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YEDITEPE UNIVERSITY

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THE EFFECT OF DIFFERENT SURFACE TREATMENTS ON SHEAR BOND STRENGTH OF VENEERING COMPOSITE TO IMPLANT-BASED PEEK ABUTMENT

MASTER THESIS

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APPROVAL

This thesis has been deemed by the jury in accordance with the relevant articles of Yeditepe University Graduate Education and Examinations Regulation and has been approved by Administrative Board of Institute with decision dated 26.10.2018 and numbered 2018/18-01

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DECLARATION

I hereby declare that this thesis is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other degree except where due acknowledgment has been made in the text.

9.10.2018

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Nora Adem

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LIST OF SYMBOLS AND ABBREVIATIONS

FPD	Fixed Partial Denture
PEEK	Polyether-Ether-Ketone
DMSO	Dimethyl Sulfoxide
PEKEKK	Polyaryl Ether Ketone Ether Ketone Ketone
CFR	Carbon Fiber Reinforced
GFR	Glass Fiber Reinforced
HA	Hydroxy Apatite
Sr-HA	Strontium-containing Hydroxy Apatite
n-FA	Nano-Fluorine Apatite
n-HA	Nano-Hydroxy Apatite
n-Tio2	Nano-titanium dioxide
W/MK	Watts per kelvin-meter
J/Kg.K	Joule/kilogram. Kelvin
K	Kelvin
ANAB	Accelerated Neutral Atom Beam
UV	Ultra Violet
RDPs	Removable Dental Prosthesis
Bis-GMA	Bisphenol A-glycidyl Di Meth Acrylate

TEGDMA	Tri Ethilene Glycol Di Meth Acrylate
UDMA	Urethane Di Meth Acrylate
HEMA	Hydroxy Ethyl Meth Acrylate
W/cm2	Watt/square centimetre
CQ	Camphoro Quinone
MEHQ	Monomethyl Ether Hydro Quinone
AS	Ablation Threshold
GC	Gradia composite
MMA	Methyl Meth Acrylate
PETIA	Pentaerythritol Thiacrylate
MPa	Mega-Pascals
ANOVA test	Analysis of Variance
SD	Standard Deviation
AFM	Atomic Force Microscope
SBS	Shear Bond Strength
µSBS	Micro-Shear Bond Strength
TBS test	Tensile Bond Strength
CAD/CAM	Computer Aided Design / Computer Aided Manufacture
H_2O_4	Sulfuric Acid
µm	Micro meter

mm	millimetre
H_2O_2	Hydrogen Peroxide
θ	surface roughness

Adem, N. (2018). The Effect of Different Surface Treatments of Shear Bond Strength of Veneering Composite to Implant-Based PEEK Abutment. Yeditepe University, Institute of Health science, Department of prosthodontic, MSc thesis, Istanbul.

ABSTRACT

Aim: The aim of this study was to assess the effect of different surface treatment methods on the shear bond strength of the veneering composite to polyether-ether-ketone (PEEK) core material.

Materials and Methods: In this in-vitro study, 48 PEEK discs were fabricated, polished with silicon carbide abrasive paper and divided into four surface treatment groups (n=12), namely air-abrasion with 50μm alumina particles at 2MPa pressure for 10 seconds, air-abrasion plus sulfuric acid etching, 98% sulfuric acid etching for one minute and no treatment control group. Visio.link adhesive with GC Gradia veneering composite was applied on PEEK surfaces and light-cured. Shear bond strength was measured using a universal testing machine and the data were analyzed by one-way ANOVA and Tukey's test.

Results: The mean ± standard deviation (SD) values of the shear bond strength of the veneering composite to PEEK surfaces were 5.39±1.36 in the control group, 6.43±1.05 air-abrasion, 13.43±1.42 sulfuric acid etching, and11.72±1.69 MPa air-abrasion plus sulfuric acid etching. The shear bond strength averages of the sulfuric acid group were significantly higher than the air-abrasion, air-abrasion + acid etching, and control groups ($p < 0.05$). Shear bond strength averages of air-abrasion + acid etching group were significantly higher than air-abrasion and control groups ($p < 0.05$). There was no statistically significant difference between shear bond strength averages of air-abrasion and control groups ($p > 0.05$).

conclusion: Different surface treatments that were applied on PEEK framework were found to be effective on the bond strength between veneering composite and PEEK core material. Sulfuric acid etching group has the highest bonding strength and the control group has lowest bonding strength. The difference between the air-abrasion group and the control group was not statistically significant. The sulfuric acid etching and combination of air-abrasion and acid etching were suggested to be an acceptable surface treatment to improve adhesion between PEEK and the resin composite.

Keywords: Polyether-ether-ketone; PEEK; Shear Strength; Composite Resin.

Adem, N. (2018). Farklı yüzey işlemlerinin polyeter-eter-keton alt yapı ile veneer kompozit arasındaki bağlanma dayanımına etkisi. Yeditepe Ünıversitesi Sağlık Bilimleri Enstitüsü, Protez Bölümü, Master Tezi, istanbul.

ÖZET

Amaç: Bu çalışmanın amacı, farklı yüzey işlemlerine tabi tutulmuş polyeter-eter-keton (PEEK) alt yapı ile veneer kompozit arasındaki bağlanma dayanımının incelenmesidir.

Gereç ve Yöntem: Yapılan çalışmada, 48 adet PEEK alt yapı bloğu hazırlandı. Uygulanan yüzey işlemlerine göre örnekler hiçbir yüzey işlemine maruz bırakılmadan kontrol grubu, 50µm alumina parikülleri ile kumlama yapılan grup, %98 sülfürik asit ile asitleme yapılan grup ve hem kumlama hem asit ile pürüzlendirme yapılan grup olmak üzere 4 gruba ayrıldı (n=12). Yüzey işlemi uygulanan her PEEK yüzeyine Visio.link adeziv ve GC Gradia veneer kompozit uygulandı. Bağlanma dayanımı üniversal test cihazı kullanılarak ölçüldü ve verilerin analizi için One-way ANOVA ve Tukey’s test kullanıldı.

Bulgular: Polyeter-eter-keton (PEEK) yüzeyi ile veneer kompozitin ortalama bağlanma dayanımı değerleri kontrol grubunda 5.39±1.36 MPa, kumlamada 6.43±1.05 MPa, asit ile pürüzlendirmede 13.43±1.42 MPa ve kumlama ve asit ile pürüzlendirmede 11.72±1.69 MPa olarak tespit edilmiştir. Asit ile pürüzlendirme yapılan yüzeylerde ortalama bağlanma dayanımı diğer yüzeylere oranla en yüksek bulunmuştur ($p < 0.05$). Kumlama ve asit ile pürüzlendirme yapılan grupta, kumlama yapılan grup ve kontrol grubuna oranla istatistiksel olarak anlamlı fark elde edilmiştir ($p < 0.05$). Kumlama yapılan yüzeyler ile kontrol grubu yüzeyleri arasındaki fark anlamlı bulunmamıştır ($p > 0.05$).

Sonuç: Polyeter-eter-keton (PEEK) alt yapı materyaline uygulanan farklı yüzey işlemlerinin veneer kompozit ile PEEK arasındaki bağlanma dayanımına etkili olduğu bulunmuştur. Yüzey işlemlerinden sülfürik asit ile pürüzlendirme yapılan yüzeylere bağlanma dayınımı en yüksek tespit edilmiştir. En düşük bağlanma dayanımını ise kontrol grubu göstermiştir.

Anahtar Kelimelar: Polyeter-eter-ketone (PEEK), komozit, bağlanma dayınımı

1. BACKGROUND

Implant-supported fixed partial dentures (FPD) are routinely utilized as an alternative to conventional full coverage FPDs, especially for restoring missing or hopeless upper anterior teeth. Despite implant-supported restorations have an excellent success rate in prosthetic dentistry, implant-supported crowns are still considered to be an obvious challenge specifically in the esthetic region. (1)

Dental implant placement needs an appropriate healing period for the osseointegration process. During this period, an interim restoration is required for the attainment of the patient’s functional and esthetic needs. (2)

The anatomical provisional restoration is used for preservation of the soft tissue profile in the coronal part of the peri-implant mucosa, this includes the formation of a gingival contour in balance with the soft tissue of the adjacent dentition. In addition to that the provisionalization being in harmony with the adjacent teeth. (3)

After the insertion of implant with suitable three-dimensional position in relation with the adjacent teeth, the soft tissue from the gingival margin to the implant can be shaped using a temporary restoration following the placement of implant or at the time of second-stage surgery. (3)

Different approaches and several designs have been presented for preparation of implant-based provisional restorations. (1) These restorations could be constructed either at the dental laboratory or chairside. Regardless of the technique used to fabricate an interim restoration, the criteria that must be considered in the selection of the temporary prostheses include the esthetic demand, patient comfort, duration of the treatment, laboratory cost, durability, ease of removal, occlusal clearance, and ease of adjustment. Selection of the suitable provisionalization for single-implant treatment has an effect on the esthetics only during this stage of therapy. But there is no relation between the interim restoration type and the esthetic outcome of the final restoration. (4) (5)

The obvious advantages have been attributed to implant-based fixed provisional restorations include: (1) improved soft tissue contours in proper relation to emergence profile, (2) shaping of an interdental or interim plant papillae, (4) a guided healing that avoid the need for another soft tissue surgery, (5) stabilization of the prosthesis, and (6) provisionalization during the healing duration to produce an esthetically contoured restoration. (6)

The main disadvantage of the implant supported temporary restoration is the expensive cost of the laboratory-made temporary prostheses and time-consuming for its fabrication at chairside. (7)

Regarding abutment material, it has been informed that abutment material plays a significant role in the prevention of soft tissue recession. The most commonly used materials are: titanium, gold, base metals, aluminium oxide ceramics. (8) Provisional solid titanium abutment is frequently used as a temporary abutment. The major drawbacks of the titanium are the color. The application of opaque veneering composite is suggested to improve the color of the temporary restorations. Also, adjusting the titanium abutment in the dental clinic makes it difficult for a chair-side application. (8) (9)

As an alternative to titanium abutments, PEEK material has only lately been introduced into implant dentistry, and thanks to the fact that the PEEK abutments decrease stress shielding between the adjacent alveolar bone and dental implant. (9) Furthermore, the PEEK abutment is inexpensive, easily modified, and its color makes it easier to reach an acceptable provisional aesthetic outcome. (10)

Because PEEK provisional abutments exhibited less fracture resistance than titanium abutments, the use of PEEK abutments is recommended to support implant based provisional prosthesis for 1-3 months, in contrast to titanium temporary abutments, which are suitable for longer periods in the mouth (6-12 months). Moreover, prosthetic abutments made from this polymer can be expected to have good torque efficiency and it can be removed easily in case of fracture. (11) (12)

As the bonding of untreated PEEK and veneering composites is very weak, numerous surface pre-treatment techniques have been used to improve their bondability. These treatments involve sandblasting, using functional monomers, silicoating, acid etching, and physical treatments. Previous studies reported that the treatments have been effective at improving bond strength. (9) (11)

For successful temporization, dentists need to know the different materials and products available in the market and their properties. Elastic behaviour, strength, and bondability to coverage materials of implant-prosthetic abutment will affect their survival rate in the mouth. So, when it comes to select one abutment type or another, dentists must evaluate whether the provisionalization requires being of short, medium or long-term duration.

2. INTRODUCTION

2.1. Polyether-ether-ketone (PEEK)

2.1.1. What is PEEK?

High-performance polyether-ether-ketone (PEEK) is a new member of high-temperature semi-crystalline thermoplastic polymer, which is assigned to the main group of polyaryl-ether-ketones (PAEK). This methacrylate-free polymer is consisting of linear aromatic backbone molecular chain, interconnected by ketone and ether functional groups. The aromatic rings make PEEK unaffected to thermal, oxidative attacks, mechanical forces and high temperature, its notable mechanical properties and its biocompatibility and stability with organic and inorganic chemicals, make PEEK attractive for medicine and dentistry. (13)

2.1.2. Synthesis of PEEK

PEEK is synthesized by polycondensation of aromatic dihalides and biphenolate salts via nucleophilic exchange reaction where DMSO solution acts as a solvent and NaOH as a base. It belongs to an important high-performance engineering thermoplastics group, amorphous PEEK is formed in three grades of viscosity (high, medium and low) based on the same basic formula ($-C_6H_4-O-C_6H_4-C_6H_4$). (14)

2.1.3. Chemical Structure of PEEK

Polyether-ether-ketone (PEEK) is a semi-crystalline linear polycyclic aromatic thermoplastic with a unique combination of mechanical and physical characters. It is a member of the polyaryl-ether-ketone group, the linear homogenous aromatic backbone of PEEK adapts to a resonance stable arrangement, where the ether and ketone functional groups located at the opposite end of the benzene rings (Fig. 1). (13)

PEEK is classically 20-35% crystalline and therefore has a two-phase morphology made up of crystalline regions dispersed in amorphous regions. Nevertheless, a broader range of crystallinities (0-40%) can be reached, depending on the prior processing. (13) (15)

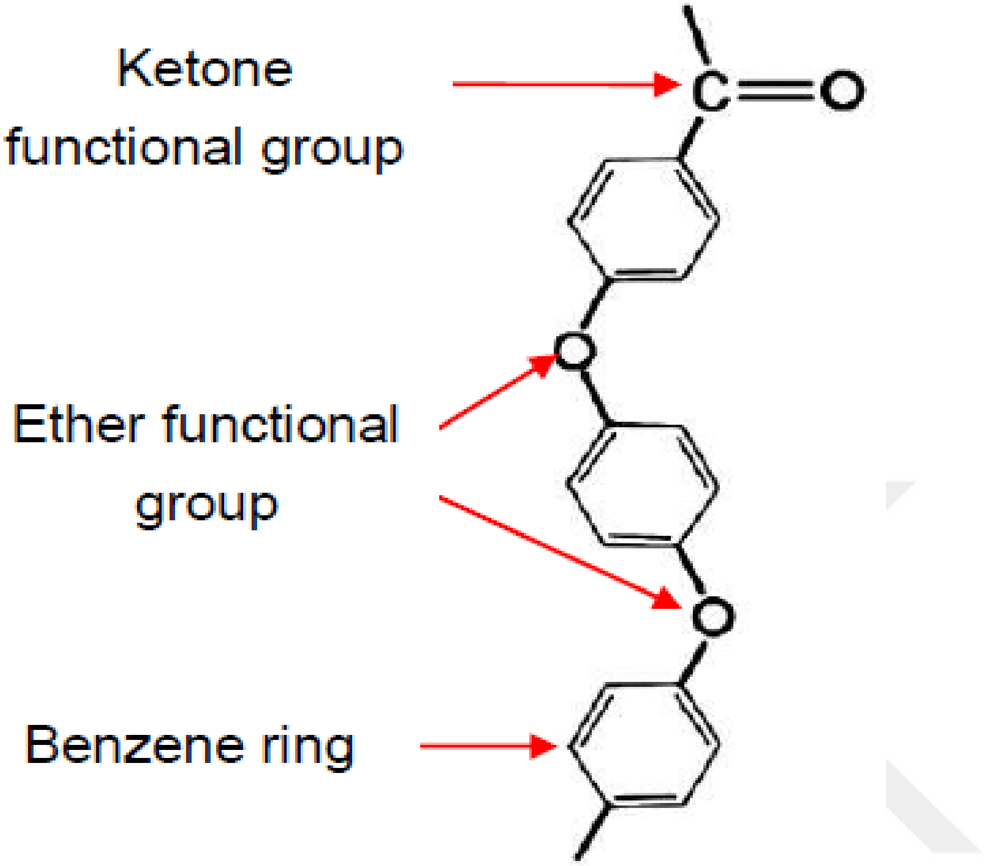

Figure 1; Chemical Formula of PEEK (13)

2.1.4. PEEK History

Two decades ago when researchers confirmed its biocompatibility, polyaryl-ether-ketone (PAEKs) has been increasingly utilized as an appropriate biomaterial for implantable medical devices. Two PAEK polymers used earlier for spinal implants and in orthopaedics, which involve polyaryl-ether-ketone-ether-ketone-ketone (PEKEKK) and polyether-ether-ketone (PEEK). (16)

PEEK was first presented into the market by ICI (Imperial Chemical Industries) in 1981, under the trade name of Victrex® PEEK for industrial application. At the end of the 1990s, PEEK had appeared as an important high-performance thermoplastic substitute for metal implant materials, particularly in orthopaedics and trauma. (13) (17)

For dental applications in 1992, PEEK was used first as an aesthetic abutment and later as implant. Since then many modifications in the composition have been done to change and improve the features of the implant. In April 1998, PEEK was first presented in the market as a biomaterial that could be used for long-term implant (Invibio Ltd., Thornton-Cleveleys, UK). Studies on PEEK biomaterial progressed and are expected to continue to progress in the future. (16-18)

2.1.5. Fabrication of PEEK

Regardless of PEEK being a high-performance thermoplastic, it can be easily fabricated using traditional methods for example; extrusion, injection moulding, etc. Extrusion followed by machining is the main technique for construction of PEEK-based implant. Also, PEEK can be milled by the CAD/CAM technique. (18)

2.1.6. PEEK Classification

The PEEK composites were divided into two groups according to the size of the incorporating bioactive materials:

1. Conventional PEEK composites such as carbon fibre-reinforced PEEK (CFR-PEEK), glass fiber-reinforced PEEK (GFR-PEEK), hydroxyapatite/PEEK (HA/PEEK), strontium-containing hydroxyapatite/PEEK (Sr-HA/PEEK).

