used in this work, which needs less equipment and specimen preparation and is also simple to execute ⁸⁹. In this method, the loading blade was placed as close as possible to the bonding interface and moved parallel to it at a constant crosshead speed of 0.5 mm/min, which causes a localized stress concentration at the point of loading. Shear bond strength was obtained by the formula:

$$\text{Shear bond strength (MPa)} = \text{fracture load (N)} / \text{bond surface area (mm}^2\text{)}$$

COMPARISON OF SHEAR BOND STRENGTH AMONG THE GROUPS

SBS values of the two groups are shown in Table 1 and Table 2. The mean shear bond strength of the Group 1 sample is 1.24 N and Group 2 is 1.16 N.

Group 1 - All the samples in Group 1 showed an adhesive type of failure. There was no cohesive failure and mixed failure. Group 1 sample showed the adhesive type of failure at a higher force compared to Group 2 samples.

Group 2 - All the samples in Group 2 showed an adhesive type of failure. There was no cohesive failure and mixed failure. Group 2 sample showed adhesive failure at a lower force compared to Group 1 samples.

In our study we have found that Group 1 samples showed adhesive failure between PEEK and composite at higher force compared to Group 2 samples this indicates that the bonding between PEEK and composite is more in Group 1 compared to Group 2 but with no statistical significant difference (Table – 2). Hence we can say that both the CAD CAM milled and 3D printed PEEK samples has a sufficient bonding with composite and can be used clinically. This study result was similar to a previous study done by **Jiaqi Z et. al.** in 2021⁷³.

Also study done by **Diogo D. et. al** in 2021 found no significant difference in shear bond strength between CAD CAM milled and 3D printed PEEK bonded to composite. In this study, the surface treatment was done with airborne-particle abrasion with 110-micrometer aluminum oxide particles⁷¹.

Liaw et. al. in 2021 studied 3D printed PEEK and found that in 3D printed PEEK, printing factors such as nozzle temperature, layer height, and wait time were shown to have a significant impact on interlayer bonding strength⁹⁰. This can be the reason behind the less shear bond strength in 3D printed PEEK compared to CAD CAM milled PEEK.

Valentam B et. al in 2013 studied PEEK and found that the artefacts such as cavities and air inclusions inside the 3D printed specimens may have compromised the components mechanically, resulting in reduced values of the 3D printed specimens. The presence of moisture in the filament is indicated by these artefacts⁹¹.

In our study, we have found that more and wider pores are seen in SEM analysis of 3D printed PEEK after etching (Fig. 27) and small pores are seen in milled PEEK after etching (Fig. 26).

Jiaqi Z et. al. in 2021 found that the ideal etching time for 3D printed PEEK is 30 seconds, while for CAD CAM milled PEEK is 60 seconds. The longer the etching period, the broader the etching pores for the primer to permeate and build a thicker mixing layer will be. It weakened PEEK's surface structure, lowering the material's surface strength. These findings suggested that a prolonged etching time might cause surface damage, hence the authors do not advise it^{52,73}. In our study we have done acid etching for 60 seconds that also might be the reason behind more porosity and less shear bond strength in the 3D printing group.

Yang X et. al. in 2018 investigated the mechanical properties of 3D printed PEEK and found that temperature control and cooling processes are other important considerations. The produced specimens were all taken from

the building platform immediately after the 3D printing procedure was completed and cooled down slowly at room temperature in the current study. This begs the question of how the mechanical characteristics of the component will react whether it is left in the heated building chamber for a lengthy period of time or is quickly cooled down. Because PAEK materials are low-crystallinity polymers, their mechanical characteristics are influenced by crystallinity⁹².

Due to a rapid temperature shift, a lesser degree of crystallisation and fractures may occur if cooling is done too quickly⁹³. However, Valentan et al. discovered that if a component is held at a high temperature in the construction chamber for 12 hours, its strength drops. As a result, it should be withdrawn from the printer as soon as the printing process is completed in order to attain the greatest mechanical qualities⁹¹. Hence we can say that the mechanical properties of 3D printed PEEK material depends on the temperature of the nozzle, time of removal of material from machine and contamination of moisture during printing of samples which ultimately have a slight effect on bonding with veneering material. In our study, we have found that CAD CAM milled group showed slightly higher shear bond strength compared to 3D printed group but no statistically significant difference was seen.

TYPE OF FAILURE AND SEM ANALYSIS

SEM analysis was used for microanalysis of the specimens by generating high-resolution images at high magnification.

Scanning electron microscopy images of the surface of each group is as shown for CAD CAM (Fig. 28) and for 3D printing (Fig. 29) under 40X. These images are clearly indicative of the adhesive failure of all the samples from both groups.

