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Master Thesis

Effect of surface treatment with aluminum oxide and plasma spray on shear bond strength between veneering resins and Ceramic filled PEEK versus Glass filled PEEK: An in-vitro study

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Abstract: In this study the effect of different surface treatments on the shear bond strength between PEEK and a composite resin was tested. Following ISO 10477 guidelines, two different PEEKs (ceramic & glass filled PEEK) were used by preparing 30 specimens of each type for 3 different surface treatment groups (reference, sandblasting and atmospheric plasma treatment). Bonding procedures started using visiolink adhesive followed by opaquer application then veneering resin. Surface roughness of the specimens was measured and scan electron microscopy (SEM) pictures was taken then thermal cycling for 5000 cycles between 5 and 55 °C in distilled water was done. Finally shear bond strength test was determined. Means and standard deviations were calculated using one-way ANOVA. Probability value (p-value) ≤ 0.05 was considered statistically significant result. Additionally, multiple comparison between different surface treatments of both types were done using POST HOC Tamhane. A statistically significant higher bond strength and surface roughness values were found only in sandblasting group in both types of PEEK. This was further confirmed with scan electron microscope. Sandblasting is still the best convenient method to provide good bonding of PEEK composites to veneering resins. Ceramic filled PEEK yielded higher bond strength than glass filled PEEK after sandblasting.

Keywords: PEEK, Surface pretreatment, Shear bond strength, SEM, Thermocycling, ISO 10477

1. Introduction

In construction of fixed and removable dental prostheses, different materials and techniques have been used to improve the function and esthetics of final restorations, as well as patient's satisfaction.

Metals like nickel chromium, cobalt chromium alloys and titanium are well known materials for framework construction in different dental prosthetic applications such as single unit or multi-unit's crowns, metallic removable partial dentures, definitive maxillofacial obturator, dental implant abutments and hybrid prostheses on dental implants.

Metallic frameworks offer good mechanical properties, high corrosion resistance and long-term survival rate. Unfortunately, some problems developed on the long term as discoloration at the margin of restorations, chipping or fracture of porcelain or acrylic veneering [1].

Zirconia is a metal-free alternative which has high optical properties, biocompatibility and mechanical properties. This material has the potential to address the esthetic problems encountered with metals and gained considerable interest as framework or full contoured restorations in fixed

dental prostheses. However, these materials couldn't solve completely all the problems associated with metals. Moreover, they introduce their own set of related problems such as higher cost, framework fracture, abrasion of remaining natural dentition and high rate of chipping of veneering than porcelain fused to metal restorations [1]–[4]. These complications will increase the need for repair, increase number of patient visits and finally will increase the cost of overall treatment and maintenance [5].

The continuous development and enhancement of materials used in dentistry and their applications gave rise to a new group of dental materials which solve specific problems in dental clinics especially in the field of prosthetic dentistry. Among these, Polyetheretherketone (PEEK) which is introduced recently as non-metallic replacement of metal or zirconium frameworks in different fixed and removable prosthetic applications [6].

Historically, most polymer-based frameworks needed to be bulky to attain a certain strength. On the contrary, PEEK offers high strength and can be constructed in thinner section without affecting its strength which is advantageous in producing light weigh restorations that is more comfortable to the patients [6].

PEEK frameworks can be fabricated very easily via computer aided design/computer aided manufacturing. In case of metals, the milling process is very time consuming and the life span of milling burs is short, while milling of ceramics and zirconium is sensitive as it can affect adversely their mechanical properties. Unlike metals or ceramics, PEEK provides perfect balance as it is not time consuming nor technique sensitive [6].

Because of its high mechanical properties and their advantages during fabrication, PEEK became recently the material of choice for construction of single crowns, fixed bridges, removable partial denture frameworks, dental implants and abutments [6].

PEEK is more esthetically acceptable than metals and its low translucency is adequate in most dental applications. However, in situations where maximum esthetics is required, PEEK should be veneered with more translucent and esthetic materials as veneering composite resins. Unfortunately, PEEK has an inert hydrophobic surface which needs to be treated before bonding to avoid shipping of veneering material in clinical applications [6].

A question thus arises, what is the effect of different surface treatments on shear bond strength of PEEK and veneering resins.

2. Review of literature

2.1. Definition

Polyetheretherketone (PEEK) is a polyaromatic semi-crystalline linear polymer and a member of a big family of polymers called Polyaryletherketone (PAEK), these polymers consist in general of an aromatic backbone molecular chain interconnected by ketone and ether functional groups between aryl rings. PEEK monomer polymerizes via step-growth dialkylation reaction of bis-phenolates to form poly-ether-ether-ketone. Commonly, PEEK can be synthesized via the reaction between 4,40-difluorobenzophenone and the disodium salt of hydroquinone in a polar solvent such as diphenyl sulphone at 300 °C [6]. PEEK can be modified either by the addition of functionalized monomers (pre-polymerization) or by chemical processes such as sulfonation, amination and nitration (post polymerization) [6].

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Owing to their chemical structure, PEEK has a good combination of strength, stiffness, toughness and chemical resistance [6], [7]. Therefore, they are known as high performance thermoplastic polymers [8].

2.2. Properties of Polyetheretherketones

PEEK has excellent biological and mechanical properties. It shows good stability at high temperatures (exceeding 300 °C), high chemical resistance in corrosive environment and resistance to radiation damage, compatibility with many reinforcing agents such as glass and carbon fibers, chemically inert and insoluble in nearly all organic and inorganic solvents at room temperature, greater strength weight ratio and high wear resistance than polymethylmethacrylate (PMMA) & composite resins. All these characteristics make PEEK a highly attractive material in medical and dental applications as well as industrial applications such as aircraft and turbine blades [8]–[10].

Regarding biocompatibility, PEEK is a highly biocompatible material as it can resist degradation and does not induce any mutagenic or cytotoxic activity [11]. PEEK is also considered as bioinert material, this is advantageous since it does not cause any adverse reaction nor release any ions or constituents to the human tissues [8]. On the other hand, the hydrophobic nature of PEEK surface decreases cell adhesion and protein absorption which subsequently can reduce the wound healing capacity during osseointegration [12].

Studies tried to overcome this issue by enhancing the PEEK surface to stimulate cell attachment and proliferation through coating or incorporating bioactive materials such as hydroxyapatite into PEEK. [8], [12]– [14].

As for water solubility, PEEK has a water solubility of 0.5 % but as mentioned earlier it is not chemically damaged by long-term water exposure, even at temperatures of up to 300 °C [8]. Furthermore, PEEK showed the lowest solubility and water absorption values under different aging solutions as sodium chloride, artificial saliva, physiological saliva, and distilled water [15].