2. Nano-sized PEEK composite include Nano-TiO2/PEEK (n-TiO2/PEEK), Nano-Fluorineapatite (n-FA/PEEK), Nano-hydroxyapatite/PEEK (n-HA/PEEK).

2.1.6.1. CFR-PEEK

Carbon fiber is a type of linear material with a special size effect from some microns to tens of microns. As a significant reinforcement material, carbon fibers have been broadly applied in many fields. PEEK has the advantages of adequate strength, low modulus of elasticity (close to the bone) and so on, which make it an excellent implant material considering human bone tissue repair. (19)

2.1.6.2. GFR-PEEK

Glass fiber has the advantages of high elastic modulus, high strength and constant expansion coefficient, good thermal stability. GFR-PEEK is consisting of 10% glass fibers and PEEK with diameters ranging from a few microns to tens microns and has an elastic modulus comparable to bone. Most of all, suitable environment for the production of osteocalcin can be established by application of GFR-PEEK. This can stimulate the bone formation process so that GFR-PEEK can create a good connection with the surrounding bone, which can progress the success rate of oral implants. (20)

2.1.6.3. HA/PEEK

Hydroxyapatite is a kind of inorganic substance, which is the main component of the inorganic substance in human bone tissue. The size of HA particle is 3～100 micron. It has been detected that with the increase of HA content, the rate of differentiation and proliferation of osteoblasts will increase consequently. It has demonstrated that when the volume portion of HA was 20%-30%, the elastic modulus of the PEEK is 5-7 Gpa, which is analogous to the human cortical bone. In addition, the HA/PEEK composite with a volume portion 20% that PEEK has good bioactivity and biocompatibility. (21)

2.1.6.4. Sr-HA/PEEK

Strontium is a bioactive element, which can support the adhesion and mineralization of osteoblasts, stimulate bone repair and decrease the risk of bone fracture. More apatites were produced on the Sr-HA/PEEK composite surface than HA/PEEK composite representing that Sr-HA/PEEK have improved bone-bonding ability than HA/PEEK composite. Therefore, the Sr-HA/PEEK composite not only improves the mechanical performances of PEEK but also have good biological properties. (22)

2.1.6.5. n-TiO_2/PEEK

TiO_2 has good bioactivity, biocompatibility, and hydrophilic nature. The preparation of n-TiO_2/PEEK composite by the integration of n-TiO_2 with PEEK can seriously improve the biological activity of PEEK. (23)

2.1.6.6. n-FA/PEEK

Polymer and metal implants are susceptible to bacterial infection during the implantation, finally leading to implant failure, which is one of the most serious complications of the implant procedure. Regarding the selection of bone implant materials, not only good mechanical performances and biocompatibility but also antibacterial properties of the material should be considered. The fluoride ions from the n-FA can inhibit the metabolism and enzyme activity of the bacteria, so n-FA/PEEK composite have antibacterial action. (24)

2.1.6.7. n-HA/PEEK

Because of the low physical bond energy between PEEK and HA, the mechanical behaviours of the HA/PEEK composites were declined compared with that of pure PEEK. However, when n-HA was incorporated into PEEK to form the n-HA/PEEK composite, the composite had high mechanical properties and excellent bioactivity. More significantly, no debonding happened between the PEEK matrix and the well dispersed HA nanoparticles. (25)

2.1.7. Properties of PEEK

2.1.7.1. Structural Properties

PEEK is white, radiolucent, rigid material that is chemically inert, non-toxic and has low plaque affinity. (11) (26) (27) It is insoluble at room temperature in all conventional substances apart from 98% sulfuric acid. Distinct chemical structure of PEEK exhibits stable chemical and physical characters. At temperatures between 390 and 420^{0}C, PEEK can be processed either by extrusion, injection molding or compression molding. However, PEEK remains in its ‘glassy’ state at body and room temperature, as its glass transition temperature is almost 143^{0}C. The crystallization peak is about 343^{0}C. (13)

PEEK shows a high resistance to electron and gamma beam radiation. Previous studies reported that the irradiation of PEEK resulted in a generation of free radicals with a lifetime less than 20 minutes, therefore PEEK is not estimated as a source of secondary radiation after gamma sterilization. PEEK has the low solubility and water absorption rates. (28) (29)

2.1.7.2. Chemical Stability

The structure of PEEK displays good chemical resistance, wherever the aryl-rings are interconnected by ketone and ether groups which positioned at opposite sides of the ring. The stable chemical building of PEEK makes it highly unreactive and intrinsically unaffected to thermal, chemical, and post-irradiation degradation. PEEK cannot be affected by exposure to organic and inorganic substances except concentrated sulfuric acid. Because of the inertness of its chemical structure, PEEK is defined as biocompatible material. (29) (30)

2.1.7.3. Thermal Stability

Thermal degradation of PEEK arises at temperatures between its glass transition temperature and melt transition temperature, yet temperature more than its processing temperature is required to form volatile degradation products. Based on previous studies reveal that Polyether-ether-ketone is stable against hydrolysis even at high temperatures (like sterilization processes). The thermal deterioration of PEEK biomaterials is not a concern throughout its clinical use in the human body (37ºC). (31)

2.1.7.4. Mechanical Properties

Regarding its mechanical properties, PEEK is a rigid material with Young’s (elastic) modulus (3-4 GPa), Flexural modulus (140-170 MPa), density (1300 kg/m3) and thermal conductivity (0.29 W/mK), The Young’s (elastic) modulus of PEEK is close to that of cortical bone, enamel, and dentine, suggesting the chance for a more homogenous stress distribution to the supporting tissues. (25) (32) (33)

Because of its unique characteristics such as high-temperature performance, wear properties, superior strength, hydrolytic stability and outstanding toughness, good creep-resistance, and corrosion-resistance, polyether-ether-ketone (PEEK) is nowadays considered as one of the most efficient thermoplastics. The mechanical properties of

PEEK are normally associated with molecular weight besides to the orientation and size of the crystalline areas. Overall, with increasing crystallinity, both of the modulus and yield strength of PEEK increase, while the molecular weight has no obvious effect on these properties. In contrast, the toughness is affected by both molecular weight and crystallinity. Toughness increases by increasing molecular weight and decreases with increasing crystallinity. (18) (34)

Reinforcing it with carbon fibers can modify its mechanical behaviours. The carbon reinforced PEEK (CFR-PEEK) was the first PEEK composite used for biomedical applications. With increasing of the carbon fibers ratio in PEEK, the tensile strength and the elastic modulus increases. Simultaneously the tensile elongation performance of the material declines, subsequently the material becomes stronger and less elastic. For medical uses, the modulus of elasticity of materials must be near to that of human cortical bone (18 GPa). Table 1 summarizes the general properties of PEEK. (35)

Table 1; General properties of PEEK (35)

Mechanical properties		Thermal properties	
Elastic Modulus (GPa)	3.6	Thermal conductivity (W/Mk)	O.29
Poisson’s ratio	0.38	Specific Heat (J/kgK)	2180
Density (Kg/m3)	1300	Glass Transition temperature (K)	416
Yield stress (MPa)	107	Melt transition temperature (K)	616

2.1.7.5. Biocompatibility of PEEK

Biocompatibility has been known as ‘the ability of a material to react with a suitable host response in a particular application. (36) It is a basic critical concern in materials selection for clinical applications. The biocompatibility includes toxicity and cytotoxicity, genotoxicity, radiolucency.

A- Toxicity and Cytotoxicity

PEEK toxicity has been assessed in a number of published studies. The polymers' testing has been undertaken according to ISO 10993 to demonstrate its toxicological safety. (36) (37)

The cytotoxicity and the tendency to release substances in the cytotoxic environment by steam, and gamma irradiation sterilization cycles, using worst-case conditions have been examined. Extensive chemical analysis of sterilized and non-sterilised specimens has been undertaken according to ISO 10993-18. The result from these studies confirmed that there is no release of substances in cytotoxic concentrations from either sterilized or non-sterilised PEEK. (38) (39)

B- Genotoxicity

Sensitization and gene toxicity test methods were selected to examine PEEK polymer for mutagenicity. These tests established that PEEK does not result in chromosome aberrations and it was not mutagenic. (40)

C- Radiolucency

PEEK polymer is generally radiolucent and compatible to imaging procedures such as X-ray, MRI, and CT. PEEK dental polymer permits clinical diagnosis without the need for its removal and replacement. PEEK is available in natural and white colour for improved aesthetics. (41)

2.1.7.6. Bioactivity of PEEK

A material is classified as bioactive if it has a definite biological response to the interface of the element, which results in the creation of a bond between the substance and the tissue. A critical problem with most thermoplastic polymers, such as PEEK, is their surface characteristics, including low-surface energy, chemical composition. This hydrophobic property neither permits protein absorption nor enhances cell adhesion. The absence of the biological medium response with PEEK makes it be labeled as bioinert. (35) (42) (43)

The bioinert performances of PEEK in the orthopedic region mean the creation of soft tissues on the surface of PEEK implant in place of bone formation, however, one of the most common applications of PEEK is for the orthopedic region. The responses of the adjacent tissue to PEEK implant can be enhanced, which could extend its uses in the medical area, where direct bone contact is critical. Many approaches have been planned to progress the bioactivity of PEEK, and these approaches classified into two categories: incorporating of a bioactive material with PEEK and through surface modification. (23) (44-46)

2.1.8. Improvement of PEEK Bioactivity

Different modification techniques have been applied to change the bioactivity of PEEK for long-term implantation, but do not change the bulk characteristic of the material. These techniques can be classified into two groups: direct surface modification and deposition. (46) Figure 2 illustrates the general classification of the existing techniques for improvement of the PEEK bioactivity.

2.1.8.1 Direct Surface Modification

Direct surface modification approaches are methods where the surface properties of the materials are altered without depositing any layer of other substance on the surface. These methods involve the following:

A- Wet Chemical Treatment

This is a technique that depends on altering the surface chemistry of PEEK and modifies the bioactivity of the surface.

Many studies stated that pre-osteoblast functions including osteogenic differentiation, proliferation, and initial cell adhesion on the PEEK surface could be improved by wet chemical treatment or sulfonation treatment. (47) (48)

B- Physical Surface Treatment

I. Plasma Surface Treatment

Plasma is commonly defined as the fourth state of matter in which the electrons are separated from their atoms by the ionization of gases. There are two kinds of plasma, cold plasma, and hot plasma. Plasma treatment of PEEK displayed a modification in its chemical and physical surface properties without altering the mechanical, electrical and optical properties of the material.

Previous studies examined the differentiation and proliferation of osteoblasts and fibroblasts on plasma-treated PEEK surface. They reported that the osteogenic proliferation on treated PEEK surfaces was improved. (49) (50)

II. Laser Surface Modification

the laser is known as a high-energy photon origin which is able to change the wettability and roughness of the polymer surface. Laser treatments are widely used because of their high-operating speed, low cost, high resolution, and lasers do not affect the bulk properties of PEEK implant. For these factors, lasers become very attractive to researchers in order to progress the surface properties of the implants. (51)

III. Accelerated Neutral Atom Beam (ANAB) Surface Treatment

The ANAB is a method that can increase the bioactivity of PEEK surface without the incorporation of other bioactive elements and without alteration of surface chemistry. In vitro trials established that the treatment of PEEK surface by ANAB enhance the growth of human osteoblast cells and progress the bone-implant integrity compared with untreated PEEK. (52)

IV. Ultraviolet/ Ozone Surface Treatment

The exposure of the polymer to sunlight displayed degradation due to the chemical reaction stimulation by photon-activation cross-linking and short wavelengths of ultraviolet (UV) of sunlight or destruction of the polymer. In the presence of oxygen, UV treatment technique termed as photooxidation, could modify surface properties of PEEK from inert to bioactive material and improve the bioactivity. (53)

2.1.8.2. Deposition Techniques

Numerous methods are available for depositing bioactive elements on PEEK surface such as vacuum deposition, plasma spraying, dip coating, and immersion in SBF technique. Hydroxyapatite is a vital material that has been broadly applied for coating of biomaterials. (54)

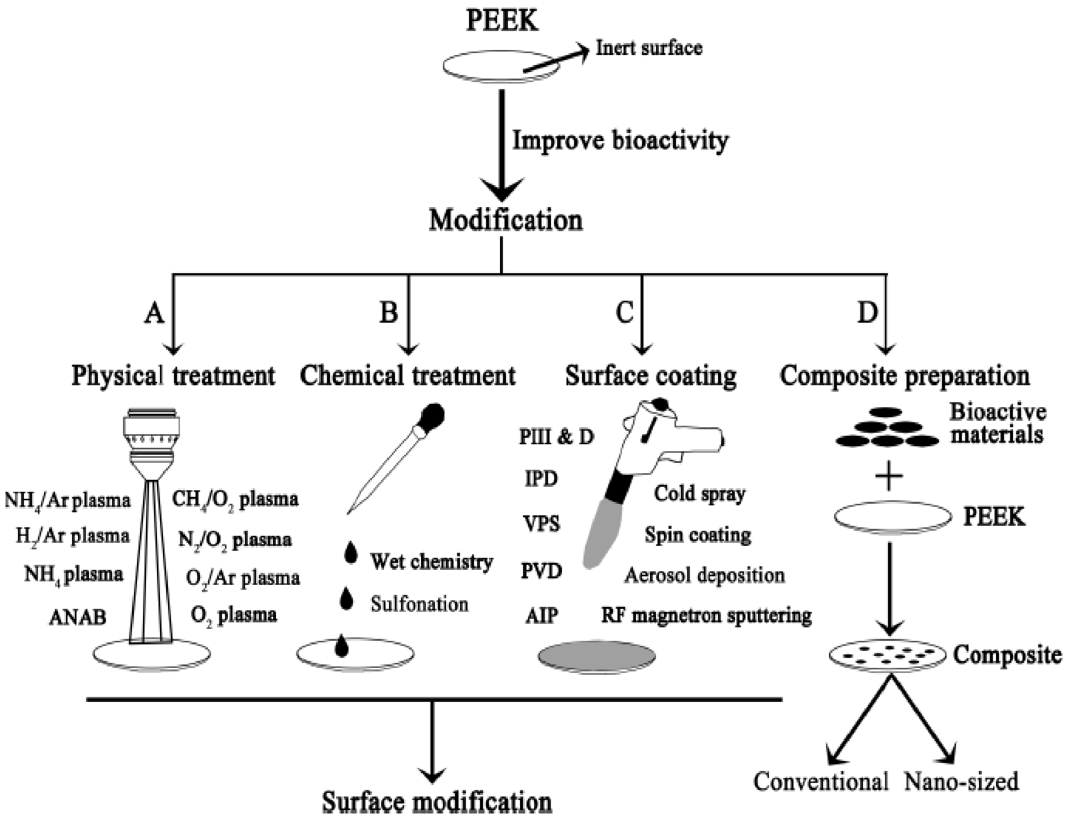

FIGURE 1; Current Methods to Increase the Bioactivity of PEEK

2.1.9. Industrial Application of PEEK

PEEK is extremely attractive for industrial applications, including aerospace, electronics, automobile industry because of its excellent mechanical properties, for example, thermal stability, solvent resistance, good wear resistance, high fatigue resistance, and appropriate electrical insulation. Hence, their field of application extends to medical apparatus. (13) (55)

2.1.10. Medical Application of PEEK

2.1.10.1. PEEK Implants for Cranial and Face Reconstruction

The complexity of cranial and maxillofacial anatomy requires reconstruction of the orbital walls and forehead with typical symmetry and accurate functional, anatomical and aesthetic outcomes. Therefore, biocompatible materials such as methyl methacrylate or titanium mesh, are inaccurate to restore the orbital wall. Furthermore, these materials are hard to adjust and shape during the restoration of fronto-orbito-temporal area. Bone resorption likewise frequently occurs. (56)

In the recent years, PEEK was presented as a biomaterial for cranial and maxillo-facial reconstruction. This was possible with CAD/CAM technologies (the computer-aided design and computer-aided manufacturing) which permit construction of an accurate implant with complex morphology. (56) (57)

2.1.10.2. PEEK in Orthopedic Surgery

A. PEEK Implant for Femoral Bond Reconstruction and Hip Replacement

Because of their quality, both CFR-PEEK and pure PEEK are applied in many orthopedic applications, involving total hip replacement, the restoration of the femoral component, and hip construction. (58)

B. Orthopedic Devices from CFR-PEEK

New advances in fiber reinforced composite processing (with a PEEK-OPTIMATM) offer new application options. The studies have continued on the growth of fiber oriented PEEK fracture fixation plates, besides extruded PEEK screws and pins.

Bone pins and screws made up of PEEK materials exhibit mechanical qualities that are comparable to titanium alloys. (13)

2.1.10.3. PEEK implant in spine surgery

Cervical disc surgery is one of the most common operations in the daily neurosurgical field. Historical cervical fusion surgery with autologous bone graft has some difficulties, therefore, new cage biomaterials were recognized. PEEK materials presented as interspinous system were applied to stabilize the anterior column of the cervical spine or lumbar and enable non-rigid fusion as a therapy for low- back pain due to spinal instability and/or degenerative disc disease. (13) (59)

2.1.10.4. PEEK Implant in Cardiac Surgery

In current years, PEEK polymer was used in cardiovascular applications. Various types of materials have been applied in the operation of heart valve prostheses. In 1994, Leat et al. (60) considered a new design for the heart valves formed by polyether-ether-ketone (PEEK).