Bond quality should not be judged just on the basis of strength, since the manner of failure is also essential, as this information may be used to predict clinical performance. The de-bonded samples of both groups were analysed under the SEM 40x in this investigation. Adhesive failure, cohesive failure, and mixed failure were the three failure modes identified. De-bonding on the interface between PEEK and composite resin was defined as adhesive failure, whereas fractures within the composite resin were defined as cohesive failure. When a specimen failed due to a mixture of adhesive and cohesive failures, it was referred to as a mixed failure. Because no cohesive failure was discovered in this work, the shear bond strength values obtained can be considered as the representative of the composite- PEEK interfacial bond strength. The results revealed that 100 percent of the samples from Group 1 and group 2 showed the adhesive type of failure. (Fig 4, 5) Hence, it can be inferred that the fracture was initiated and propagated at the interface, which proves that the interface was the weakest area. This in turn can be correlated with the low SBS values of these groups. Similar results are described by Schmidlin et al and Caglar et al who reported the high adhesive failure mode in the weakest interface ^{41,94}.

In both Group interface was the weakest area but in Group 1 mean shear bond strength was **1.24N** and the mean shear bond strength in group 2 is **1.16N** which indicate that the group 1 sample shows higher shear bond

strength compared to Group 2 samples and adhesive failure at higher force seen in Group 1 compared to Group 2 but the bond strength was not statistically significant.

THE LIMITATIONS OF THE STUDY

1. The investigation was conducted in vitro.
2. The Shear Bond Strength test does not accurately reflect the mechanism of stress application in clinical practice.
3. Using such highly corrosive solutions (98 percent sulfuric acid) in a clinical setting is not practical due to the necessity for careful handling. It might also suggest that the etched PEEK surface has been destroyed. This might degrade the PEEK structure and result in bond weakening at the interfaces.

CLINICAL IMPLICATIONS

1. PEEK can be used in fixed dental prostheses and as a framework in removable dental prostheses.
2. The use of newer technologies CAD CAM and 3D printing for the fabrication of PEEK material based restorations increases its mechanical properties significantly if all other parameters are standardised.
3. The use of 3D printing technologies also reduces the time of fabrication and the cost of restoration.
4. 3D printed and CAD CAM milled PEEK material can be easily bonded to the composite resin after surface treatment with 98 percent sulfuric acid and can be used clinically.

5. The role of the clinician and laboratory personnel is equally important in relation to the longevity of the prosthesis in-service; owing to its technique sensitivity, one must be thorough with the knowledge of the materials in concern as well as newer digital technologies.
6. CAD CAM milled PEEK and 3D Printed PEEK can be used in clinical practice.

FURTHER SCOPE OF THE STUDY

1. There is a lack of data regarding the effect of different percentages of sulfuric acid on 3D printed PEEK, hence further research on its use is recommended.
2. The use of other surface treatment options available are recommended to use on 3D printed PEEK and further research in properties of 3D printed PEEK is needed.
3. Further study should be done on 3D printed PEEK on duration to keep it in heated building chamber and its effect on mechanical properties of PEEK.

SUMMARY

Polyetheretherketone is extensively used in dentistry because of its excellent properties such as better strength, stability with all materials, inertness and elastic modulus similar to the bone making it one of the best materials in dentistry.

The disadvantage of PEEK is its greyish white colour which makes its use in the aesthetic area limited. Composite veneering is done on a PEEK surface to give its natural tooth colour appearance. Most commonly 98 percent sulfuric acid treatment is done to increase the surface area of PEEK and composite bonding is done.

The shear bond strength between PEEK and composite plays a very important role in the survival of prostheses for a long time. PEEK can be fabricated with CAD CAM and 3D printing techniques.

This study was conducted to comparatively evaluate shear bond strength of composite resin with polyetheretherketone (PEEK) fabricated by CAD CAM and 3D printing techniques. A total of 30 samples was made. 15 samples made were made by CAD CAM as Group 1 and 15 samples by 3D

printing as Group 2. All samples were surface treated with 98 percent sulfuric acid. Composite veneering was done.

A universal testing machine was used to evaluate the shear bond strength of both groups. Type of failure evaluated with a scanning electron microscope. Results show that the mean shear bond strength of the Group 1 sample is more (**1.24 N**) compare to the shear bond strength of Group 2 samples (**1.16 N**). All samples showed the adhesive type of failure.

CONCLUSION

Within the limitations of this study the following conclusions were derived:

1. The shear bond strength of CAD CAM milled PEEK with composite resin were higher compared to the shear bond strength of 3D printed PEEK with composite resin but no statistically significant difference was seen.
2. All samples in Group 1 and Group 2 showed an adhesive failure when seen under a scanning electron microscope at 40X.
3. CAD CAM milled PEEK samples bonded with composite resin showed an adhesive failure at higher force compared to 3D printed PEEK samples bonded with the composite resin group.