Concerning thermal stability, the thermal stability of PEEK has been studied because of its high temperature industrial applications and processing conditions. It exhibits a melting point around 335 °C. Studies have shown that thermal degradation occurs in PEEK at temperatures between the glass transition 143 °C and melting transition 340 °C. So to avoid production of degradation products, the processing temperature of PEEK should be below glass and melting temperature [8].

In respect to sterilization of PEEK, the chemical structure of PEEK ensures that they are extremely stable against hydrolysis even at elevated temperatures. Therefore, repeated sterilization using pressurized steam as autoclaving is possible without degrading their mechanical properties [8], [16]. PEEK shows also high resistance to gamma and electron beam radiation consequently using gamma radiation and ethylene oxide as a means of sterilization for some medical devices shows no deterioration for PEEK and its carbon composites [8], [16].

Radiographically, Medical imaging methods such as computer tomography (CT) and magnetic resonance imaging (MRI) are not metal friendly and the presence of metallic objects in the area being scanned can create artifacts and affect negatively the quality of the resulting images. PEEK polymers are compatible with modern imaging technologies as they inherently radiolucent which is beneficial during follow up of implant surgeries [8].

2.3. Types of PEEK used in medical and dental fields

The aim of adding fillers is to improve its mechanical and biological properties to suit more the different needs in biomedical and industrial applications [9]. PEEK with the added fillers produce

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composites. Each composite has its unique physical, bioactive, and mechanical properties [8]. There are several types of PEEKs according to type of fillers and additives used to modify or reinforce them.

1- Unfilled PEEK

Unfilled PEEK is not reinforced general-purpose grade that offers steam and wear resistance. It provides the greatest elongation and toughness of all PEEK grades. It also is well suited for seal components where ductility and inertness are important [8].

2- Carbon-Fiber Reinforced PEEK (CFR-PEEK)

Carbon fillers were among the first reinforcement additives for PEEK to increase its strength and stiffness. The addition of 30 % carbon fibers enhances the compressive strength, stiffness, wear-resistance and load-carrying capability of PEEK while dramatically lowering its expansion rate. This grade also provides greater thermal conductivity than unreinforced PEEK, allowing for increased heat dissipation from bearing surfaces. CFR-PEEK biomaterials are used in dental implants and medical implant for spine fusion and joint replacement [8].

3- Glass-Fiber Reinforced PEEK (GFR-PEEK)

The addition of glass fibers increases the strength and modulus of elasticity of PEEK. This grade is especially good for structural applications that require greater strength, stiffness, or stability especially at higher temperatures as in aircraft and train industry. Medically, glass fiber fillers enhance bioactivity of PEEK through proliferation and osteocalcin production of human osteoblastic cells [16,17].

4- Ceramic filled PEEK

Ceramic Fillers significantly improve its mechanical properties and machinability. It allows for production of different white shade grades which are more aesthetic than opaque carbon filled PEEK. The fine granularity of the filler is the basis for the extremely good polishing properties. The deposit of plaque is prevented and the degree of discoloration is reduced due to the fact that the surfaces are polished to a high shine [18].

5- Bioactive PEEK

Bioactive fillers such as hydroxyapatite, β-tricalcium phosphate, titanium , calcium silicate, strontium containing hydroxyapatite, nano-fluorohydroxyapatite, nano-hydroxyapatite and carbon fibers and 3-D braided carbon fiber are added into PEEK to improve biological and mechanical properties of medical and dental PEEK implant [8,9].

6- Radio-opaque PEEK or image contrast PEEK

Radio-opacifiers such as barium sulfate are incorporated into PEEK to improve visualization and contrast in medical imaging. This is useful for imaging PEEK implants and are used nowadays in spinal implants [8].

2.4. Processing of PEEK

PEEK can be processed and prepared through different techniques including injection molding, extrusion, compression molding, powder coating and milling of previously pressed PEEK blanks. This allows for flexibility in manufacturing different designs of medical and dental devices [8], [19].

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In dental field, PEEK can be processed by two methods. The first approach is pressing the PEEK material in the form of pellets or granules utilizing a special vacuum-pressing machine in a dental laboratory. In this method, a preheated muffle with the press plunger is placed into the vacuum-pressing device and pressed [8].

Another approach is milling using computer aided design and manufacturing technologies (CAD/CAM) where PEEK blanks are prepressed under standardized parameters such as pressure, temperature and time [20].

2.5. Applications of PEEK

In general fields, PEEK and its composites are good candidates in structural applications in aerospace, biomechanics, automotive, electrical & chemical industries [21]–[24]. In medical field, it was first introduced as effective biomaterial for medical implants in April 1998 (Invibio Ltd., Thornton-Cleveleys, UK) [25]. Since then, PEEK has been increasingly applied in every area where titanium is being used. Titanium and alloys suffer from potential ion release and significantly higher stiffness than that of the adjacent cortical bone by a factor of 10 to 20 times. This stiffness mismatch can lead to bone resorption because of stress shielding which can finally lead to reoccurrence of fracture. Compared to stainless steel and titanium, PEEK implants have the advantages of bio inertness, weight reduction and compatibility with different x-ray imaging techniques [8], [16], [19], [26].

CFR PEEK has many medical applications that interact with bone such as compression bone plates, bone screws, intramedullary nails, hip prostheses, joint replacement systems, implants in cranial and spinal surgery especially for cages used in vertebral fusion surgery [27]. Suture anchors in applications such as anterior cruciate ligament repair [8].

Current developments and application are in cardiovascular field as a replacement of heart valves and pacemaker devices. Also, it can be used as intracardiac pumps for minimal invasive surgery [16], [28]. Another application in craniofacial fields where patient-specific craniomaxillofacial implants such as skull plates can be formed of PEEK through computer-aided design and computer aided manufacturing technologies which perfectly matches the defect area [28]–[30].

In dental field, there is an increased demand for metal-free restorations because of increased demand for aesthetics. PEEK became a promising material as non-metallic replacement in many dental applications owing to unique mechanical and physical properties. In addition, these polymers are cheaper, lighter in weight and easier to work in dental laboratories compared to titanium or ceramics.

1- Dental implant

As previously mentioned, titanium implants have an elastic modulus significantly 10 times (110 GPa) higher than that of the cortical bone (approximately 18-30 GPa). This mismatch causes overloading resulting in bone resorption and implant loosening and finally failure [6], [9]. Other complications also associated with titanium implants like hypersensitivity, ion leakage and compromised esthetic in cases of thin biotype gingiva where the implant appears as dark shimmer. So, it became necessary to search for alternative materials as zirconium and PEEK [31].