2.1.11. Dental Application of PEEK

Polyether-ether-ketone (PEEK) is a thermoplastic material that has attracted progress in medicine and is now gaining attention in the dental ground. (26)

Some superior biological and physical features of PEEK are compatible with the prosthetic requirement in the dental field. Enhanced properties are reached when filler ingredients such as silicate or glass are integrated. PEEK can be moulded in thermopressing processes (e.g. BioHPP, Bredent, G) or processed via CAD/CAM system (e.g. Juvora dental disc, Juvora, UK). Standard burs for dental resin materials can be used for final adjustments. (61)

2.1.11.1. PEEK for Tooth Replacement

Some PEEK polymers have biomechanical properties close to the human cortical bone and this can reduce the bone resorption and improve the implant osseointegration. Lately, different companies were offered a new design of PEEK implants for tooth replacement. (62)

2.1.11.2. Implant Abutment

Because of its acceptable biocompatibility, PEEK has been broadly used in the fabrication of implant provisional abutments. A randomized, controlled clinical trial (RCT) directed by Schwitalla A et al. (62) proposed that there is no notable difference in the soft tissue inflammation and bone resorption around metal and PEEK abutment. Additionally, there is a close match between the modulus of elasticity of PEEK and bone which improve bone remodeling and decrease the stress shielding effects. From now, PEEK could establish to be a practical substitute to titanium in preparing implant abutments. (9) (62)

Additional studies and clinical researches should be undertaken with the purpose to improve the PEEK qualities and enable its use as a permanent abutment material with dental implants. (9)

2.1.11.3. PEEK as a Removable Prosthesis Material

Conventional removable dental prostheses (RDPs) with chrome cobalt framework and clasps have been a cost-effective and probable treatment choice for the restoration of partially edentulous patients.

The metallic framework has many drawbacks such as the undesirable display of metal clasps, the increased weight of the prosthesis; taste of metal, and allergic reactions to metallic components. Because of these disadvantages, a number of thermoplastic materials such as nylon and acetal resins have been introduced in clinical practice. (26)

A modified PEEK material with 20% ceramic fillers can be applied as an alternative to metal. The advantages of PEEK material for removable prosthesis are owing to its high strength, white color, and biocompatibility. Therefore, it can be used to construct metal-free components that are esthetically more acceptable. (26)

The elasticity of PEEK material has a modulus of elasticity of 4GPa, which is near to the human bone and dentine. This will decrease the distal torque and the stress on the abutments in cases of distal extension. Therefore, it has been expected that dentures manufactured from this polymer will routinely be applied in near future. (13)

2.1.11.4. In the Fabrication of a Maxillary Obturator Prosthesis

In comparison to conventional methods and materials, the use of PEEK polymer largely simplifies the construction of the antral part of the palatal appliance and produce a lighter palatal obturator. The PEEK is biocompatible with adjacent mucous tissues, retention, the patient pleased with esthetics result and it is more comfortable in comparison to the earlier prosthesis.

The absence of a chemical adhesion between the PEEK and acrylic resin material can be resolved by making a groove through the PEEK to create mechanical retention with acrylic resin and by using silica microabrasion to produce a mechanical-chemical bond. Hence, fabrication of obturator prosthesis with PEEK-Optima is a suitable substitute for conventional materials and techniques. (63)

2.1.11.5. PEEK Crowns

Previous studies recommended that PEEK material can be applied as a coping material. As the mechanical characteristics of PEEK are near to those of dental tissue (enamel and dentin), PEEK might have an advantage in comparison to ceramic and alloy restorations. (64) But, the grayish color and opacity of PEEK restrict its uses in full-coverage restoration. Consequently, for good appearance, the surface of PEEK restorations has to be veneered by other material such as resin composites or lithium disilicate. (61)

However, the bond strength of the PEEK with composite veneering material is low owing to low surface energy and inert chemical structure of the polymer, it is difficult to modify its surface in order to increase the bond strength and adhesion with composites. Moreover, composite as a veneering material of the PEEK may destroy with time. So, if the PEEK frame remains intact, it is essential to repair the coating material. These are extra costs to the patient. (64)

Unfortunately, there was not enough clinical trial made to demonstrate PEEK’s advantages over other materials. There is still no adequate data stated about its complications. (9)

2.1.11.6. PEEK CAD-CAM Milled Fixed Partial Dentures

PEEK is a respectable material for constructing fixed and removable prostheses with CAD-CAM because it can be milled easily, its mechanical features are unaffected by the milling procedure, and its fracture resistance is superior to that of other materials used for CAD-CAM restorations. (61)

CAD-CAM milled PEEK fixed dentures have a fracture resistance which is higher than those of alumina (851N), zirconia (981-1331N), lithium disilicate glass-ceramic (950N). The abrasive performance of PEEK is excellent. In spite of significantly low modulus of elasticity and strength, PEEK has an abrasive resistance that is competitive with metallic materials. But, there is no clinical research has tried to make a comparison in term of the abrasion resulted from PEEK crown on the tooth to that resulted from other materials such as alloy and ceramic. (65) (66)

In view of good mechanical properties, abrasion resistance and aforementioned suitable adhesion to composite and tooth structures, a fixed partial prosthesis made of PEEK are expecting to have an acceptable survival rate. (61)

Additional study and clinical trials are considered to recognize PEEK material and suitable modifications for more dental applications. (66)

2.1.11.7. PEEK for Endocrown Restorations

Endocrowns are commonly used in patients with endodontically treated molar with short roots, short clinical crown, and weak axial walls. But over the years it has been detected to have significantly superior fracture strength than classical crowns restored with a custom-made post and core or with a resin core and a fiber post. But materials with high stiffness such as alumina can produce excessive loading of the abutment teeth and the restoration. PEEK and composite resins Materials have been established to decrease occlusal stress by acting as stress breakers because of their lower modulus of elasticity. (67)

The only disadvantage of PEEK is that the detection of secondary caries on the x-ray would be a matter of concern as PEEK is a radiolucent material. It can be overcome by periodical examination for recurrent caries. (67)

2.1.12. PEEK Versus Titanium

Although implants based on titanium and titanium alloys are well evidence-based, it was established that the use of titanium is correlated with a range of drawbacks, such as hypersensitivity and allergy to metal, stress concentration on surrounding bone because of the remarkable variance in the modulus of elasticity of a titanium implant and bone, consequently this may result in stress concentration at the implant-bone interface during force transfer, probably causing peri-implant bone resorption. As well, metallic appearance may also cause aesthetic problems due to its lack of light transmission. This can create a dark shadow of the peri-implant tissue in cases of thin mucosal tissue and/or gingival recession around a metallic implant, subsequently, lead to unacceptable aesthetics especially in case of high smile line. Furthermore, most of the patients prefer dental restorations of entirely metal-free materials. (11)

The major advantage of PEEK material over the metallic one remains its Young (elastic) modulus. The titanium and its alloys have elastic moduli which is significantly high compared to that of the bone, this is could result in severe stress-concentration and failure, the elastic moduli of carbon-reinforced PEEK and PEEK is close to those of dentin and bone, so the PEEK could display lesser stress concentration in comparison to titanium and its alloys which used as implant materials. In addition to that, the PEEK material has tensile properties that are also similar to those of enamel, dentin and cortical bone making it an appropriate restorative material as concerns the mechanical properties. (11) (13) (61)

However, titanium implant distributes the load in a more homogenous way in relation to the CFR-PEEK implant because of the smaller deformation of titanium and its alloys. The CFR-PEEK implant did not show any advantages in comparison to the titanium implant concerning load distribution to the peri-implant bone. (32)

2.2. Composite Resin

A “composite”, in material sciences, means that two dissimilar materials are mixed together to produce a new material. (68)

Composite-based resin materials are a physical mixture of substances that is known as a “three-dimensional integration minimum of two dissimilar materials with a separate border separating the ingredients". Dental composite is basically made of three materials which are chemically different: i) the organic phase (organic matrix), ii) the filler or disperse phase (inorganic matrix), and iii) coupling agent (organosilane) to bond the organic resin with the filler. (68)

2.2.1 History

Early desire and demand for tooth coloured restorations were focused on silicate cement until direct filling methyl methacrylate was developed in Germany by Kulzer GmbH in 1950. This acrylic-based material permits the production of a dental restoration in a desired contour and shape. Each of these original materials, even though realize the “aesthetic need”, had characteristic limitations, namely solubility problem for the cement and extreme polymerization shrinkage (and thus micro-leakage) for the methacrylate-based acrylic resins. (69)

In 1962, Bowen introduced the Bis-GMA based composite to be the first actually successful dental resin composite with a view to decreasing the problems of the acrylic resins and silicate cement in a challenge to improving the structural properties of acrylic resins. This hydrophobic dimethacrylate monomer (Bis-GMA*)* establishes the basis of current composites due to its limited shrinkage and fracture resistance. Bowen’s resin is highly viscose and consequently restricted the ratio of filler particles that could be combined. Subsequent trials considered triethilene glycol dimethacrylate (TEGDMA) as a diluent or viscosity controller to reduce viscosity. This monomer incorporation has become one of the most broadly applied matrix monomer mixtures for dental composite so far. (70) (71)

The photo-polymerized resin composite system developed in 1970 by the application of ultraviolet light to initiate the polymerization reaction. Such technique allowed probable esthetic restorations with the ability to accelerate the polymerization of the composite, five years later, composite resin curing was achieved by visible light stimulation of camphoroquinone, which lead to enhanced setting time and colour stability while avoiding the iatrogenic side-effects to the eye which associated with ultraviolet radiation. (72)

First presented at the beginning of 1970s, composite resin material development concentrated mainly on two aspects: filler loading and curing technique. A variety of fillers, differing in size and type, have been combined to display an extensive range of composite resin with attention to strength and ease of polishability. Filler elements decrease the ratio of polymerizable organic matrix needed; which is in sequence lead to reduce polymerization shrinkage. By means of ceramic and glass fillers usage, the resin composites have a total coefficient of thermal expansion that is lower than that of the entirely organic composition. (73)

2.2.2. The Composition of Composite Resins

According to Lutz et al, composite resins are very complex mixtures made up of four major components, namely, an organic matrix, inorganic filler, a coupling agent that enhances filler/resin interaction and the initiator system. (74)

2.2.2.1. Organic Polymer Resin Matrix

The organic matrix forms the body of the resin composite and in most commercially available composite resins it comprises of a mixture of several polymerizable monomers for example; Bisphenol A-glycidyl dimethacrylate (Bis-GMA) and/or urethane dimethacrylate (UDMA). In addition to polymerization initiator and diluent monomers and activator systems. (75)

Bisphenol-A glycidyl dimethacrylate (Bis-GMA) is a high molecular weight monomer with two methacrylate groups available for cross-linking polymerization (Fig. 3). It is highly viscous; therefore, once activated, the chemical reaction of these dimethacrylate monomers leads to hardening of the dental composite due to the development of covalent bonds, subsequently reaching the gel point of photopolymerization. Also, the high viscosity limits the filler ratio of dental composites.

In order to reduce this viscosity monomers with low molecular weight are added to the organic matrix; the most broadly incorporated diluent monomers are 2-hydroxyethylmethacryalte (HEMA) and triethylene glycol dimethacrylate (TEGDMA), Composite production with high TEGDMA ratio usually allow increased filler concentrations but also display higher polymerization shrinkage show the chemical structure of TEGDMA. (Fig. 4) (75) (76)

Urethane dimethacrylate (UDMA) is used either in combination with or as a substitute to, Bis-GMA monomer. (Fig. 5) It has lesser viscosity and good flexibility that provides better strength. Additionally, it improves the mechanical properties of the material as compared to Bis-GMA monomer. (76)

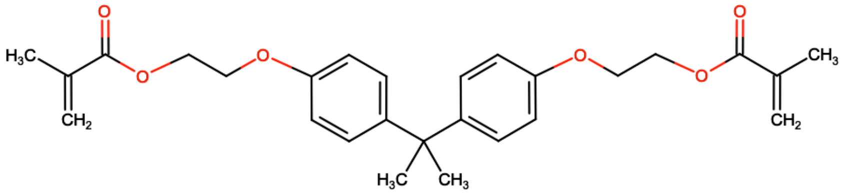

FIGURE 2; Chemical Structure of Bis-GMA Unit (75)

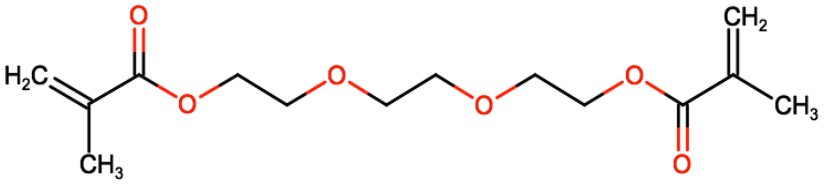

FIGURE 3; Chemical Structure of TEGDMA Unit (75)

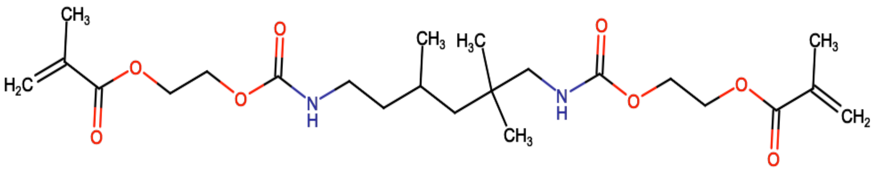

FIGURE 4; Chemical structure of UDMA unit (69)

2.2.2.2. Initiator/ Activator System:

In general, composite resin materials are hardened by the production of free radicals from a free radical polymerization reaction which is activated by two systems: light activated and chemically activated.

I. Chemically Activated System

In this system, a tertiary amine and reacting benzoyl-peroxide stimulate the polymerization reaction of chemically activated composite resin. Chemically cured composites are available as a two-paste system (one tube containing a chemical initiator and the other containing a chemical activator). When these pastes are mixed together, leads to the formation of free radicals by the chemical reaction between peroxide-amine systems, to initiate the polymerization process. (74)

II. Photoactivated Systems

The majority of the composite resins now available are light-cured resins. Camphoroquinone (CQ) is the most common photo-initiator used with light-activated resin composites that are stimulated by a tertiary amine, typically an aromatic one. The Camphorquinone (CQ) is sensitive to light in 400-500 nm regions to produce an activated complex with the combination of the tertiary amine. Afterward, this complex breaks down to form free radicals, which in sequence initiate the polymerization process. (74)

2.2.2.3. Inhibitors and Stabilizers

Inhibitors such as hydroquinone monomethylether (MEHQ) and phenols are added in order to avoid spontaneous polymerization during storage. UV photostabilizers can decrease the discoloration and the effect of UV rays on the amine component within the initiator system, which can induce later discolouration over a long period. (77)

2.2.2.4. Pigments

Dental resin composites have the capability to approximate the natural tooth colour. There is a wide range of shades and translucencies have been introduced for dental restorative materials which offered an enhancement in the aesthetic result of restorations. Dental composites are coloured (shading) by addition of different pigments. Metal oxides pigments are the most commonly used pigments. (77)

2.2.2.5. Coupling Agent

The coupling agent (silane) serves as a bond to induce adhesion between the inorganic filler phase and the organic resin matrix of the composite resin. This bond has a critical role in order to progress the properties of the resin composite. (78)

2.2.2.6. Inorganic Filler

Most of the mechanical and physical properties of composite restorations are considerably enhanced by raising the loading of filler particles. Fillers are added to the dental composite material to improve strengthening, abrasion resistance, toughness, reduced dimensional and thermal change, influenced radiopacity, improved aesthetic outcomes, and easy handling. (79) There is a direct effect of the volumetric amount of the fillers on the total Polymerization shrinkage of the resin composite. (80)

Nowadays there are a variety of fillers available in the market. New dental composite resins contain filler particles such as quartz, colloidal silica, and silica glass containing strontium, zirconium, and barium. Glass particles are commonly employed, because of their improved optical performances. (81)

The filler phase is classified according to the size of particles into microfillers or macrofillers. The macrofillers are attained by milling and mechanical grinding of larger quartz or glass particles and have an average size of (0.2-20 µm). The microfillers are usually pyrogenic silica particles that are produced by heat treatment procedure of silicon chloride ($SiCl4$) to about 0.04 µm in size. (81)

2.2.3. Classification of Resin-based Composites According to Filler Type

Composite are generally categorized according to the mean size of the inorganic filler particles, either conventional, macrofilled or hybrid composites (Fig. 6), and this system of classification is useful up to now.