4. As there is no statistically significant difference seen in shear bond strength between CAD CAM and 3D printed groups so both can be recommended for clinical use.

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TABLES AND GRAPHS

Table 1: Descriptive statistics of shear bond strength of composite resin with PEEK fabricated by CAD CAM (Group A) and 3D printing techniques (Group B) respectively.

Shear bond strength (in MPa)	Group A (CAD CAM)	Group B (3D Printing)
Mean	1.24	1.16
Standard deviation (SD)	0.14	0.19

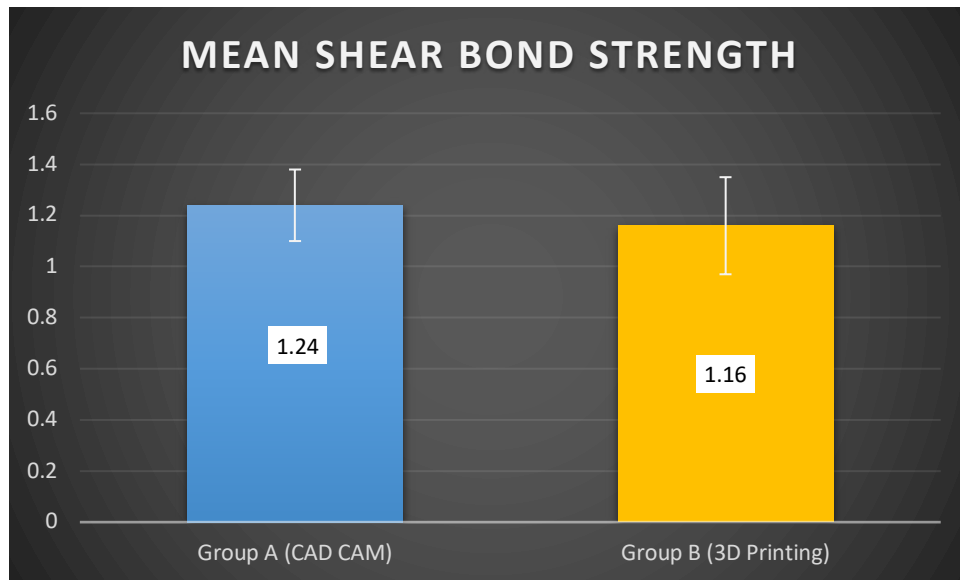
Standard error (SE)	0.03	0.05
Minimum (Min)	0.93	0.79
Maximum (Max)	1.46	1.54

Table 2: Comparative statistics of shear bond strength of composite resin with PEEK fabricated by CAD CAM (Group A) and 3D printing techniques (Group B) respectively

	Mean	SD	Mean Difference ± S. E	Unpaired t test	p value, Significance
Group A (CAD CAM) (n=15)	1.24	0.14	0.08 ± 0.06	t = 1.246	p = 0.223 (No Statistical significant difference)
Group B (3D Printing) (n=15)	1.16	0.19			

***p < 0.05 – statistical significant difference**

Graph – 1 Comparative evaluation of mean shear bond strength of composite resin with PEEK fabricated by CAD CAM (Group A) and 3D printing techniques (Group B) respectively



ANNEXURE

Master Chart

Group – A (shear bond strength of composite resin with PEEK fabricated by CAD CAM)

Sample number	Maximum Load (N)	Maximum Strain (percent)	Maximum shear bond strength (MPa)
1	258.73	6.78	1.46
2	244.09	10.42	1.38
3	178.28	18.27	1.01
4	250.83	6.64	1.42
5	200.17	16.09	1.13
6	196.81	15.21	1.31
7	241.69	12.71	1.16
8	262.81	7.01	1.28
9	174.17	14.61	1.19
10	212.51	11.61	1.19
11	229.65	12.49	0.93

12	265.23	8.43	1.31
13	183.87	11.89	1.36
14	221.48	16.29	1.27
15	252.18	12.81	1.34

Group – B (shear bond strength of composite resin with PEEK fabricated by 3D printing)

Sample number	Maximum Load (N)	Maximum Strain (percent)	Maximum shear bond strength (MPa)
1	229.56	33.9	1.3
2	186.75	17.93	1.06
3	272.77	30.29	1.54
4	251.67	31.32	1.42
5	139.92	18.49	0.79
6	142.43	21.57	0.91
7	189.29	16.39	1.01

8	227.61	28.03	1.12
9	156.21	24.61	1.08
10	186.37	28.38	1.21
11	264.34	31.71	1.34
12	251.18	25.03	1.31
13	221.69	24.61	1.26
14	198.51	19.01	1.17
15	134.80	16.29	1.02