- Stress shielding of PEEK

The major beneficial property of PEEK is its lower Young's (elastic) modulus which is close to human bone. The unfilled PEEK has a modulus of elasticity 3 - 4 GPa while for example carbon reinforced PEEK has an increased modulus of elasticity up to 18 GPa which is more comparable to those of cortical bone [6], [9]. PEEK also showed long term dimensional stability under cyclic loading tests that replicate mastication process [32]. So, these polymers being biocompatible with excellent

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mechanical properties could exhibit lesser stress shielding when compared to titanium when used as an implant material [6].

Regarding the stress shielding of PEEK implants, finite element analysis (FEA) of carbon-fiber reinforced PEEK (CFR-PEEK) studied the stress distribution in the region of the peri-implant bone in four different models composed of titanium abutment with implant, CFR-PEEK abutment with titanium implant, titanium abutment with CFR-PEEK implant, and CFR-PEEK abutment with implant. The results showed that distribution of the stresses is more homogenous with titanium in relation to the CFR-PEEK implant due to the smaller deformation of this material. Moreover, CFR-PEEK implant are not advantageous than the titanium implant regarding stress distribution to the peri-implant bone [33]. On the contrary, another FEA of carbon-fiber reinforced PEEK implants concluded that they could induce lesser stress shielding than titanium [6], [34].

Because PEEK dental implants have not been used widely in clinical practice, there is still controversy if there is a difference between the bone resorption around PEEK and titanium implants in human subjects. As a result, there is an obvious need for clinical trials to conclude whether or not PEEK implants produce lesser stress-shielding than titanium implants [6]. If PEEK implants are proven to produce more stress shielding, then further researches are needed to improve the biomechanical behavior for more homogenous stress distribution to the surrounding bone [35].

- Bioactivity of PEEK

As to bioactivity of PEEK implants, unmodified PEEK is bioinert with hydrophobic surface and shows limited inherent osteoconductive properties [36]. Therefore, different methods have been suggested to improve the bioactivity of PEEK [31], [37 – 45].

The first approach is surface modification where PEEK surface is activated through surface treatment alone or in combination with a surface coating. The surface modification of PEEK includes physical treatment through plasma using different gases like oxygen, nitrogen, ammonia and argon. chemical treatment through wet chemistry as sulfonation, amination, fluorination and nitration [6], [46], [47].

Surface coating can be done by many techniques as cold spray technique, radio-frequency magnetron sputtering, spin coating techniques, aerosol deposition, ionic plasma deposition, plasma immersion ion implantation and deposition, electron beam deposition, vacuum plasma spraying, physical vapor deposition, and arc ion plating. The second approach is impregnating bioactive materials into PEEK substrate to produce bioactive PEEK composites [31], [41], [48].

An in-vivo study conducted on rabbits where PEEK implants with nanocoating of HA of 20–40 nm thickness were used. After 12 weeks follow up, histological sections showed osseointegration of PEEK implants and higher bone implant contact values of test implants compared to controls uncoated PEEK implant [49]. Another study conducted on dogs showed an osseointegration of PEEK implants optimized with carbon fillers and nanohydroxyapatite composite to improve its mechanical properties as well as bioactivity. After 8 weeks follow up, the implants were well osseointegrated with no resorption of bone around the implants [50].

PEEK implants demonstrated that they are biocompatible and offer favorable osseointegration which is promising as a dental implant material. Yet, the numbers of in vivo animal and human studies are still limited and not enough to make conclusions for clear recommendation as dental implants [51].

2- Implant fixed structures

Implant bars, abutments combined with titanium base can be made of PEEK [52]–[54]. Because of its biocompatibility, PEEK can be used as implant healing abutments without change in oral microbial

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flora attachment to the abutment as compared to titanium, zirconia and polymethylmethacrylate (PMMA) abutments [55]. Moreover, there is no increased risk for marginal bone loss and soft tissue recession during the healing period [56,57]. PEEK can be also used as a temporary abutment which is cost-effective and easily modified, supports a provisional prosthesis that is delivered at the time of implant placement [58, 59].

3- Orthodontic wires

A study assessed the properties of PEEK as non-metallic orthodontic wire and the results showed that PEEK has good esthetics and low water absorption. In addition, it offered the highest bending strength and creep resistance at 1.0×1.0 mm cross sectional area and it can deliver orthodontic force similar to NI-TI wire [60].

4- Maxillofacial implants & prostheses

Maxillofacial defects can result from trauma, surgical resection of neo-plastic disease, infection and congenital or developmental deformities. Some defects are large & complex which necessitate the use of alloplastic materials and autogenous bone to rebuild the facial skeleton [61]. A case series described the use of prefabricated PEEK implants for reconstruction of extraoral maxillofacial defects as orbitomaxillary, superior orbitocranial and anterior table of frontal sinus defects [29], [61]. As for intraoral defects, PEEK can be used as a framework for the construction of a removable obturator [62].

5- Removable prostheses

PEEK has the advantages of high strength, low weight, more esthetics when used as a framework in removable prostheses. It can be used as a framework in removable dentures through computer-aided design and computer-aided manufacture systems or vacuum pressing technique [6], [63,64]. Retention clips made of PEEK can be used in implant retained dentures [65]. Also, denture retentive clasps made of PEEK can provide adequate retention which is maintained for significant time period of usage [66]. PEEK can be also used for construction of secondary crowns in telescopic overdenture prosthesis [67].

6- Fixed prostheses

In fixed prosthodontics, PEEK can be used as coping or substructure in single crowns or bridges [68, 69]. It can be constructed via Vacuum pressing technique or CAD/CAM technology [6]. The CAD-CAM milled PEEK fixed dentures have a fracture resistance higher than those of lithium disilicate glass-ceramic, alumina and zirconia [6]. Also PEEK has high abrasive resistance which is competitive with metallic alloys [70].

- Benefits of PEEK in prosthodontics

As previously mentioned, PEEK provides high strength, low weight, biocompatibility, ease of construction and compatibility with modern imaging techniques. Beside these properties and as the applications of PEEK expands more and more in the field of prosthodontics, discoloration of any dental prostheses over a certain period is evident [71]. A study assessed the discoloration and the stain removal potential of PEEK, PMMA and composite materials after their storage in different staining media. The results showed that PEEK has significantly lowest discoloration over all different coloring media as compared to PMMA and Composite which is another important benefit of PEEK [71].

- Drawbacks of PEEK in prosthodontics

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As described PEEK suffers from inherent drawbacks mainly its low translucency and grayish discoloration which limits their applications when high esthetics is required as in anterior restorations. The solution was layering the surface of PEEK with veneering composite resins but unfortunately this material has a chemically inert and hydrophobic surface with low surface energy. This raised difficulties toward achieving good bonding with veneering resins.