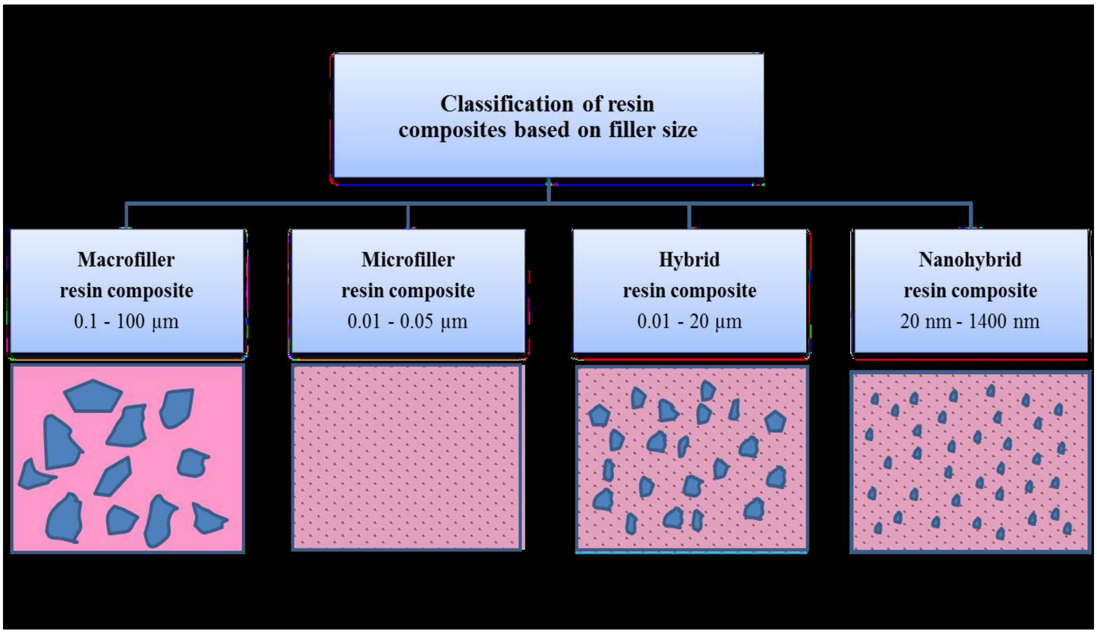

FIGURE 5; Composite Classification According to Filler Size (82)

2.2.3.1. Macrofilled (Conventional) Composites

Macrofilled composite was presented in the late 1950s. It produced by mechanical grinding of larger particles containing radiopaque quartz, ceramics or glass into smaller particles via mechanical methods. Macro Fillers particles are with a size of 10-100 µm, mixed to the organic resin phase up to 70-80% of the weight, which results in an improvement of composite resin properties in comparison to the unfilled resin. (82)

High filler ratio results in the interaction of the particles with each other, this contributes basically in the reinforcement mechanism of dental composite. Macrofilled composite is stronger than microfilled composite. They are broadly applied in stress-bearing restorations such as Class III and IV restorations. (82)

However, they have also many disadvantages, including clinical wear because of their poor wear resistance, which in sequence leads to a rough surface with trapped plaque and reduced polishability; in addition to the staining and discolouration because of surface roughness. (82)

2.2.3.2. Microfilled Composites

Homogeneous microfilled composite resins were developed at the end of the 1970s. colloidal silica filler particles with size ranging from 0.04 to 0.1µm are added to an organic phase, to attain a filler ratio of 35% by weight. Achieving a higher filler content maybe by pre-polymerization of resin holding the colloidal silica, ground into particles and integrating it as fillers. This would provide an increase by 50-60% by weight. (75) (82)

Compared to the macrofilled composite resins, microfilled composite resins give a higher degree of smoothness to finished restoration, with less surface degeneration with time and better color stability which is highly advantageous, but they did not have as good physical properties, thus They are mostly used where a moderate load is applied in combination with an aesthetic demand. Also, they can be used for veneering the cores made up of fine-particle size composite resin or hybrid resin in extensive anterior restoration so that both strength and aesthetics can be improved. (82)

2.2.3.3. Hybrid Composites

Hybrid composites are the most recently established group of composite resins. They have designed to blend the enhanced mechano-physical features of microfills with higher filler ratio accomplished in traditional resins. Hybrid composites have a wide range of filler particle sizes. This variety of particle sizes could allow high loading of filler with subsequent high strength. Classically, hybrid composite resins have a filler particle with a size ranging from 15 to 20 µm in addition to 0.01- 0.05 µm. Several particles such as barium silicate and borosilicate glasses may also be used as fillers to the hybrid composite. (82)

2.2.3.4. Nanofilled Composites

Nano-composites are the current trend introduced to the market. It is available as nanohybrid systems, the sizes of their filler particles are less than 10 nm (0.01 μm) that is aimed to increase the filler proportion to enhance the mechano-physical features and clinical performance.

In order to increase the filler content, it is necessary to decrease the dimensions of the particles this subsequently decreases the polymerization shrinkage and enhances the mechanical properties, for example, hardness, strength, polishability, and appearance which make this category are superior to those of macrofilled composite and better than those of microfilled composite. (83)

TABLE 2; Classification of Filler size and Material in Composite Resin

Composite type	**Filler size (μm)**	**Filler material**
Macrofilled	10 – 40	Quartz glass
Microfilled	0.01 – 0.1	Colloidal silica
Hybrid	15 – 20 and 0.01 – 0.05	colloidal silica and Glass
Modern hybrid	0.5 – 1 and 0.01 – 0.05	Zirconia, Glass and colloidal silica
Nanofiller	< 0.01 (10 nm)	Silica or Zirconia

TABLE 3; Indication of Composite Resin

	High-esthetic restorations	Stress-bearing restorations
Micro filled	×	-
Micro hybrid	-	×
Nano filled	×	×

2.2.4. Properties of Composite Resins

2.2.4.1. Polymerization Shrinkage

The contraction of dental composites during polymerization is termed polymerization shrinkage. Such Polymerization shrinkage is important because of its negative sequelae on cavosurface margins that led to poor marginal seal and marginal staining resulting in an esthetic matter and recurrent caries. Marginal adaptation of composite resins restoration is related to many factors including: polymerization shrinkage, adhesion between restoration material and the cavity walls, hygroscopic properties, the coefficient of thermal expansion, and the finishing methods. (Table 4) Such shrinkage may lead to microcracks within the composite resin that may in sequence led to premature failure of the composite restoration. The shrinkage properties of a composite resin are directly correlated with the degree of conversion, the factors affecting the conversion of the monomers into polymers (and thus the polymerization shrinkage) are including: curing time, resin thickness, temperature, curing distance, type of filler, amount of organic material. (84) (85)

Integration of a high content of filler particles along with a proper composition of the monomer matrix theoretically would ideally minimize the associated polymerization shrinkage. (84)

TABLE 4; Factors that Affect the Polymerization Shrinkage of Composite Resin (85)

Factor	Clinical repercussion
Curing time	It depends on; light intensity, curing through tooth structures, resin shade, resin thickness, box deep, composite filling.
Shade of resin	Composites with Dark shades cure less deeply and more slowly than those with lighter shades (one minute at a maximum depth of 0.5 mm)
Temperature	Room temperature is suitable for a rapid and complete curing cure of composite.
Thickness of resin	Ideal thickness is (1-2 mm)
Type of filler	Heavily loaded composite is easier to cure than Microfine composite.
Distance between light and resin	Ideal distance <1 mm, the source of light located at 90 degree from the surface.
Light source quality	Wavelength (400-500 nm). A power density 600 m W/$cm2$ passes through the first increment of the dental composite in posterior teeth.
Polymerisation shrinkage	Depends on the ratio of the organic phase.

2.2.4.2. Water Absorption

The technical properties of dental composite restorations are associated with water sorption where water acts as a stress corrosion agent and plasticizer, Deterioration the matrix particles interface weakening of the mechanical and physical properties can arise as a consequence of localized swelling at the filler-matrix interface in the mouth. This is mainly because of hydrolytic debonding between the matrix and filler interface or silane/filler particles. Solvent effects and temperature changes further accelerate this breakdown of the composite surface. The higher temperature is associated with a faster water absorption. Other drawbacks of water absorption are including tensile strength, flexural strength, modulus of elasticity, and wear resistance. (86) (87)

2.2.4.3. Hygroscopic Expansion

The polymerization shrinkage of the composite resin may be compensated by the Hygroscopic expansion and, consequently, make possible improved marginal sealing. In the polymerization process, the inside movement of water ions leads to saturation of molecules within the matrix. However, outside movement of ions and unset monomers removed from fillers and activators. Extracted components result in weight loss and more shrinkage, however, hygroscopic expansion causes weight gain and swelling. (88)

2.2.4.4. Wear

Wear is defined as progressive loss of hard material from the surface due to mechanical impact. The conventional large-particle composite resins consist of filler particles with a large size that is significantly harder than the resin matrix. During mastication, forces are diffused onto the restoration surface and mostly the particles prominent from the occlusal surface. As the filler particles are harder than the resin matrix where they are implanted, most of the load is transferred through the particle into the resin. Stress will accumulate and become extremely high where resulted in the wear of restoration or irregularly shaped surface. (89)

A new development of composite resin has been introduced which hold filler particles of decreased sizes but increased filler content. The total stress around each particle is decreased which results in a serious reduction in anatomical form wear. (89)

2.2.4.5. Fracture Toughness

The main cause of clinical failure for composite resin restorations is a bulk fracture. Fracture toughness is a mechanical character for defining the brittleness of material, several features may affect fracture toughness; for example, chemical structure, fillers (content and size), the degree of polymerization of the resin matrix, or bond between matrix and filler interface. A larger value of fracture toughness means a material rarely to crack or fracture easily. Nano-filled and hybrid resin composites are expressively having a larger fracture resistance than micro-filled composites. (90)

2.2.4.6. Surface Properties

I. Colour Stability

The composites resin restorations are most commonly replaced because of colour shade mismatch since the discolouration of composite resin restoration is considered as the main cause of aesthetic failure.

The discoloration of composite filling occurs as a consequence of intrinsic and/ or extrinsic causes. Intrinsic causes include changes in the chemical structure of the resin composite. The chemical discoloration is associated with the oxidation of amine accelerator, storage in water for a long period, and exposure to various energy sources. Extrinsic causes include staining or spreading of stains from drink and food for example stained drinks and beverages. Colour alteration may happen for material associated with changes in absorption and reflecting of light after aging. As a result of an insufficient resin polymerization, so, because of stains absorption, the colour of the resin composites may change easily. (91)

Hydrophobic composite resin shows more colour stability than Hydrophilic resin because of the solubility of hydrophilic stain in aqueous solutions and easy penetration into materials. (91) (92)

II. Gloss

The gloss is known as the ability of the material to reflect direct light. The gloss is determined by the shape and size of filler particles in addition to the resin matrix. Chemical degradation and wear of the surface may affect gloss and cause discolouration. Clinically, restorations that display a high gloss surface show a better aesthetic result. (93)

III. Hardness

Hardness is the most significant property, which linked to wear resistance, compressive strength and the degree of polymerization. Hardness affected by subjected load and time through the test. The hardness of composite resin can be decreased by the hydrolytic breakdown and water sorption. A low hardness rate of a dental composite indicates weak chemical and physical bond between the matrix and filler particles. (94)

2.2.5. Improving Esthetics in Composites

The esthetics of composite resin is affected by the contour and shape of the restorations, esthetics is determined by the availability and proper shade selection– the translucency and fluorescence, value "degree of lightness or darkness", hue, chroma "intensity of the shade", polishability, wear resistance, the stability of gloss. All of these factors have a role in creating and maintaining ideal esthetic outcome (table 5). (74)

TABLE 5; Factors Influence Composite Resin Esthetics

Shape and contour close to the natural teeth.
Functional contours with esthetic.
Use of a suitable technique.
Prevention of moisture contamination.
Use of a proper bonding system.
Selection of accurate shades.
Polishability of the materials.
Wear resistance.
Stability of glass and polish.

2.3. Bonding of Composite to PEEK

There are some aesthetic problems which restrict the application of PEEK for full-coverage monolithic restoration. As a result of the optical appearance of PEEK included its grayish-white color and low translucency. Thus, additional dental composites for veneering are still necessary to obtain satisfactory esthetics. (11)

PEEK exhibits a hydrophobic, chemically inert surface, as well as its resistance to surface modification by various mechanical and chemical treatments, these are responsible for its limitation in prosthetic dentistry because of difficulty to obtain durable bond strength with the composite resin material to guarantee an appropriate functional result and long-term stability. This adds an extra challenge, for attaining sufficient bonding between PEEK surface and veneering composite. (11) (50) (51)

The mechanical retention of the composite resin veneer is related to its viscosity and consequently on the loading of the filler content. The viscosity is increased as a result of an increase in particle percentage. The main requirement for durable bonding is spreading of the adhesive material on the surface of adherent or substrate. Adequate spreading will only occur if the surface free energy of adherent is higher than the surface free energy of the adhesive. typically, the surface energy of adhesives is higher than that for untreated PEEK of poor bonding properties. Because of difficulty to change the surface energy of the adhesive, several trials are made to improve surface energy of PEEK by using different surface modification methods. (50) (51)

In general, several material features such as adhesive bonding properties, reflectivity, wettability, and coefficient of friction are significantly affected by surface treatment. (50) (51)

2.4. Surface Treatments

Many surface treatment methods have been planned to increase the bond strength of PEEK to the matrix in a composite resin. These surface treatment methods are broadly classified into four groups: surface cleansing, mechanical, chemical and physical surface treatment.

2.4.1. Surface Cleansing

Regarding all surface treatment methods, surface cleansing is the easiest technique; its primary aim is to eliminate the contamination from the surface. This is by wiping the material with a specific solvent or with vapour, according to previous trial the solvent-wiping treatment is obviously inadequate and it looks to have no influence on PEEK and its veneering composites. (96)

2.4.2. Mechanical Surface Treatment

The micromechanical retention surface treatment is possibly the easiest and inexpensive modification method since the cost for tools is low. There are several options to produce simple mechanical roughness ranging from silicon carbide paper to sand/grit blasting. This produces surface defects in the PEEK surface that with polymer result in an increase in surface roughness and surface area. Firstly, PEEK should be prepared with acetone then roughened and cleaned again to eliminate debris. In order to improve the cleaning effect, the usage of ultrasonic bath with solvent should be appropriate. The irregularities of the surface should not be intense because adhesives with low viscosity cannot wet and infiltrate through severe rough surfaces. The main goals of mechanical abrasion are to increase the surface roughness and eliminate any weak layers of the adherend.

Studies have established that Surface roughening of PEEK can be an effective surface modification to improve the bonding strength between composite resin and PEEK to values 4.6 times higher than those without roughening. (97) (98)

2.4.3. Chemical Surface Treatment

Chemical surface treatment can cause chemical and physical modifications when a polymer is immersed in a highly oxidative chemical solution and treated under appropriate conditions. Previous studies evaluated etching by sulfuric acid solution as a method of PEEK surface treatment technique and approved that it results in a higher bonding strength with different composite materials than after pre-treatment by air-abrasion technique. Polar components are introduced to the polymer surface and can cause surface properties improvement, but these are toxic methods and pollute the environment. (98)

2.4.4. Physical Surface Treatment

These methods are generally very effective with polymers and do not result in pollution or health hazards.

2.4.4.1. Plasma Treatment

A cold plasma treatment is a significant method for surface treatment that chemically modifies the surface of the polymer and also has an effect of surface roughening. The most commonly used gases for surface treatment of polymers are oxygen, air, helium, argon, ammonia, and nitrogen. It is better to clean surfaces before plasma treatment.

Plasma treatment seems to be an acceptable method to improve the adhesive bond strength of PEEK. In comparison to other gases using air as process gas seems to produce lower bond strengths. However, air is easy to use and always available. Plasma treatment method is a discontinuous procedure because of the low-pressure condition that needs a chamber, this is the main drawback of plasma treatment. (50)

2.4.4.2. Corona Discharge Treatment

Corona treatment is the alteration of material’s surface energy and bonding capacity by the excitation of molecules between two electrodes by a corona or a high voltage power supply and the substrate to be treated is placed between these electrodes (99).

It is very close to plasma treatment except the former, it has both a disadvantage and an advantage for example, it is created in air, which is simply arranged process, inexpensive and also easily used in the industry; the difficulty of the corona discharge is its composition which is harder to control than that in plasma treatment. (99)

2.4.4.3. Laser Treatment

Among most of the surface treatment methods, laser micromachining is a capable alternative due to its high resolution, high working speed, technique flexibility and unchanged bulk properties. Moreover, there are many publications on altering PEEK surface morphology by laser treatment; the energy density applied was above the ablation threshold (AS) which mean that the chemical alteration of the surface was associated with surface roughness. In this case shear bond strength improved from about 3MPa to 18MPa. (100)

Laser treatments either with a solid or a gas are excited to release light of a specific wavelength. it may be performed in air or in different gaseous atmospheres by means of a chamber. Generally, laser treatment takes place in ambient conditions: air and atmospheric pressure. (100)

2.4.4.4. UV-Light

The UV activation process is basically a continuous oxidation method which starts with the reactive oxygen and carbon radicals. Previous trials have been revealed that UV surface treatment is an effective means to increase adhesive bonding behaviours of PEEK. (97) (98) (53)

2.5. Bond Strength Testing Method

Testing methods for assessing bond strength the load must be applied in such a way that is concentrated at the interface. Bond strength is evaluated using various mechanical tests. These tests are generally divided into three groups shear, tension and peel.

2.5.1. Tensile Test

The tensile test is a very simple test. A load of failure divided by the contact area calculates the tensile bond strength.

In all tensile test methods, it is important to align the samples in the testing machine accurately. Any error may lead to an improper distribution of load and result in data scatter. Alteration in adhesive thickness is another problem which can cause non-uniform Loading in the adhesive and great scatter in the bond strength result. It should be mentioned that it is hard to compare the tensile bond strength attained from different test procedures. (101)

2.5.2. Shear Tests

Shear tests are very common because of simplicity to fabricate the Sample with accurate geometry. When loads are applied in the adhesive plane, the adhesive bond is seemed to be in a shear state. The shear bond strength is measured as the load of failure divided by the bonding contact area. There are two aspects should be considered in the shear test, firstly is that the stress is not distributed uniformly, so the maximum stress in the bond layer may vary intensely from the average; secondly is that generally the applied stress is not pure shear, hence the real state of stress affects by other features such as adherend stiffness and adhesive thickness. (101)

2.5.3. Peel Tests

The peel strength is defined as force per unit width. There are numerous kinds of peel tests. The simplest and common one is the T-peel test. (101)

3. THE AIM

The aim of this study was to evaluate the shear bond strength between veneering composite and PEEK core material to investigate the effect of different surface treatments including air-abrasion by 50μm alumina particles, acid etching with 98% H_2SO_4, and combinations of the two treatments.

We hypothesized that pre-treatment with either mechanical and/or chemical means would result in possible bonding of composite resin to PEEK. Secondly, the micro-roughness of PEEK surfaces is the main factor to ensure durable bonding of veneering composite to PEEK.

4. MATERIALS and METHODS

I- Materials:

The materials used in this study, along with their specifications, chemical composition, batch number, and manufacturers are listed in Table 6.

TABLE 6; Material name, Specifications, Chemical composition, Batch number and Manufacturers

Product Name	**Manufacturer**	**Composition**	**Application steps as recommended by the manufacturer**	**Lot. No**
PEEK KETRON	Invisibo PEEK CLASSIC Germany	Polyether-ether-ketone		
Visio.link	Bredent Senden Germany	MMA, PETIA, Photoinitiators	1.Apply adhesive on PEEK surface with brush 2. Light cure for 90s	164371
GC Gradia (Finehybrid)	GC Corporation, Japan.	UDMA, EDMA, 75% wt filler: ceramic, prepolymer, SiO_2)	light cure for 45seconds	151124D
Sulfuric acid		H_2SO_4 98%	Application for 60 s; rinsing with distilled water for 60 s	
Air-abrasion	KOROX Renfert Germany	50 µm Al_2O_3		54299

II-Methods:

Forty-eight specimens were manually sectioned out of a PEEK blank (KETRON CLASSIX LCG PEEK, Invisibo, Germany) (Fig. 7) using a diamond cutting disk (BUEHLER, ISOMET 1000, Germany), with dimensions of 8 mm diameter and 2 mm thickness. Figure 8 show samples after cutting.

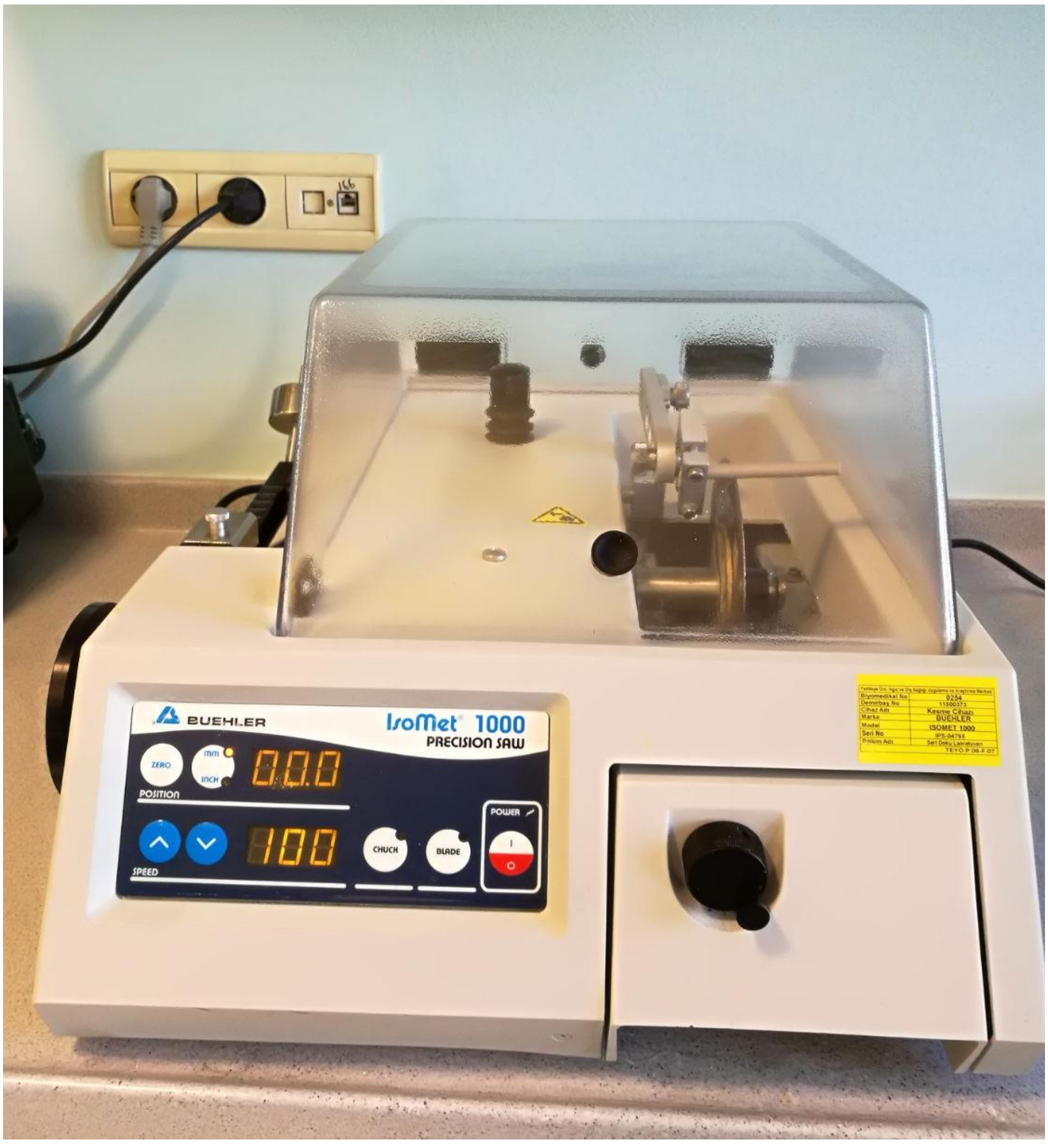

Figure 6; **ILLUSTRATION OF CUTTING OF SPECIMENS**

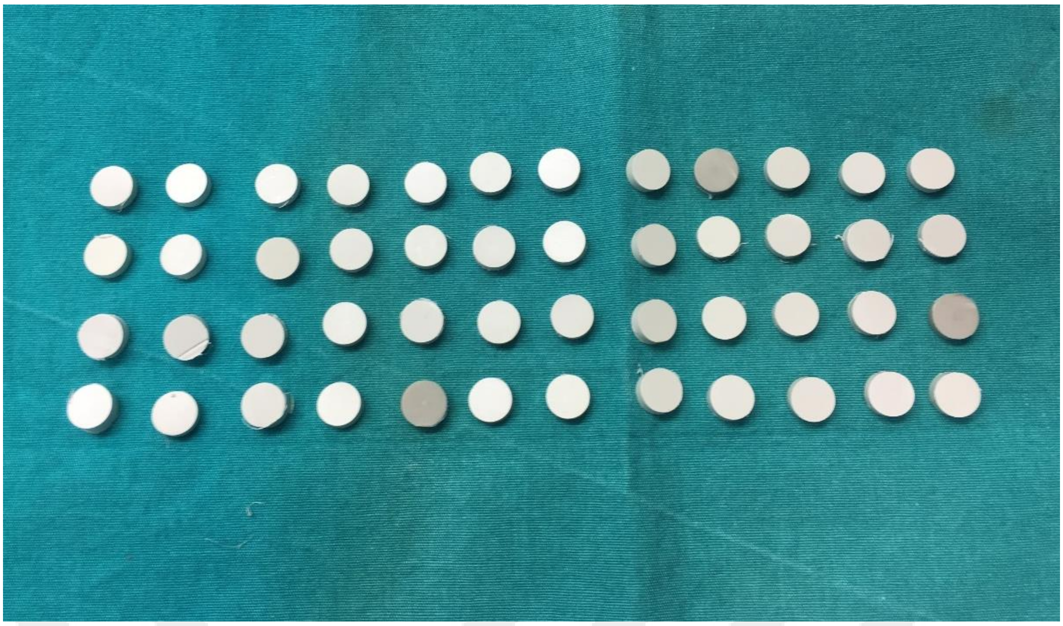

FIGURE 7; PEEK Samples after Cutting

The bonding surface of each cylinder was polished with the polishing device (PHOENIX BETA, BUEHLER, Germany) under water cooling with series of rotating silicon carbide abrasive paper (600 grit, 800 grit, 1200 grit) (Figure 9).

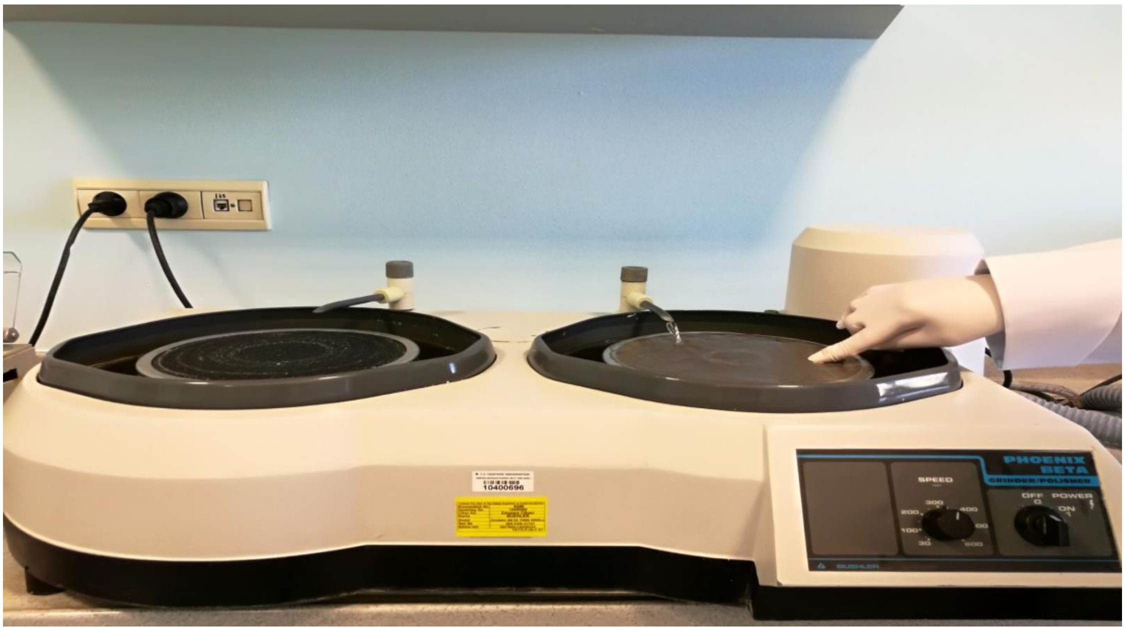

FIGURE 8; Polishing of PEEK Specimens with Water Cooling

Before starting surface treatment and veneering procedure, the value of surface roughness (Ra) of the disks was observed by a surface profile-meter (Perthometer M1, MAHR, Germany)

Grouping of the samples

The 48 disks were randomly grouped into four different groups according to the different surface treatment that would be used before veneering the composite to the disks. Each group contained twelve discs (n=12/group). Figure 10 shows the samples after they were divided into their respective groups.

FIGURE 9; Samples divided into their Respective Groups

Surface Treatment

Forty-eight PEEK specimens were randomly divided into four groups according to the surface treatment protocol as follows:

- Group #1: This group acted a control group and the disks did not receive any surface treatment (control).

- Group #2: Disk surfaces were subjected to air-abrasion with (Basic Master, RENFERT, Germany) by 50µm alumina powder in a direction perpendicular to the surface and at 10 mm distance from the puzzle to the specimen for 10 seconds with a pressure of 2 MPa (Figure 11).

FIGURE 10; Illustration of Air-borne particle Abrasion of PEEK Disks

- Group#3: Disk surfaces were etched with 98% sulfuric acid for one minute, after etching the surface were rinsed carefully with distilled water then air-dried at room temperature (Fig. 12, 13).

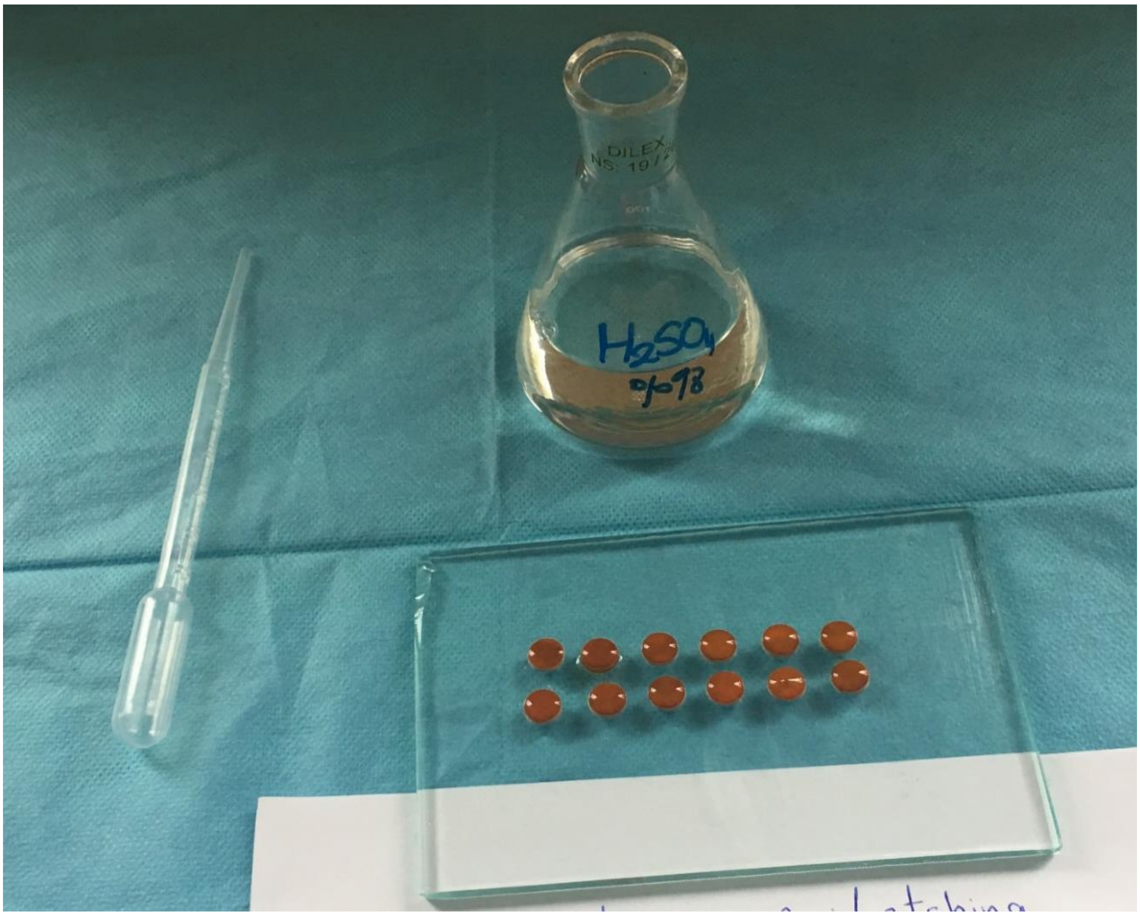

FIGURE 11; Specimens Being Acid Etched

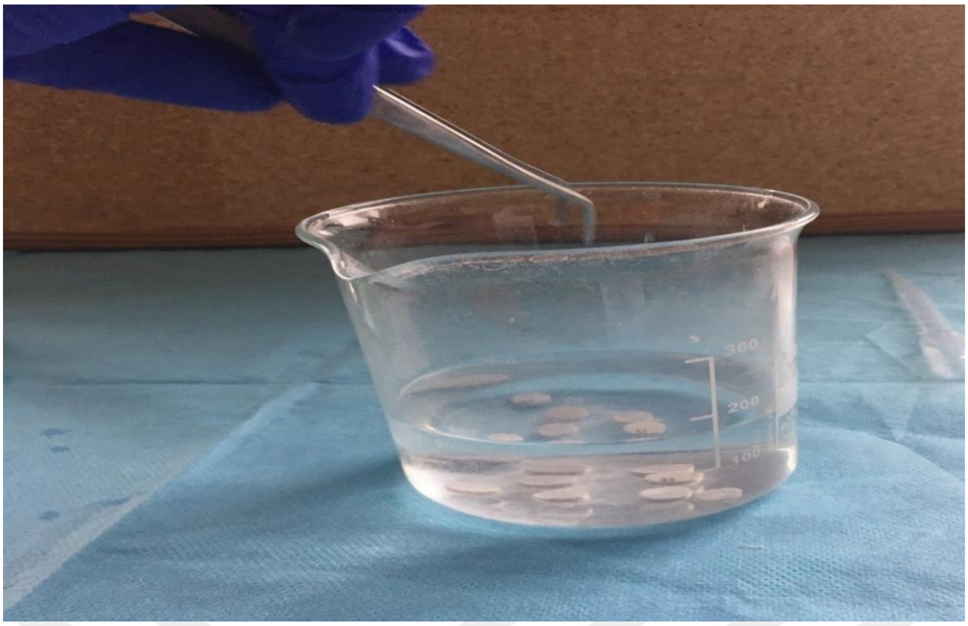

FIGURE 12; Illustration of Cleaning of Specimens in Distilled Water

- Group#4: Disk surfaces were subjected to air-abrasion by alumina particles 50 µm at 2 MPa pressure and 10 mm distance for 10 seconds and were then etched with 98% sulfuric acid for one minute. After etching, the specimens were rinsed thoroughly with distilled water and air-dried at room temperature. (Fig. 14)