2.6. Surface treatment of PEEK

Nowadays, there are several methods of surface treatments to modify polymer surfaces for different biomedical applications. This allows for improvement of surface bioactivity and cell adhesion for better osseointegration and improvement of bonding to polymer surfaces. Treatments fall into three main categories chemical treatments like (solvent degreasing and chemical etching), mechanical treatments as (paper abrasion and sandblasting) and finally physical treatment such as (plasma and laser treatments).

1- Chemical surface treatment

Chemical treatment of surfaces aims to increase surface roughness for better micromechanical bonding and create new chemical/functional groups at the surface. Different chemicals have been used for etching including sulfuric acid, hydrofluoric acid, piranha solution (which is mixture of sulfuric acid and hydrogen peroxide). The type of acid used and duration of etching affect the surface topography & amount of roughness produced which eventually change the bonding characteristics [72].

2- Sandblasting surface treatment

Sandblasting or air abrasion are one of the most competitive methods for preparing thermoplastic material surfaces before adhesive bonding. Sandblasting changes the surface morphology and creates micro roughness that provides micromechanical interlocking with adhesives that ultimately increase bond strength [73]. This treatment has the advantages of low cost and convenience. It consists of projecting fine abrasive particles at high velocity to clean or etch a surface. Different conditions of sandblasting can be obtained by varying projection time, particle size and pressure [73]. Different particles are used for sandblasting but the most common are alumina particles (Al_2O_3) which have an irregular shape with abrasive angles and available in three different particle sizes 50 μm, 110 μm and 250 μm [73].

3- Plasma surface treatment

Plasma is defined as the fourth state of matter [8]. It is an ionized gas with an equal density of positive and negative charges in given volume. It can exist over an extremely wide range of temperature and pressure [74,75]. It is formed when supplied energy ionizes the gas used during the treatment which release the ions from their atoms within a gas [76]. In general, plasma has two main applications in dentistry. Firstly, plasma shows antibacterial effect to variety of microorganisms therefore it can be directly applied on human living tissue for disinfection & decontamination purposes without producing resistant bacteria nor inducing toxic side effects. Secondly, plasma can be used as surface treatment method to improve quality of dental materials needed for their subsequent special dental applications [77].

There are two types of plasma, hot (thermal) plasma which refers to the high temperatures and the high degree of ionization within the gas and used for depositing hard and passivating coatings. Cold (non-thermal) plasma is performed at low temperature and require low pressure. A vacuum chamber is used to maintain the pressure and to supply different gas feeds. Treatment depend on vacuum chamber geometry, gas used, gas flow rate, and electromagnetic parameters input power [76].

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In dentistry, cold plasma surface treatment is used to etch surfaces or coat surfaces by deposition. The deposited films are chemically bonded, resistant to delamination and very thin with thickness of 200 to 2000 nm [76,77].

Plasma treatment is not limited to polymers, it can also be used on ceramics and metals. This method can modify different types of surfaces including chemically inert ones, without affecting the bulk chemistry [76].

- Effect of plasma on polymer surfaces

There are four main effects of plasma on surfaces. These effects always occur to some degree. However, one effect may be favored over another depending on substrate chemistry, reactor design, gas chemistry, and processing conditions.[74,75]

1- Cleaning of the polymer surfaces

Any surface is contaminated even after any cleaning process that ends with a liquid rinse, which results in decreased bonding strength. Plasma can remove all organic contamination from inorganic surfaces and polymers, This results in hyperclean surfaces which provide very reproducible bonds and stronger bonds than normally cleaned surfaces [74].

2- Ablation (micro-etching) of the polymer surface

Ablation is low molecular weight removal for the cleaning of badly contaminated surfaces. It is effective in removing weak boundary layers formed during the fabrication of polymers. This results in an increased surface area and can improve micromechanical bonding [74].

3- Crosslinking of the polymer surfaces

This feature occurs in polymer surfaces exposed to plasmas which are effective at creating free radicals like noble gas plasmas. Helium and argon are crosslinking plasmas when they are used in the total absence of oxygen or other free radical scavengers. These free radicals can migrate across polymer chains and react with other radicals resulting in branching and interconnection of chain molecules (crosslinking). This improves the heat resistance and cohesive strength of the surface. also, it can act as a barrier layer hindering diffusion across the interphase [74].

4- Activation of polymer surface

Activation is the process of increasing surface energy, wettability plus addition of functional groups [74]. This is very useful in medical and dental implant applications where surface activation can result in an increased cell adhesion and improved osseointegration. Polymers have inherently low surface-energy which hinders the wetting and interaction with adhesive systems. Plasma increases the surface energy which in turn improves wettability of the polymer's surface. This means that the adhesives can wet the polymer's surface with less voids in the bond line and improve much their bonding quality [74,75].

Plasma also adds polar functional groups on the surface. These chemical groups can interact with adhesives and improve bonding. Oxidizing gases like O_2, Air, H_2O, N_2 act as scavenger and remove organics by oxidation and leave oxygen in the polymer surface. Reducing gases like H_2 or H_2 mixtures can replace fluorine or oxygen from surfaces and can remove organics from surfaces that are sensitive to oxidation. Noble gases as Argon or Helium generate free radicals in surfaces to cause crosslinking. Active gases as NH_3 will leave amino groups in the surface that can react covalently with adhesives [74].

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2.7. The effect of surface treatment on bond strength

Different studies focused on how to modify PEEK surface to achieve highest bond strength and durability with the veneering resin. Furthermore, they introduced the previously mentioned methods for surface treatment of PEEK which included chemical treatment, air abrasion and plasma surface treatment.

Sproesser et al [78] investigated the effect of different etching durations with sulfuric acid on the shear bond strength between PEEK and different luting resin cements. PEEK specimens were milled and etched with sulfuric acid for 5, 15, 30, 60, 90, 120, and 300 seconds. Then luted with one of the following resin cements RelyX ARC, Variolink II and Clearfil SA. Specimens were stored in distilled water for 28 days at 37 °C and shear bond strengths were measured. It was noted that the highest bond strength of the 3 resin cements occurred with etching durations up to 120 seconds. Moreover, etching duration of more than 120 seconds resulted in decreased bond strength measurements. Specimens of the non-etched control group demonstrated no bond strength to resin cements. This study demonstrated that sulfuric-acid etching can improve bond strength of resin cements to PEEK surfaces. However, chemical treatment cannot be used in dental clinics due to the hazardous effect of sulfuric acid.

Stawarczyk et al [79] examined the effect of two different acids (sulfuric acid and piranha acid) on the tensile bond strength between PEEK and two different veneering resins (Sinfony and Vita VM LC) after application of 2 different adhesive systems visio.link and signum PEEK bond. Specimens were stored in distilled water at 37 °C for either 24 hours or 60 days before bond testing. Higher bond strength measurements were obtained after adhesives application than control group but in general the results didn't show significant improvement in bond strength compared to untreated groups.