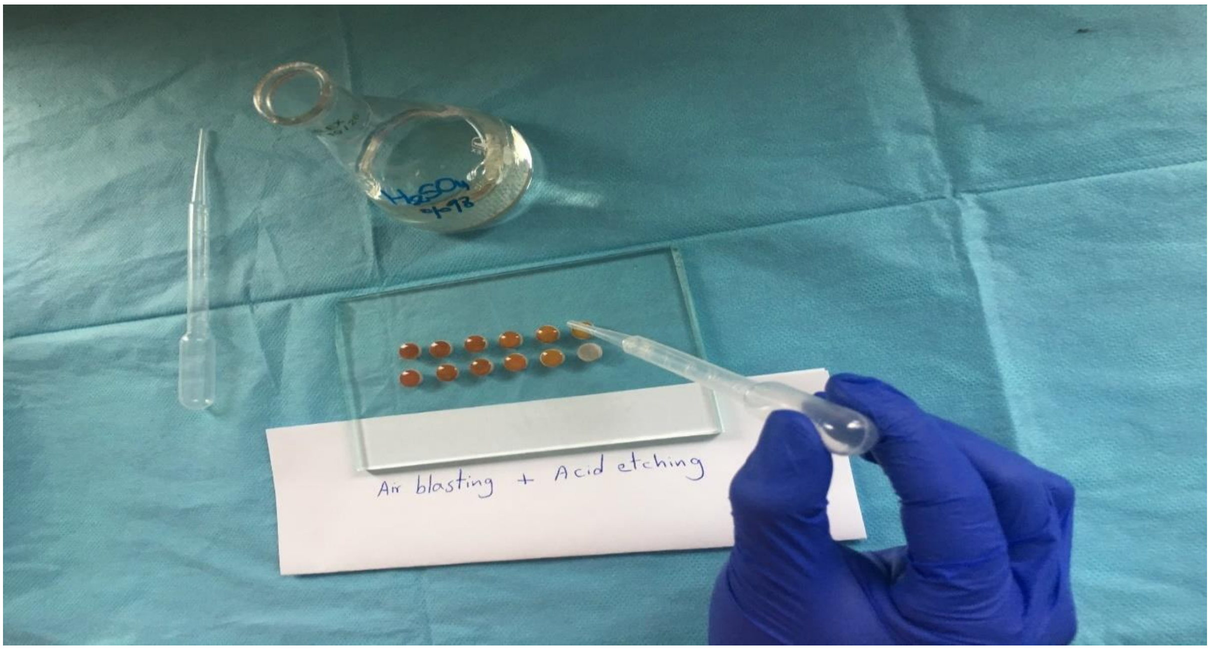

FIGURE 13; Acid Etching of Disk Surface After being Abraded with Al_2O_3

Before the application of coupling agents, all specimens were cleaned in an ultrasonic bath with distilled water (ALEX, JAPAN) (Fig. 15) for 5 min and dried on a clean bench at room temperature.

FIGURE 14; Cleaning of Specimens in Ultrasonic Bath

The average surface roughness (Ra) of PEEK disks were assessed using an Atomic force microscope (AFM) (QUESANT, INSTRUMENT COOPERATION, UNIVERSAL SPM, USA). The microscope was operated in the non-contact mode under dry condition at ambient temperature, the specimens were placed below the cantilever of the AFM to obtain three-dimensional images (10 μm x 10 μm) of the surface (Fig. 16) displays the AFM that was used.

FIGURE 15; The Atomic Force Microscope

Application of Adhesive

After surface roughness measurement, an adhesive consisting of MMA, PETIA and photoinitiators (Visio.link, bredent, Senden, Germany, LOT #. 164371) (Fig. 17) was applied on the bonding surfaces of samples using a small brush and immediately light polymerized by curing machine (OPTILUX 501) for 90 seconds.

FIGURE 16; The Visio.link Adhesive

For reproduction and similarity, a cylindrically shaped acrylic mold with an inner diameter 4 mm and height 4 mm was used to define the veneering area. (Fig. 18)

FIGURE 17; Illustration of the Acrylic Mold

Application of Composite Resin

The specimens were inserted in that mold. A veneering composite of Gardaí (GC corporate, GC Dental Product Group, Japan, LOT 151124D) was applied to the specimens in two 2 mm increments (Fig. 19). Each increment was cured for 45 seconds by curing lamp (OPTILUX 501) with the light perpendicular to the surface (Fig. 20). All materials were applied according to the manufacturer’s instructions (Table 6).

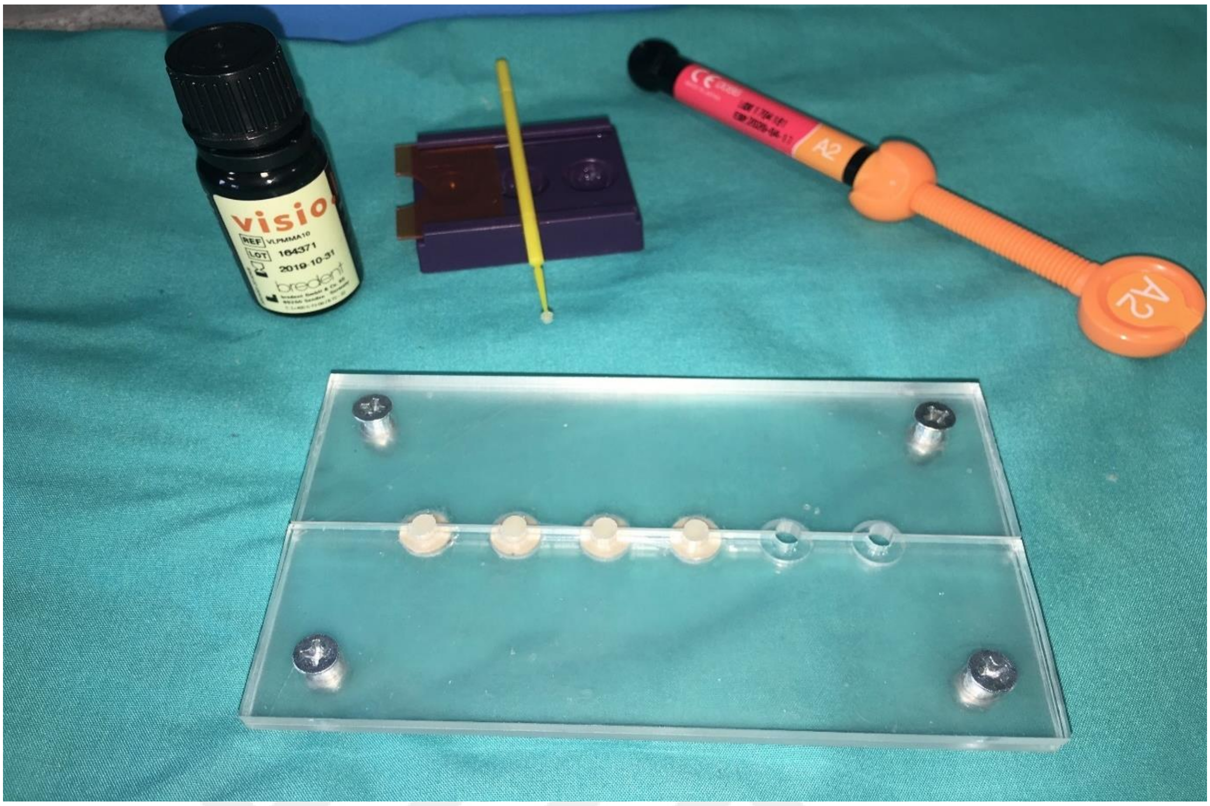

FIGURE 18; Composite Application

FIGURE 20; Illustration of Composite Resin Curing

After polymerization, the veneered samples were removed from the acrylic mold and stored in distilled water at 37°C for 24h.

FIGURE 19; Illustration of Veneering Composite on the PEEK Specimen

Measurement of Shear Bond Strength

Specimens were stabilized in an acrylic resin mold by Type 4 stone (Fig. 22), for an accurate positioning in the horizontal plane. (Fig. 23)

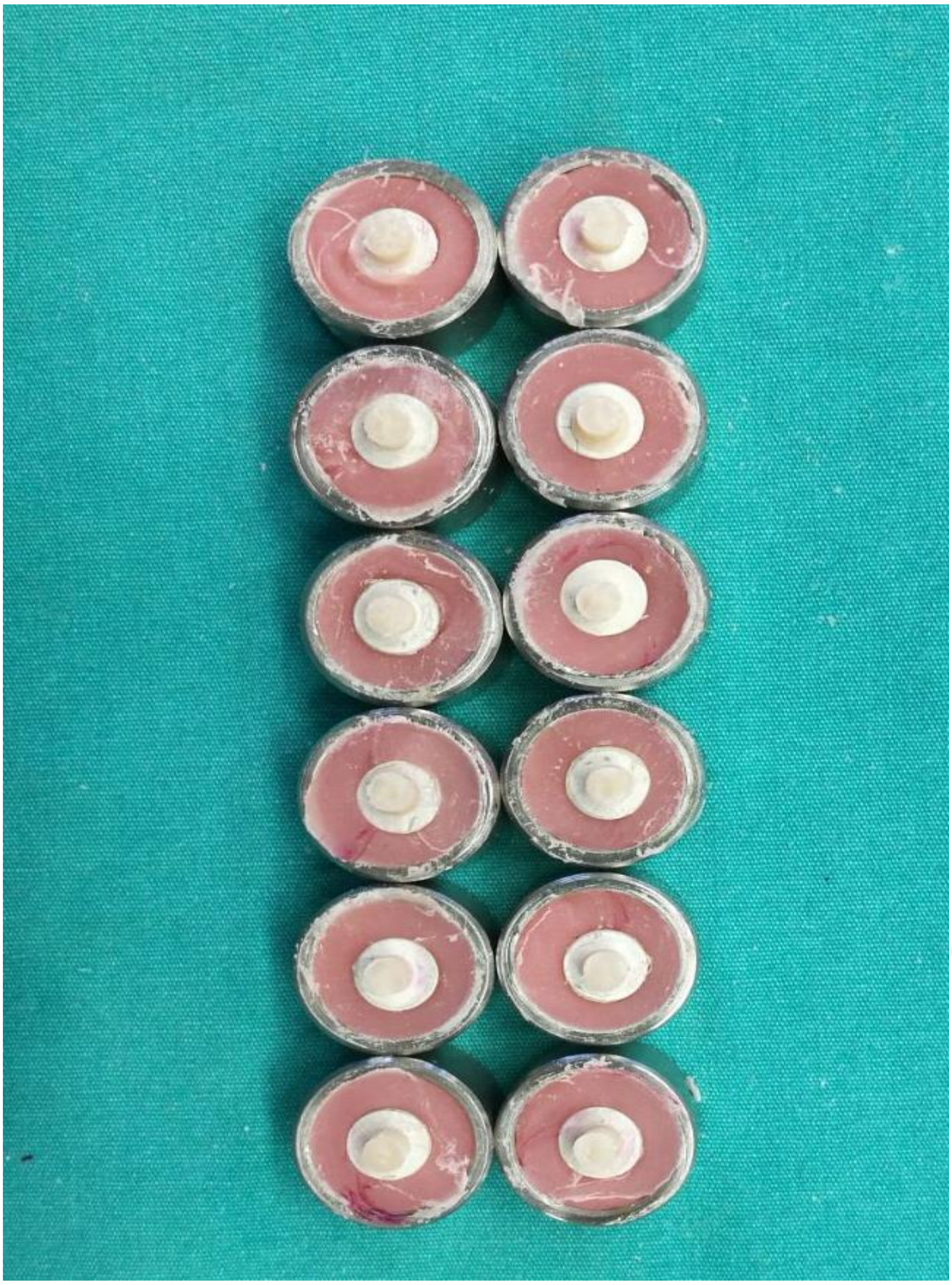

FIGURE 20; Illustration of the Specimens Embedded in the Mold with Type 4 Stone

Shear bond strength was measured with the universal testing machine (INSTRON, 3345, 3345J7324, USA). The samples were securely mounted in the holder with a bonding surface parallel to the loading force. The force was applied by means of a knife-edge shaped with a cross-head speed of 1mm/min. The maximum load before the separation of the resin composite from the PEEK surface was measured as a load at failure. The shear bond strength then calculated and expressed in Mega-Pascals (MPa) using the following formula: Shear bond strength (MPa) = Load (N)/area (mm^2).

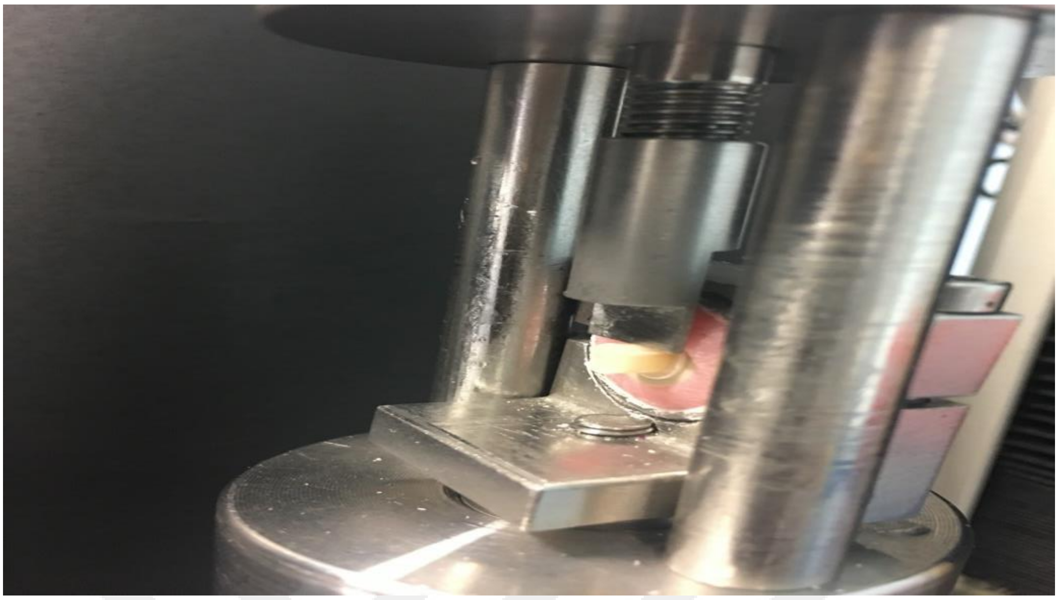

FIGURE 21; Specimen Placed in the Shear Testing Machine

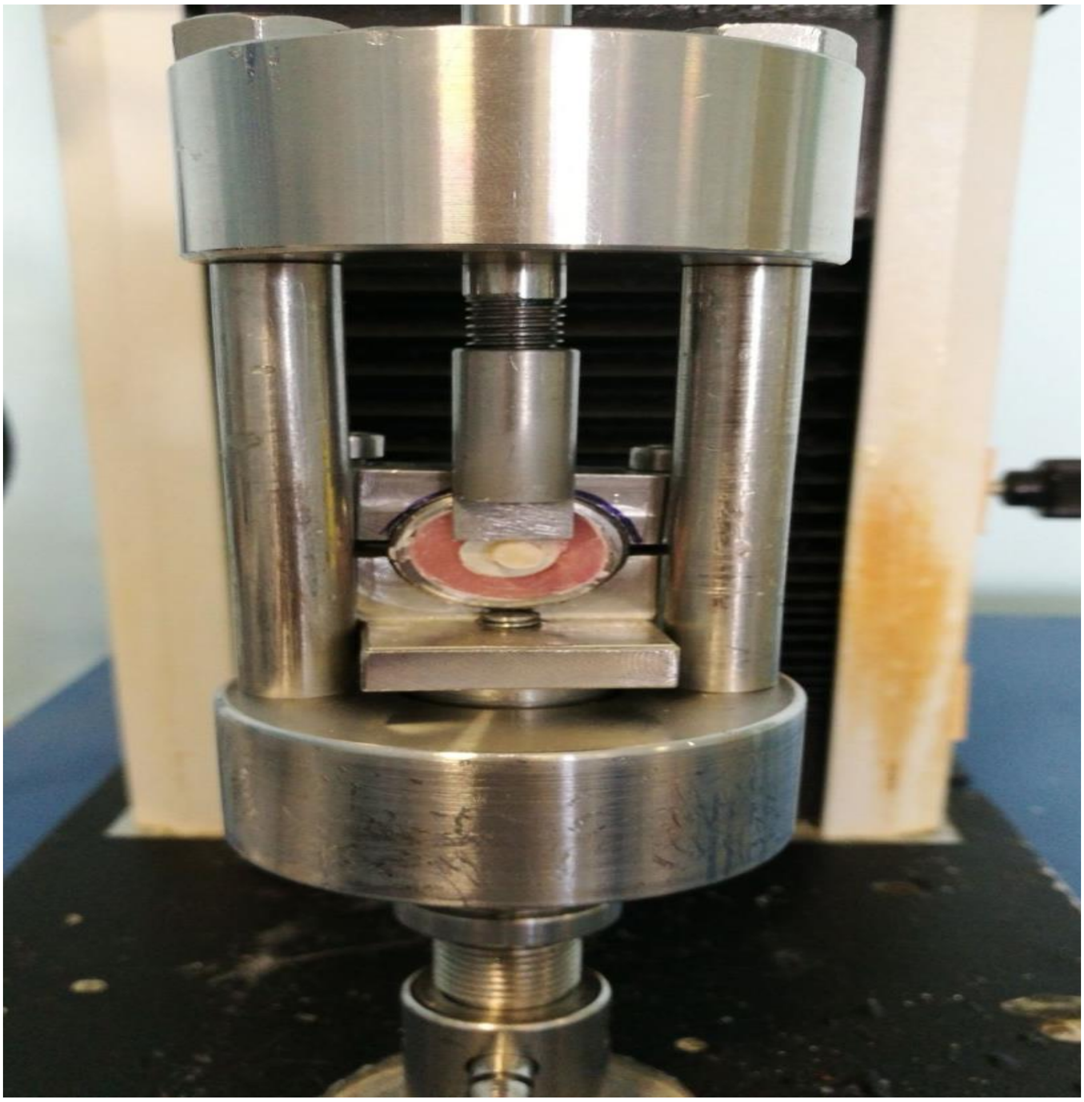

FIGURE 22; Illustration of the Universal Testing Machine with Mounted Specimen

Statistical Evaluations

During the assessment of the result achieved in this study, IBM SPSS Statistics 22 (IBM SPSS, Türkiye) programs were used. The normal distribution of the parameters was measured by the Shapiro Wilks test and it was determined that the parameters were conformed to the normal distribution. Regarding the comparisons of quantitative data One-way ANOVA test was used for the intergroup comparisons and Tukey test was used for the determination of the group of significance. The study data was evaluated at a level of $p<0.05$.