Kern et al [80] examined the effect of air abrasion on the tensile bond strength and durability between PEEK and provisional resin (Luxatemp Fluorescence). Different techniques of chair side air abrasion were used 110 μm alumina particles (Rocatec pre) and tribochemically silica-coated particles (Rocatec plus). Also, different adhesive systems were applied (Ecusit Composite Repair, Luxatemp Glaze & Bond, Clearfil Ceramic and Espe Sil). Artificial aging by storage in distilled water at 37 °C either for 3 days without thermal cycling (TC) or for 150 days with additional 37,500 thermal cycles between 5 and 55 °C with dwell time 30 seconds. The results showed that strong and durable bond can be achieved when Luxatemp Glaze & Bond adhesive and alumina 110 μm air abrasion (Rocatec pre) were used.

Stawarczyk et al [81] investigated the effect of different adhesives only on tensile bond strength (TBS) between one type PEEK and different veneering resins. The used adhesives were Z-Prime Plus, Ambarino P60, Monobond Plus, Visio.link, Signum PEEK Bond and control group without treatment. The applied resins were Sinfony, GC Gradia and VITA VM LC. All specimens were pretreated with air abrasion using 50 μm aluminum oxide particles. After bonding, half of each group was tested directly and the other half was thermo-cycled. The results showed that pre-treatment and Z-Prime Plus and Ambarino P60 gave 0 TBS values. While The highest TBS before and after thermo-cycling between PEEK and all tested veneering resins was observed for groups pretreated with Visio.link and Signum PEEK Bond.

Fuhrmann et al [82] studied the effect of different adhesive systems on the bond strength between luting resin cement (multilink automix, Ivoclar vivadent) and three types of PAEK (glass fiber filled PEEK, crystalline PEKK and amorphous PEKK). Surface treatment was done using air conditioning by alumina particles (Rocatec pre, 3M) and Tribochemical silica-coating (Rocatec soft, 3M). The used adhesive systems were primer Luxatemp Glaze & Bond - universal primer Monobond Plus. Then long-term storage and thermal cycled between 5 and 55 °C for 10,000 times (30 days) or for 37,500

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times (150 days). Results showed that glass fiber-reinforced PEEK exhibited higher bond strengths in all groups and at all three storage times than crystalline and amorphous PEKK.

Stawarczyk et al [83] investigated the effect of different adhesives & sandblasting surface treatments on the tensile bonding strength (TBS) between composite resin and PEEK. The five applied air abrasion methods were 50 μm Al_2O_3 (0.05 MPa), 50 μm Al_2O_3 (0.35 MPa), 110 μm Al_2O_3 (0.05 MPa), 110 μm Al_2O_3 (0.35 MPa), Rocatec 110 μm (0.28 MPa). These pretreatments were combined with the following different adhesive applications visio.link - Monobond Plus/Heliobond - Scotchbond Universal and dialog bonding fluid. Then aging for 28 days in distilled water at 37 °C plus thermocycling for 20,000 cycles at 5/55 °C. The results showed that grain size of the air-abrasion powder has no effect on bond strength in contrast to air abrasion, pressure & adhesives which had a major impact on TBS. Surface treatment with 110 μm Al_2O_3 and 0.05 MPa resulted in higher survival rates compared to other groups. Visio.Link showed the highest survival rates and the TBS values higher than 25 MPa independent of the pretreatment method.

Schmidlin et al [84] assessed possible bonding techniques of PEEK to dental composite resin materials. PEEK discs were treated by etching with sulfuric acid, sandblasting with 110 μm, sandblasting with 50 μm, sandblasting with Rocatec system. The composite materials were 3M universal composite resin cement, hybrid composite resin and the used adhesive was Heliobond. Following bonding procedures, the specimens were stored in distilled water at 37 °C for 24 h. Surface roughness increased with all treatment conditions. Results showed that there was no adhesion with resin cement after sandblasting surface treatment while high bond strength measurements found with chemical sulfuric acid treatment. PEEK bonded to composite resin after adhesive applications showed high bond strength measurements after sandblasting with alumina 50 μm and Rocatec system while higher values obtained with sulfuric acid pretreatment.

Keul et al [85] examined the effect of two surface treatments (chemical and air abrasion). PEEK specimens were either treated with air abrasion 50 μm or etched with piranha solution or both air abrasion followed by piranha acid etching or untreated. Different adhesives were used for bonding procedures including heliobond, visiolink, clearfil ceramic primer and Signum PEEK bond. The results showed higher surface energy and surface roughness with air abrasion group and air abrasion/piranha acid etching group. Higher bond strength measurements resulted after air abrasion only while highest bond strength measurements occurred when combining the air abrasion and chemical treatment.

Hallmann et al [86] examined the effect of two surface treatments chemical and air abrasion on the bond strength between PEEK and resin cement RelyXUnicem. The treatment groups were control specimens (no treatment), piranha solution etching, abraded with 50 μm alumina particles followed by piranha etching, abraded with 110 μm alumina particles and piranha etching, abraded with 30 μm silica-coated alumina particles and piranha etching, abraded with 110 μm silica-coated alumina particles and piranha etching. The adhesives used were Heliobond and Clearfil Ceramic Primer. Each specimen was stored in distilled water (37 °C) for 3 days. The results showed that the highest bond strength of 21.4 MPa was obtained when air abrasion with 50 μm alumina particles followed by etching with piranha solution was used with the application of Heliobond. Control group PEEK didn't bond with composite resin. Tribochemical silica coated/etched PEEK surfaces did not influence the bond strength.

Rosentritt et al [87] studied also the effect of chemical treatment and sandblasting on shear bond strength between PEEK and veneering composite. PEEK surfaces were untreated, etched (H_2SO_4 98 % 1 min; H_2O_2/H_2SO_4 1:130 s), air-abraded with Al_2O_3 (50/120 μm, Harnish & Rieth, G) or abraded with silica-modified alumina oxide treatment (Rocatec 30 μm/110 μm, 3 M, USA). Surface roughness (Ra) was determined after different treatments. After surface treatment, different dental surface conditioning was applied including Espe Sil, signum connector, solidex solibond, composite primer,

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New outline primer, clearfill alloy primer, clearfill ceramic primer, new outline adhesive, metal bonder, Cera resin bond 1+2, ML primer, metal primer 2, plaquit adhesive, zirconium bond 1&2. In addition, 2 different opaquer was applied standard and flowable. Aging in distilled water for 24 hours and for 90 days plus thermal cycling for 12000 cycles was done. Results showed that etching with sulfuric acid increased significantly roughness in comparison to other groups. Highest bond strength was achieved after sandblasting with 50 μm alumina and application of signum connector adhesive in combination with opaque application.