5. RESULTS

This study was designed to evaluate the effectiveness of the use of surface treatment with intermediate agents on the shear bond strength of the composite veneer to PEEK. Following the surface treatments, all the specimens were examined by using the Atomic force microscope. Data were displayed as mean and standard deviations values (SD). Three-way analysis of variance (ANOVA) was used in testing the significance of each variable alone and their interactions on the shear bond strength. Tukey's post-hoc test was used in order to make a pair-wise comparison between the means, the ANOVA test was significant at $p \leq 0.05$.

The mean (±SD) bond strength of the veneering composite to PEEK discs was 5.39±1.36MPa in the control group, 6.43±1.05MPa in air-abrasion group, 13.43±1.42MPa in the sulfuric acid etching group, 11.72±1,69MPa in air-abrasion plus sulfuric acid etching group. (Table 7) (Figure 25) According to the results of one-way ANOVA, the difference in shear bond strength of the veneering composite to PEEK discs was statistically significant among the groups ($p<0.05$).

TABLE 7; Shear Bond Strengths of the Different Surface Treatment Groups (±SD)

Surface treatment	Shear bond strength (Mpa)
Control	5.39±1.36
Air-abrasion	6.43±1.05
Sulfuric acid	13.43±1.42
Air-abrasion+ Acid Etching	11.72±1.69

Oneway ANOVA Test was used * $p<0.05$

SD standard deviation

There was a statistically significant difference in shear bond strength averages between the four groups ($p:0.000$, $p<0.05$) (Table 7). After bilateral comparison, the shear bond strength averages of the sulfuric acid group were significantly higher than the air-abrasion, air-abrasion + acid etching and control groups ($p<0.05$). Shear bond strength averages of air-abrasion + acid etching group were significantly higher than control and air-abrasion groups (*$p<0.05$*). There was no statistically significant difference between shear bond strength averages of air-abrasion and control groups (*$p>0.05$*) (Table 8).

TABLE 8; Post Hoc Assessment Chart

		Shear bond strength (Mpa)
		P
Air-abrasion	Air-abrasion+Acid Etching	0.000*
	Sulfuric acid	0.000*
	Control	0.278
Air-abrasion+Acid etching	Sulfuric acid	0.022*
	Control	0.000*
Sulfuric acid	Control	0.000*

Tukey HSD Test was used. * $p<0.05$

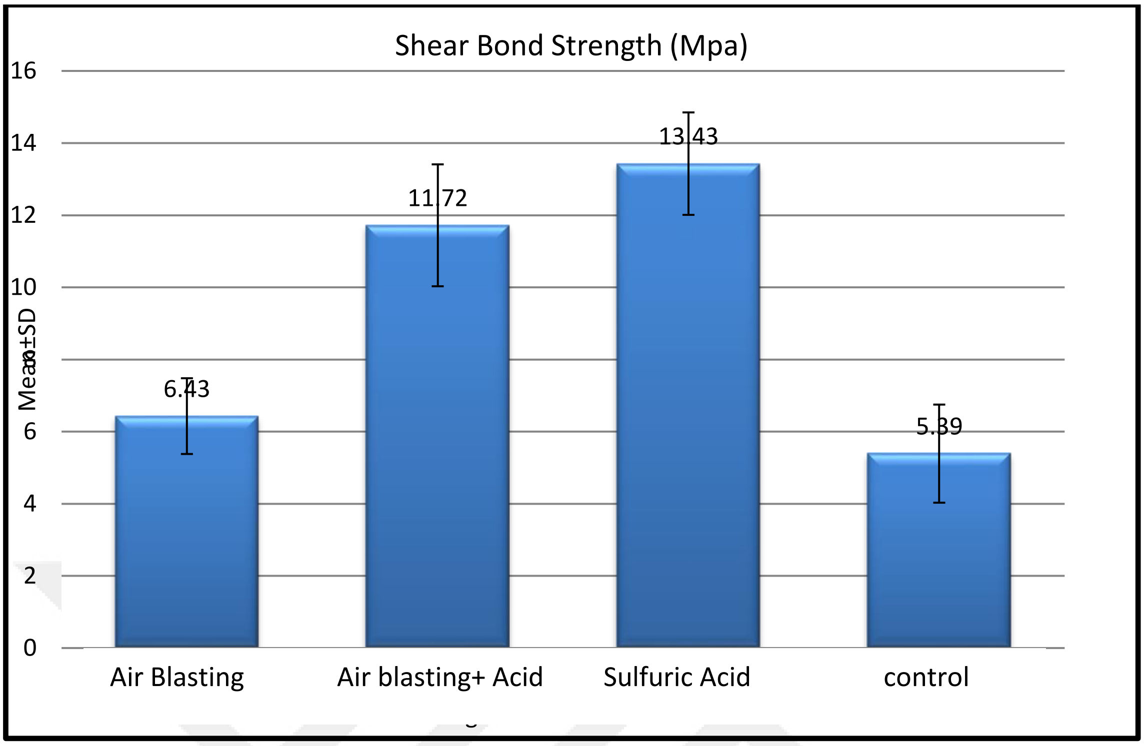

FIGURE 23; Bar Chart Illustrates the mean Shear Bond Strength of the Tested Groups

Table 9; Evaluation of Groups in term of Surface Roughness (NM)

	Surface Roughness (nm)
	mean±SD
Control	293.43±103.14
Air-abrasion	1378.09±279.43
Sulfuric Acid	737.2±198.12
Air-abrasion+ Acid Etching	784.58±263.8
P	0.000*

Oneway ANOVA Test was used. * $p<0.05$

Surface roughness

The mean surface roughness values are summarized in Table 9. There was a statistically significant difference between groups in terms of surface roughness averages (*p:0.000, p<0.05*) (Table 10). After bilateral comparisons, surface roughness averages of the air-abrasion group were significantly higher than air-abrasion + acid etching, sulfuric acid and control groups (*p<0.05*). Surface roughness averages of the control group were significantly lower than air-abrasion + acid etching and sulfuric acid groups (*p<0.05*). There was no statistically significant difference between surface roughness averages of air-abrasion + acid etching and sulfuric acid groups (*p>0.05*).

TABLE 10: Post Hoc assessment Chart

		Surface Roughness (nm)
		P
Air-abrasion	Air-abrasion+ Acid Etching	0.000*
	Sulfuric Acid	0.000*
	Control	0.000*
Air-abrasion+ Acid Etching	Sulfuric acid	0.953
	Control	0.000*
Sulfuric acid	Control	0.000*

Tukey HSD Test was used * p<0.05

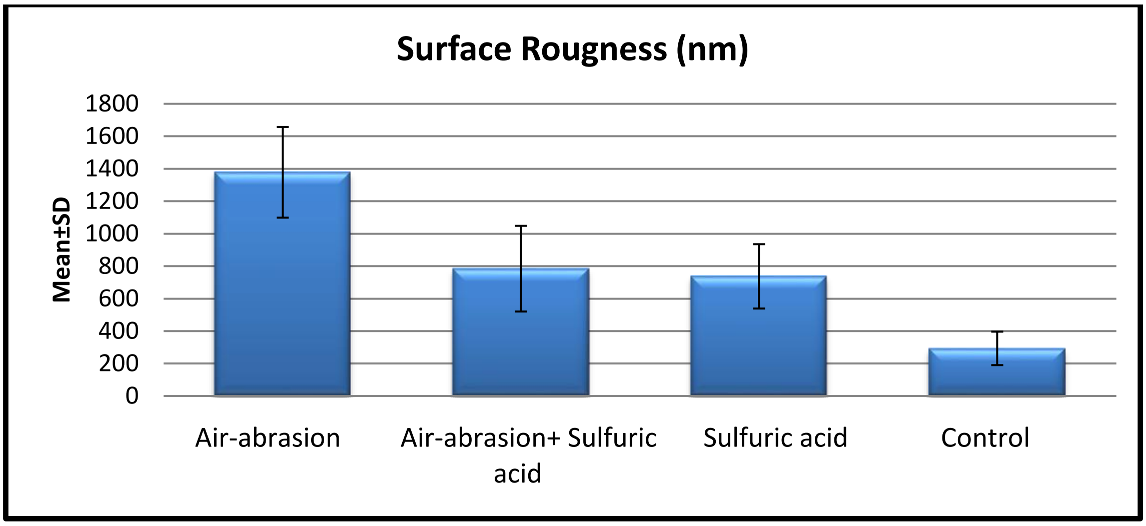

FIGURE 24: Bar Chart Illustrates the Mean Surface Roughness Values

The Morphology of Different Surface Pre-treatments by AFM;

The surface roughness of all pre-treatment groups was measured by Atomic force microscope (AFM) and the mean roughness was calculated as shown in Figure 26. The PEEK surfaces topography after the different pre-treatments is presented by the AFM micrographs. The morphology of PEEK surfaces was affected markedly by the various pre-treatments as shown in (Figure 27) (A-D)

The sulfuric acid etching group did not show any complex fiber networks but smooth and highly subsurface corrosion (Fig. 27A). PEEK surfaces air abraded with Al_2O_3 plus 98% sulfuric acid etching showed uniform pores and pits, exhibited rougher surface than did the control group (Fig. 27B). Air-abrasion by Al_2O_3 particles produced large depth and width of craters (Fig. 27C). While in the control group, the surfaces were relatively smooth, with irregular ridges from the polishing process (Fig. 27D).

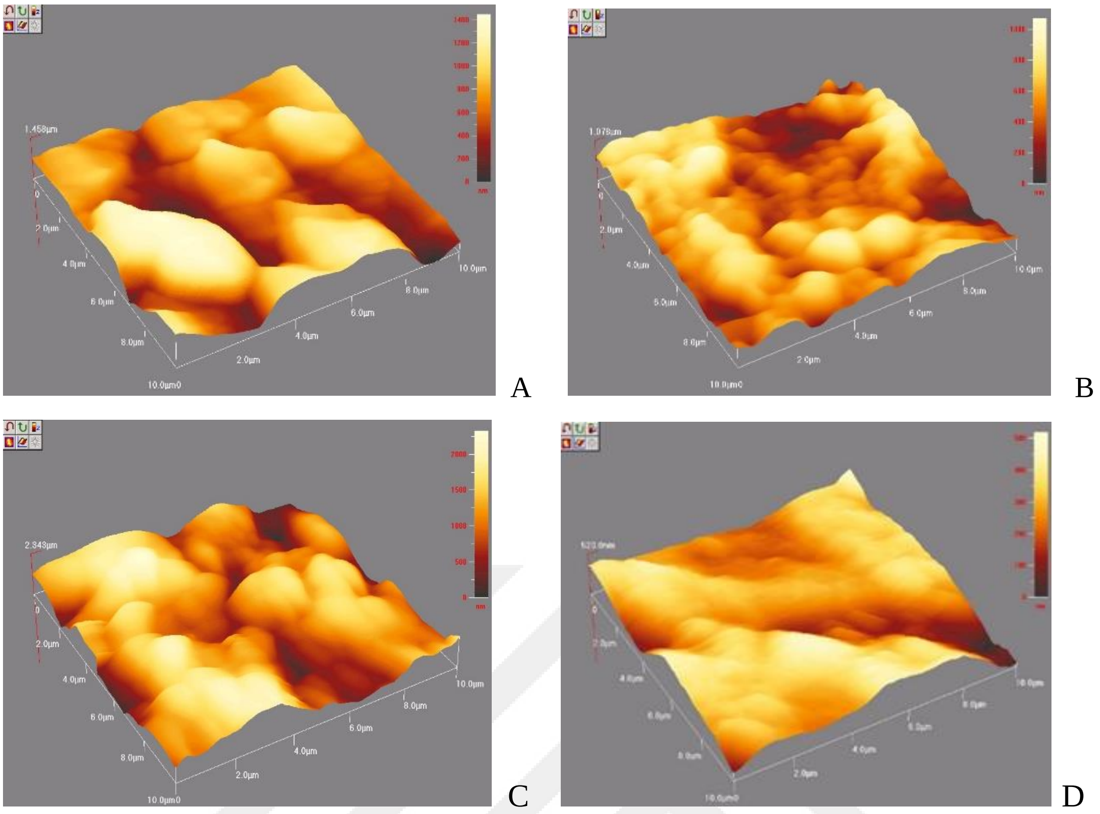

FIGURE 25; AFM images of PEEK. (A) sulfuric acid etching, (B) air abrasion plus acid etching, and (C) air abrasion with AL_2O_3 and (D) without pre-treatment

When comparing Fig. 27D and Figs. 27A-C, there is a clear difference between untreated PEEK and pre-treated PEEK surface. The untreated PEEK shows a smoother and more uniform surface whereas treated PEEK specimens show a rougher and more cross-linked surface.

As shown in Figure 27, the surface roughness of the polymer is increased after surface treatment and new cross-links are formed on the PEEK surface. It helps in improving the adhesion performance of the polymer.

6. DISCUSSION

Polyether-ether-ketone is a biocompatible thermoplastic engineering material with special properties that make it attractive for dental uses (64). Although the application of PEEK has a wide history in the industry (102) and medicine (102,103), little consideration has been given for the possible application of PEEK as a restorative dental material because the adhesion protocol of PEEK for dental use is not well established up to now. Generally, the application of PEEK as a framework for FDPs needs a permanently durable and stable bonding to veneering composite materials. The main requirements for an acceptable bonding are a good choice of adhesive, a proper joint design, cleaning of surfaces, wetting of adherends (bonded surfaces), and a good adhesive bonding process (curing and solidification).

The chemical inertness of Polyether-ether-ketone (PEEK) is very attractive for many applications; nevertheless, this inertness also causes massive difficulties with the bonding of PEEK to other materials. In order to cement PEEK, the adhesion must be improved without missing the bulk attractive properties of PEEK material. This can be reached by Alteration of polymer surface by means of some physical or chemical surface treatment methods.

The goal of any surface pre-treatment techniques is to improve the adhesive bond's durability and strength when it is subjected to environmental factors. The surface treatment includes cleanliness, degreasing, elimination of loose materials, physical and/or chemical alteration of the surfaces where an adhesive material is applied for bonding. In plastics material, surface preparation leads to improving the surface polarity, enhances surface wettability and creates areas for adhesive bonding. (98)

The research focus on the bonding properties between veneering material and framework using surface treatment and conditioning procedures is increasing, particularly when it relates to new materials such as PEEK. In the current study, the choice of different chemical and mechanical surface treatment methods aimed to assess the validity of the simplest and the most common techniques that could be used to enhance the bonding of PEEK to veneering composite resin.

The present study was in-vitro which is relatively effective in terms of cost and time compared to in-vivo studies. The aim of in-vitro studies is to be able to evaluate dental materials and particular factors in a controlled laboratory condition, with methods which are standardized and mimic clinical condition as closely as possible. (104) In vitro studies have some restrictions originating from the fact that testing the material in a laboratory condition is simplified and does not completely mimic the complexity of mechanical and physical performances of substructures, the biological environment of the mouth, or the force of chewing and the design of the restoration. This makes difficulty for direct comparison of laboratory results to clinical situations. However, in vitro studies should be considered as a test in expecting clinical performance. (104)

Bond strength can be examined by several test methods, each method is with advantages and disadvantages. These tests vary and involve tensile/micro-tensile (TBS/μTBS) bond strength test, shear/micro-shear (SBS/μSBS) bond strength test, and pullout tests. (105) the standardized test method for a durable bond strength of veneering composite to PEEK restorations has not been established. The most generally used methods for testing bond strength, including micro-tensile and micro-shear tests. (106) The most common restriction of these tests is the difficulty to apply the failure load on the surface of tested samples in the specific setup. The shear bond strength test was selected in the current study since this test is comparatively easy to perform, simple and can initiate shear stress, which is an important contributor to weakening and debonding of restorative materials. (106-108) Also, shear bond strength test is more suitable for assessing adhesive abilities of composite resin. Any modification in the surface treatment of the restorative materials may influence the shear strength, which is correlated to chemical and mechanical adhesion. (109)

However, stresses occurring at the bonded interface is more complex than the calculated load at failure and in the shear test method, forces close to the loading surface are more complex and much higher than pure shear load. (107, 108) In general, the SBS test shows lower bond strength than the TBS test method. Furthermore, some factors should be considered such as types of substrate, samples preparation, the frequency of load application, cross-section surface area, the experience of the investigator and storage conditions. (106)

Variations in bond strengths of veneering resin composite to PEEK are large and depend on the chosen test method. Results are not comparable, but they give an expectation of the obtained bond strength. (106)

The current study used air-abrasion procedures for the mechanical treatment and a sulfuric acid etching for the chemical treatment of PEEK surface, to investigate their influence on the retention and their capability to establish adhesion between PEEK and composites veneer.