Silthampitag et al [88] evaluated the effect of four different surface treatments on the bond strength between PEEK and composite resin. The surface treatments were etching with 98% sulfuric acid, etching with piranha solution and sandblasting with 50 μm alumina and control no pretreatment. The Bonding was done in two subgroups with and without adhesive. The adhesive used was Heliobond and composite resin used was flowable composite Z350XT 3M. The highest bond strength was in the group etched with 98% sulfuric acid and bonded with Heliobond.

Stawarczyk et al [89] tested the shear bond strength of PEEK to two self-adhesive resin cements (RelyXUnicem and Clearfil SA) after Helium plasma treatment and adhesive Bond application. 3 different adhesives were used Visiolink, Signum PEEK and Ambarino P60. Subsequently, all bonded specimens were stored in water for 24 h at 37 °C and two groups were further thermally cycled for 5,000 or 10,000 cycles respectively. The results showed that plasma treatment couldn't improve the bond strength by itself and in addition with an adhesive.

Zhou et al [90] studied the effect of 3 different surface treatments sandblasting, plasma treatment and chemical treatment on the bond strength between PEEK and two different composite materials. PEEK specimens were divided into 5 groups. First group etched sulfuric acid, second group etched with hydrofluoric acid, third group treated with argon plasma, fourth group is treated with 50 μm alumina air abrasion and lastly fifth untreated group. This study used RelyX Unicem resin cement and SE Bond/Clearfil composite system. After bonding, all specimens were stored in distilled water at 37°C for 24 h. Higher values of the bond strength of PEEK to resin were resulted after sulfuric acid surface treatment and argon plasma.

Schmidlin et al [91] studied the effect amine functional groups created on the PEEK surface by addition of amino acids (glycine) on the bond strength with two resin cements (RelyX Unicem or Clearfil SA). Plasma surface treatment with helium and different adhesive material (soft-liner liquid, Visio.link, Ambarino P60) were used in this study. After bonding specimens were stored in distilled water at 37 °C then half of the specimens was removed after 24 hours and the tensile bond strength was tested, whereas the other half was additionally aged for more 14 days and thermocycled for 10,000 cycles. Helium plasma pre-treatment without glycine showed no impact on initial TBS. Combining between glycine application and Softline/Ambarino P60 allowed for significantly higher initial TBS was measured after helium plasma treatment. However, this effect was no evident after thermo-cycling. All groups conditioned with visiolink showed the highest TBS values.

Schwitalla et al [92] studied the effect of cold low pressure argon/oxygen plasma treatment with and without previous sandblasting on the shear bond strength between PEEK and veneering composite. Three types of PEEK were used unfilled PEEK, titanium oxide filled PEEK and pigment powder filled PEEK. Vita Vm Lc veneering composite was used and Visiolink was the chosen adhesive. Four groups were made untreated, plasma treated, sandblasting, sandblasting followed by plasma treatment. Surface roughness and contact angle measurement were made after each treatment. The specimens were stored in distilled water for 24 hours before shear bond testing. The results showed that plasma significantly reduced the contact angle while sandblasting increased significantly the contact angle. Plasma reduced surface roughness while sandblasting increased surface roughness in comparison to control group. Highest bond strength was found in the group treated with

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sandblasting followed by plasma. Moreover, unfilled PEEK showed highest bond strength results in comparison to the other two PEEKs.

2.8. Bond strength measurements

Interfacial bond strength can be assessed by a variety of methods including laboratory tests and clinical performance. While clinical trials are the best methods for evaluating dental restorations, they cannot identify the exact reason for failure due to the presence of confounders and diverse stresses on restorations within the oral cavity [93]. On other hand, laboratory tests are effective to gather data quickly and easily on a selected parameter or property. It is possible to test one specific parameter while keeping all other variables constant [94]. So, laboratory tests can only predict the behavior of material in clinical application

The laboratory bond strength tests can be static or dynamic tests [93]. In static tests, specimen is stationery upon load application while in dynamic tests, the specimen is in dynamic state [93], [94]. Static tests are categorized into macro tests where the bond area is larger than 3 mm^2 and micro tests where bond area is less than 3 mm^2, the interface at the bonded area can be loaded and tested either in tension, shear or push out [93], [94].

- Static tests

1- Macro-shear Bond Strength Tests

The most commonly used method for bond-strength testing. It is the easiest and fastest and doesn't require further specimen processing after the bonding step [94].

After two materials are bonded via an adhesive agent, the specimen is positioned in a universal testing machine loaded in shear until fracture occurs. Through a single-edged chisel, a flat-end rod or a wire loop attached to the actuator the composite cylinder is dislodged from the substrate [94]. Chisel produce higher stresses at the area of force application. While wire loop provide better distribution of the forces on the adhesive interface [94].

The crosshead is usually applied at constant speed ranges from 0.5 mm/min to 5.0 mm/min. A load transducer is connected to the crosshead to record the force. Once in contact with the sample, the force of crosshead rises gradually, initiating from 0 N to a nominal value until fracture the sample. Then, the final force at fracture is recorded. Shear bond strength is then calculated by dividing the maximum recorded load (F) on the bonded area (A) [95].

In the shear testing, shear & tensile stresses develop at bonding interface by the bending moment which are responsible for fracture initiation and ultimately debonding[96]. The higher the loading distance from the interface the more tensile stresses because of a bending moment created in the composite cylinder. Also, the location and configuration of the loading device has an effect on the stress distribution at the bonded interface and the bond strength results. Moreover, the higher the mismatch of modulus of the elasticity between the composite and the substrate, the higher the stress concentration at the interface which decreases the bond strength measurements [94].

A finite element analysis was conducted to analyze three different protocols of shear bond test. It found that the highest shear stresses were generated at a distance of 0.3 mm below the point of force application and then decreased in all directions. In addition, the stresses were only uniform 0.5 mm below the point of force application. The author stated that data of shear bond test shouldn't be used to make inferences on susceptibility of fracture clinically but rather it should be restricted only for comparison purposes to the effect of different material properties, material microstructures and different surface treatments that can enhance resistance to fracture or debonding [97].

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2- Macro-tensile Bond Strength Tests

In a tensile bond test, the specimen is held either by active or passive gripping methods and the force will be applied on either side of the test specimen. In this test, it is important that perpendicular alignment of the bonded interface to the loading axis is present or bending stresses will be generated. Therefore, specimen preparation is difficult for tensile bond strength tests in comparison to shear bond tests [93]. Stress distribution in case of tensile tests is more homogenous and uniform than in shear bond tests. So, It provides an accurate estimate of the stress level that initiated debonding [93]. It is mainly used to measure the bond strength of cements and hard materials such as metals and ceramics [94].