According to the previous study examining the impact of various surface treatment on the bond quality of PEEK, Lubica H et al. (110) presented that bond strength of PEEK surface pre-treated with sulfuric acid etching was higher when comparing with air-abrasion, although airborne particle abrasion lead to improvement in micro-roughness, the functional benzene rings of PEEK are attacked by sulfuric acid, this chemical reaction led to production of more functional groups which bond with ingredients of the adhesive materials. Consequently, the improvement of surface energy and increase the diffusion of adhesive material into polymer can led to higher bond strengths. Another previous study, Shu S et al. (111) showed that application of sulfuric acid results in sulfonating of the functional benzene rings in PEEK molecules. As the result of these studies, the significance of chemical bonding on the polymer material was confirmed. However, the etching time effects the properties of the PEEK material, and over-etching has a damaging effect. In this study, PEEK specimens were etched by sulfuric acid for one minute, based on three other previous studies used this etching time for sulfuric acid and also achieved durable bond strengths. (64,112,113)

On other hand, Swift Jr EJ et al. (114) and Stokes AN et al. (115) recorded that surface treatment of PEEK with 98% sulfuric acid resulted in a highly porous surface and permeable to adhesive. Thus, the bonding strength was improved. However, nitric acid and hydrochloric acid solutions cannot modify the PEEK surface morphology regardless of the acid concentration. Some researchers reported that the bonding strength of an indirect resin composite etched by 9.6% HF gel to a luting cement was reduced. HF gel maybe results in the dissolution of exposed fillers on the surface. the resin matrix may also be softened because of The HF acid absorption. (115) PEEK is a resin material with high performance. Correspondingly, Hydrofluoric acid (HF) can selectively react with the silicon phase of a PEEK composite material ($6H2F2+ 2SiO2 \rightarrow 2H2SiF6+ 4H2O$) to produce tetrahedral fluorosilicate.

Most of the authors showed that etching by 98% sulfuric acid for 1 min is an efficient method for chemical Pre-treatment of the PEEK surfaces and improving the bonding activities of the PEEK material. (64,102,113,120)

In order to achieve a durable bond between PEEK restoration and composite, it is essential to enlarge the bonding surface for micromechanical retention. (110,116) Techniques to increase the roughness, and consequently, the bondability of PEEK is often restricted to machining, grinding or airborne particle abrasion. Air-abrasion by Al_2O_3 particles is the most widely used surface treatment method in dentistry and is considered an effective method of achieving micromechanical retention in PEEK to the composite or to the veneering composite. (110,116,117)

Michelle S et al**.** (118) have suggested that blasting PEEK surfaces with 50μm particles would allow sufficient micromechanical retention. However, it was observed that after 5 seconds of sandblasting the roughness parameters tends to stabilize whatever the particles size used. Bogna St et al. (64) showed that samples abraded with 110μm alumina produced higher roughness with lesser contact angles compared with the samples abraded with 50μm alumina. Subsequently, the bond strength values were higher for the group abraded with alumina particles, since the surface roughness of material has been stated to have an effect on the contact angle and bond strength. However, in 2017 the same author Bogna Stawarczyk et al. (119) reported that the size of powder particles used in the air-borne abrasion did not display any effect on the tensile bond strength. In our study, the blocks were blasted with 50μm Al_2O_3 particles for 10 seconds at a distance of 100 mm and with an air pressure of 5 bars, by gentle movements of the blasting nozzle perpendicular to the surface, according to the manufacturer's instructions.

In the current study, Visio.link treated specimens acted as a control group. It is important to mention that shear bond strength of untreated polished PEEK was not tested in present study. According to previous studies it has been reported that it is not possible to attain durable bond strength between composite and an untreated PEEK surface. (102,110,120) The selection of the tested adhesive was based on manufacture recommendation of the PEEK which suggests the usage of Visio.link to initiate sufficient bonding between PEEK surfaces and different veneering composite. Most of the authors reported very high bonding performances after the application of Visio.link as a conditioning material on different pre-treated PEEK surfaces. (103,112.121)

According to earlier studies (103,121), in the absence of an adhesive system, low bond strength value can be accomplished. The adhesive system had a strong outcome on the bonding behaviours between PEEK and veneering composite. Furthermore, the composition of the adhesive system has an effect on the chemical bonding of PEEK to composite resin. As a result of another study, Methylmethacrylate (MMA) monomers are stated to be very efficient for improving the bonding strength of PEEK to composite veneer. (64) Therefore, it can be supposed that MMA monomers caused the surface of PEEK to swell then the dimethacrylate monomers produced the linking to the composite resin with two carboxyl groups as binding sites.

This is also approved by the investigation of Kern and Lehmann (122) which reported that a strong bonding (14.5 ±2.6 MPa) to PEEK could only be accomplished using a resin containing multifunctional methacrylate on air-abraded PEEK surfaces to produce considerable chemical bonding with PEEK. Furthermore, in consideration of the composition of Visio.link adhesive and dialog bonding fluid, it can be supposed that the PETIA component has a high ability to change the surface of PEEK, consequently Visio.link adhesive gives arise to even and advanced bonding properties to PEEK restoration.

No recommendations are made for the viscosity of the composite veneer bonded to PEEK substrate. in general. Condensable materials should permit a better adaptation by pressure, while flowable composites moisten the surface of the material more efficiently. Against expectations and according to the results of earlier studies**,** Martin R et al. (116) and Bogna St et al. (123), recorded that the consistency of the veneering composite whether condensable or flowable, seemed to have no effect on bonding quality.

The results of the current study exhibited that there was a statistically significant effect on the shear bond strength according to the surface treatment, so the first hypothesis, that shear bond strength between composite and PEEK would be increased by PEEK surface treatment using acid etching, airborne-particle abrasion, and acid etching treatment after air-abrasion, was accepted. In this context, shear bond strength of more than 10 MPa was discussed to be acceptable. (124, 125) In regard to the obtained mean shear bond strength results higher than 10 MPa, acid etching and airborne particle abrasion plus acid etching of the PEEK surface may be supposed more viable surface treatment methods for the PEEK materials.

Based on the present results, the mean shear bond strength of the veneering composite to PEEK surfaces was the lowest in control group (5.39MPa) followed by air-abrasion treatment group (6.43MPa), air-abrasion plus sulfuric acid etching (11.72MPa) and sulfuric acid etching (13.43MPa) groups. As noted, sulfuric acid etching alone and in combination with air-abrasion produced the highest shear bond strength values while air-abrasion and no surface treatment produced minimum shear bond strength values. Another finding of the current study was the lower shear bond strength of the veneering composite to PEEK surfaces in air-abrasion plus sulfuric acid etching group compared to that following sulfuric acid etching alone, this result came in agreement with Hossein P et al. (126), who explained this by the absence of synergy between these two methods. While Lubica H et al. (110), disagreed suggesting that the combined use of the chemical treatment after air-abrasion showed significantly improved bond strengths (21.4 MPa) in comparison to the chemical treatment without air-abrasion (11.8 MPa). They have clarified two causes for this improvement. Firstly, the chemical surface treatment could not generate enough roughness, which is supposed to be an important factor in the bonding of the polymer in order to increase the surface contact area. Additionally, the wide contact area is associated with more functional groups following the chemical treatment, those groups are responsible for a better crosslinking of the polymer. Secondly, the surface morphology which created from the air-borne particle abrasion enhanced the mechanical anchorage of the adhesive due to the diffusion of adhesive into the polymer.

In contrast to the earlier investigation which was aimed to assess the impact of various surface treatment on PEKK bondability (127), bonding strength in our study was lower in air-abrasion groups. A possible clarification for that variance is that the air-borne particle abrasion more efficiently improving the wettability and roughness of the surface in PEKK compared to PEEK to provide more mechanical retention. Additional researches comparatively examining the influence of surface treatment methods on PEEK and PEKK are still required.

Air-borne particle abrasion by Al_2O_3 is known to increase the mean surface roughness θ, and coarser Al_2O_3 particles are known to create rougher surfaces. However, the PEEK surface/veneering composite interfaces treated by air-borne particle abrasion showed increased θ values with lower shear bond strength compared to sulfuric acid etching, suggesting that air-abrasion surface treatment procedure led to decreased wettability of the PEEK surfaces rather than the expected increase. This pheonemon is also evident in the literature (128), and this controversy was attributed to the characteristics of the wettability property being affected not only by the contact angle, but also by the surface chemistry.

Stawarczyk B et al, (116) reported that adequate surface roughness is significant for enhancing the bonding strength of dental plastic material and an adequate roughness of PEEK surface should be attained to produce good mechanical interlocking in the bonding procedure. Only a few numbers of surface roughening technique can be effectively used with PEEK because of its strength and hardness. However, in our study, the effects of the mechanical treatment were decreased and chemical reactions became dominant.

Air-borne particle abrasion mechanically modifies the PEEK surfaces with increased surface areas, whereas acid etching produces a chemically treated PEEK surface by enhancing the functional features of the PEEK. This enhancement is obvious with the development of more functional groups, once the benzene rings of the PEEK material break down due to the attack of the ether and carbonyl groups by sulfuric acid, this is also resulting in increased surface roughness values. (120)

Zhou et al, (120), showed increased the bond strength of Rely X Unicem and SE Bond/Clearfil AP-X to PEEK composite by etching with 98% sulfuric acid and treatment with argon plasma compared to no treatment, hydrofluoric acid etching and sandblasting which was in accordance with our findings. The reported bond strength values in their study ranged from 1.4MPa in the sandblasted group to 7.4MPa in sulfuric acid etching group. Their findings agreed with the current results and indicated optimal efficacy of sulfuric acid etching for enhancing the bond of composite resin to PEEK substrate.

Therefore, acidic solution is required as the PEEK is an inert polymer with high chemical resistance and low surface energy. (120)

It must be taken into consideration that sulfuric acid at such a high concentration (98%) is hazardous as it can cause serious damage upon contact. Thus, the application should neither be done chair-side nor by the technician. Also, industrially milling and pre-treatment of PEEK with 98% sulfuric acid may be a viable method. However, contamination of the pre-treated surfaces in the laboratory and the dental clinic prior to bonding must be avoided.

In comparison with a previous study (126) using the same test design and surface treatments to evaluate the shear bond strengths, bond-strength values attained in the current study for the air-abrasion plus sulfuric acid etching group and the acid etching treatment group without thermocycling are in the same range as those reported previously. However, Hossein P et al. (126) reported the mean shear bond strength of veneering composite resin to PEEK with acid etching was 30.42MPa, which was significantly higher than the results obtained in this study. In the present study, different manufactured products of PEEK were used. The PEEK specimen size and composite veneering thickness used in a previous study were different from that of the current study. The thickness of the veneering composite applied in the present study was two times larger than that study, so the greater size of the sample may slow down the polymerization reaction and decrease the bonding strength.

Due to the absence of standard laboratory conditions, accurate comparison of the results of different studies on the bond strength of composite veneer to PEEK surfaces is not feasible. Several factors, for example, the variable geometry of the samples, different modulus of elasticity of materials and variability in loading conditions can affect the bond strength values. Also, macro tests yield lower bond strength results due to larger bonded surface area compared to micro tests. (129)

In the present study, a strong difference was found between the different applied methods with Ra values ranging from 293.43±103.14 nm (without treatment) to a maximum of 1378/09±279.43 nm (Air-abrasion). the present investigation also supported by AFM analysis that clearly demonstrated a tendency of increased surface roughness and irregularities of PEEK after different surface treatment (Fig. 26).

As mentioned in earlier studies, surface roughness (Ra) was presented to have a significant role for the adhesive process and therefore several surface treatment methods were applied to increase surface roughness and contact area. (130,131) In shear bond strength testing, the roughness of the material related to a large extent to the strength of initial bonding. Nevertheless, based on the current results of AFM presented in (Fig. 26) (Table 9), the enhanced adhesive bond strength in shear bond strength by different surface treatment does not affect by the surface roughness of PEEK. The surface is more roughened by air-borne abrasion with Al_2O_3, while the higher shear bond strength was for the sulfuric acid etched group.

The achieved mean surface roughness values were 1378.09±279/43 nm for the air-abrasion PEEK surfaces, where the mean roughness values were 737.2±198/12 nm for the acid-etched PEEK surfaces. Lower mean shear bond strength values of the veneering resin/PEEK interface for the air abraded PEEK surfaces compared to the acid-etched PEEK surfaces might be associated with possible air voids in the air-abrasion PEEK surface during the resin veneering procedures, so additional studies are required to determine the ideal surface roughness value of the PEEK surface, since these voids may cause insufficient diffusion of monomers and veneering materials into the roughened PEEK surfaces. But the present data presented that roughening of the surface alone with air-abrasion or H_2SO_4 etching (or combination with H_2O_2) was not adequate to ensure a durable bonding between the veneering composite and the PEEK surface. Nevertheless, the data cannot be generalized because shear bond strength may mainly depend on the chemical attraction between Polyether-ether-ketone and specific tested systems. Variances in blasting time, as well as etching time and pressure, may lead contradicting results.

In the current investigation there was no statistically significant difference between shear bond strength averages of air-abrasion and control groups ($p>0.05$). However, in a previous study (116,121,122,132), the value of shear bond strength was higher for the air-abrasion group with alumina particles than that of the control group which explained as a surface roughening of material having an impact on the contact angle and shear bond strength. Irregularities of the surface increase the bonding area with the material to bond with, enhancing the mechanical retention and the bonding strength compared to smoother surfaces. However, these arguments cannot clarify the better shear bond strength of acid-etched specimens despite lower roughness. Because unfortunately, it is difficult to determine the type of chemical bindings that have been created between the composite resin and the activated acid etched PEEK surface on a molecular side, few studies have focused on PEEK were identified. This outcome may suggest that surface roughness would have an additive influence on the bond strength, but no significant improvement was observed.

As the result of the current study, the significance of chemical and mechanical processes on the polymer was emphasized, furthermore adhesion processes cannot be characterized by roughness measurements only so the second hypothesis, that micro-roughness of PEEK surfaces is the main factor to ensure durable bonding of veneering composite to PEEK was rejected. The complexity of interaction, surface topography as well as the mechanical and chemical process must also be considered. Therefore, a waiver of conventional bond test methods is not possible, more trial on this topic is required and clinical studies must be performed to support these results.

A general limitation of the current study is the material thickness of the veneering composite and the presence of the acrylic mold, which was used for the standardized bonding area to the PEEK surface. These factors can negatively affect the light intensity and the resulted bond strength. With regard to the actual test design, a comparison was only possible for values obtained in previous studies with the same test design. (121) (132-134)

From a methodological point of view, a shortening of the present study is the absence of artificial aging by water storage for a long-term or thermocycling. Thermocycling may influence the bond strength in two ways. On the first hand, a higher bond strength could be attained by the post-polymerization of the adhesive and the veneering composite resin. (135) On the second hand, thermal changes may result in mechanical stress caused by volumetric changes. (88) Therefore, cracks in the bonding area may originate, followed by a decrease in bond strength. Also, with regard to testing methodology, it may be that specimen geometry combined with shear bond testing parameters used may not accurately reflect the stress state observed in an actual prosthesis during function.

Clinical Significance

The test used in the present study does not simulate the reality of the clinical situation, because study was carried out in vitro conditions without chemical, physical, thermal and static (dynamic) stress, so the PEEK restoration in vivo subjected to these fatigue stresses over a longer period, in vivo may adversely affect the results. Therefore, more trial on this topic is required and clinical studies must be performed to support these results

7. CONCLUSIONS

- From the present study, we can conclude that

1. Surface treatment of the PEEK plays a significant role in improving its bonding ability with veneering composite, there was a significant difference between the shear bond strength of 4 groups ($p<0.05$). control group had the lowest SBS value (5.39±1.36), sulfuric acid etching group had the highest SBS value (13.43±1.42), air-abrasion had SBS value of (6.43±1.05) and air-abrasion plus acid etching had (11.72±1.69).

2. Since shear bond strength of more than 10 MPa is considered adequate, sulfuric acid etching and air-abrasion plus acid etching of PEEK surfaces may be considered as efficient surface treatment methods for the PEEK.

3. There was no significant difference between SBS values of control group (5.39±1.36) and air-abrasion group (6.43±1.05).

4. The roughening of the surface alone with air-abrasion or combination of air-abrasion with H_2O_2 was not enough to guarantee a durable bonding between the veneering composite and the PEEK surface.

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EDUCATION

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LANGUAGE

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PROFESSIONAL EXPERIENCE
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AWARDS AND RECOGNITIONS

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