3- Macro-pushout test

In this approach, load is exerted through a plunger mounted to universal testing machine. It is used mainly to test adhesion of root canal sealers and retention of posts. The plunger should cover completely the testing material without touching the root canal wall [93]. It requires more specimen preparation and consume more time [94].

4- Micro-shear Bond Strength Tests

The test procedure is like that for macro-shear tests but the bonded areas are of 3 mm^2 or less [98]. This test has the advantages of the ease of manipulation and the ability to test several specimens. It allows for efficient screening of adhesive systems [98].

5- Micro-tensile Bond Strength Tests

Beam-shaped or hourglass shaped specimens are used with area of 1mm^2 [94]. Specimen preparation is more time consuming than macro tests because the preparation of the micro-specimens starts after the bonding procedure. Through diamond disks, large bonded interface is sectioned into thin slices. This test has much higher values than macro-tensile tests because the size for flaws is smaller in a micro-interface [98].

6- Micro-push out test

Micro-push out test is a modification of push out test where the specimen thickness is less than or equal to 1 mm^2. It is more dependable than the micro tensile technique when measuring the bond strength of luted fiber posts [98]. This method simulates the clinical condition more closely than in shear/tensile tests because it includes constraint of the curing composite and the associated polymerization stress.

- Dynamic tests

It is necessary to supplement static bond-strength data with dynamic tests to better predict the behavior of bonded materials in clinical applications. In dynamic tests the specimens are exposed to cyclic loadings as produced during chewing [93]. Examples of dynamic tests protocols are macro/micro shear fatigue, macro/micro push-out fatigue test, micro tensile fatigue test, micro-rotary fatigue test point-bend fatigue test.

- Bond durability

Testing of bond durability is important to measure and predict the effectiveness of bonding under more clinically relevant environment. Water storage or thermo-cycling are the most common artificial aging methods that test bond durability [94].

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Thermal cycling involves repeatedly cycling a specimen between two temperatures usually 5 and 55 °C with a sufficient dwell time of 20 seconds at either extreme to ensure the thermal adjustment of the specimens before an exposure to another extreme thermal stress. This process creates stresses at the bonding area due to difference in dimensional changes between the composite and PEEK, which results in crack formation at the bonding area and propagation upon mechanical loading and ultimately fracture or debonding of veneering. 5,000 cycles in a thermocycling machine corresponds to approximately 4-5 years period in vivo [94], [99].

3. Aim of The Study

The aim of this study was to examine shear bond strength between veneering resin and glass filled versus ceramic filled PEEK after surface treatment with aluminum oxide and plasma spray. The main objective was to explore the best method of achieving high and durable bond strength between PEEK and veneering resins which might solve the problem of chipping and detachment of composite resins from PEEK surface in clinical practice.

The null hypothesis is both surface treatments will not improve bond strength and durability in comparison to untreated surfaces.

The research question: Will air abrasion and plasma surface treatment improve bonding between polyetheretherketone and veneering composite resins?

Clinical relevance: PEEK as replacement of metal and zirconium substructure in prosthodontics has many advantages as previously described. Unfortunately, insufficiency of bond strength's data between veneering composites and PEEK might affect their bond strength intra-orally on the long term with subsequent chipping and fracture of veneering resins. This will increase the need of repair frequently, increase number of patient visits and finally will increase the cost of overall treatment and maintenance.

4. Materials and Methods

1- Specimen preparation

In this study, two different PEEK blocks materials were used glass filled PEEK[1] (Figure 1) and Ceramic filled PEEK[2] (Figure 2).

Figure (1) Glass filled PEEK

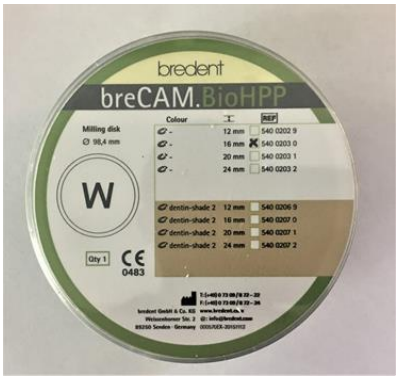

Figure (2) Ceramic filled PEEK

[1] Smile PEEK (Pressing Dental, San Marino, Italy)

[2] BreCam.BIOHPP (Bredent, Senden, Germany)

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The specimen's geometry and dimensions were planned through Solidworks software [3] then exported as STL file which can be read by the milling machine software Figure (3). In this study 60 PEEK specimens, 30 specimens per each type of PEEK (Figures 4,5), were milled with following dimension 20 mm x 10 mm x 2 mm through CAD/CAM system[4].

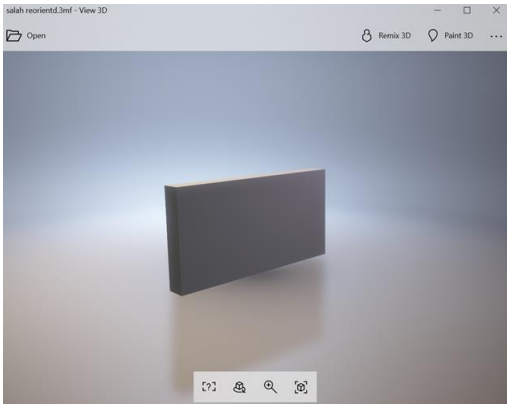

Figure (3) Exported STL file of Specimen's geometry created via Solidworks

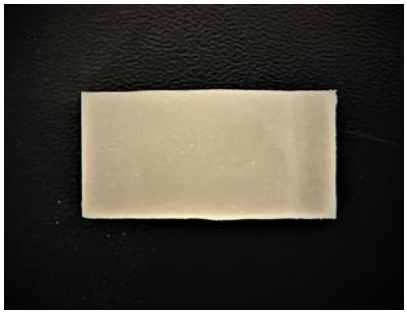

Figure (4) Glass PEEK specimen

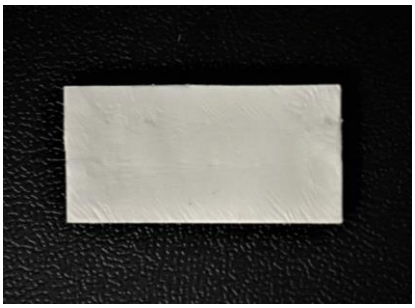

Figure (5) Ceramic PEEK specimen

After preparation of specimens, all specimens were cleaned in ultrasonic path containing 70% ethanol[5] for 15 mins using ultrasonic machine[6] then left to dry in air before surface treatment. The specimens of each type of PEEK were left air dried then numbered randomly by clerical staff from 1 to 30 and allocated to one of the following surface treatment groups control (untreated), sandblasting and plasma where the number of samples in each group was 10. Figures (6,7).

[3] SOLIDWORKS Corp, Massachusetts, USA

[4] Shera CAD/CAM (SHERA, Lemförde, Germany)

[5] Sphinx chemicals (Sphinx, Cairo, Egypt).

[6] Sonorex, Bandelin, Berlin-Germany

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Figure (6) Ultrasonic device

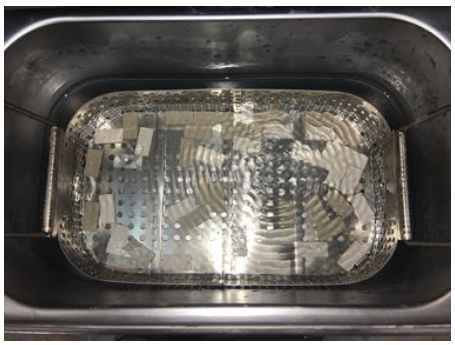

Figure (7) Ultrasonic cleaning in 70 % ethanol

- **Control group**

The Bonding procedures started without any surface treatment of the specimens. A jig was designed on Solidworks software with dimensions 20 mm x 10 mm x 2.5 mm and exported as STL file then milled from aluminum (figure 8). The jig had a hole in the center with diameter of 5 mm through which the resin was applied and bonded to the surface of PEEK specimen.

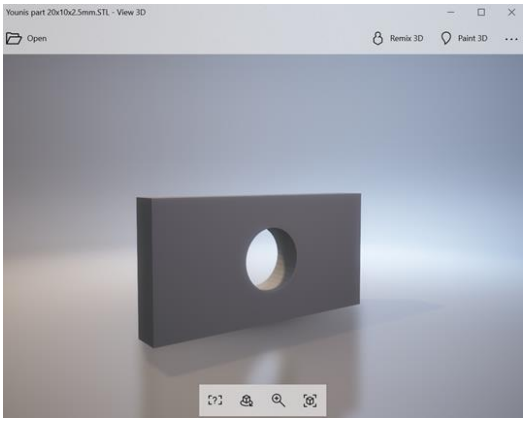

Figure (8) exported STL file of Jig's geometry

Bonding

The veneering resins used in this study was visio.lign veneering system[7]. Following manufacturer's instructions, the bonding protocol started with single application of Visiolink adhesive primer[8] (figure 11) using micro brush on the surface of PEEK specimens through the hole present in the aluminum jig. (figure 12) The specimens were immediately placed in light curing unit[9] with wavelengths range from 320 to 550 nm for 90 seconds. (figure 13).

[7] visio.lign veneering system (Bredent, Senden, Germany).

[8] visio.link (Bredent, Senden, Germany).

[9] complex lux S8 (pressing Dental, San Marino, Italy).

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Figure (11) Visio.link adhesive system

Figure (12) Adhesive bonding through the aluminum jig

Figure (13) Light curing unit

After application of adhesive and its curing, an opaquer[10] (figure 14) was then used to all the specimens before application of veneering composite. The opaquer was applied to the surface of PEEK as one layer through the hole present in aluminum jig then placed again in the light curing unit and cured for 180 seconds. Finally veneering composite resin[11] was added in two layers (figure 15). Each layer was cured for 180 seconds (figure 16). Finally, the jig was carefully removed from the specimens and then final polymerization of the composite for 6 mins (figure 17).

[10] Crea.lign opaker (Bredent, Senden-Germany)

[11] Crea.lign dentine A2 shade (Bredent, Senden-Germany).

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Figure (14) opaquer

Figure (15) veneering composite

Figure (16) composite bonded through jig

Figure (17) finished specimen

- **Sandblasted group**

1- Surface treatment was done using alumina particles with mean size 110 μm according to manufacturer's recommendation of visio.lign veneering system. PEEK specimens were blasted

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with 110 μm alumina at 2.5 bar pressure in a commercial sand-blasting chamber. The distance between the nozzle and the specimen was 5 cm. The projection time was 60 seconds. After sandblasting the specimens was cleaned with dry brush. Treatment was done on the front and back of each specimen.

2- The bonding steps were done as in control group.

- **Plasma treatment**

1- Atmospheric plasma surface treatment was done by using Piezobrush® PZ2[12] plasma device which apply plasma treatment using air under atmospheric pressure. This device was hand held and its nozzle was directed toward the surface of specimen. The distance between specimen and nozzle was 10 mm and the treatment duration was minute; figures (18,19). Treatment was done on the front and back of each specimen.

2- The bonding procedures was done as in the control group.

Figure (18): Plasma device

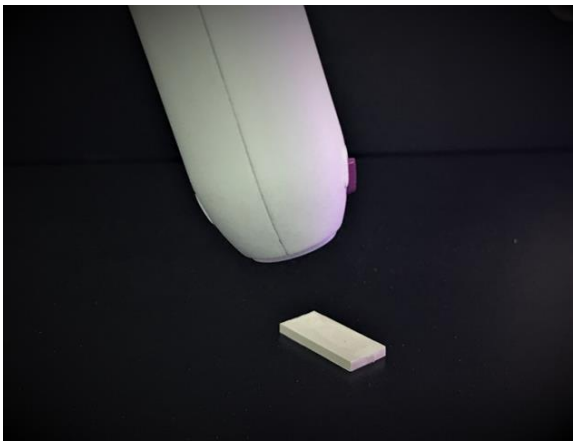

Figure (19) Plasma surface treatment

The specimens were sent to the Section Medical Materials Science and Technology, University Hospital Tübingen in Germany to test for surface roughness analysis, analysis of topography through scanning electron microscopy, surface area measurement, thermal-cycling and bond strength testing.

[12] PZ2 (Reylon Plasma, Regensburg, Germany)

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1- Surface area measurement

The surface area of bonded composite resin in all the samples were calculated through taking picture of veneered area under microscope. Then through software[13] the veneered area was measured 3 times per each sample and the mean surface area was calculated. Figure (20)

Figure (20) surface area measurement of bonded composite through Datin F software

2- Surface roughness

Perthometer[14] which is a surface roughness measuring device was used to measure surface roughness of 3 PEEK specimens per each group. The device is equipped with a contact mode stylus pickup system with a 0.5 μm diamond stylus that enabled two-dimensional tracing of a surface. The stylus was traversed normal to the surface at constant speed of 0.05 mm/s to measure the roughness of the specimen's surface. Surface roughness was described by Ra (average roughness height). Three measurements passing through the center of the specimen were performed and the average was obtained. Figure (21)

[13] Datinf software (Tübingen, Germany)

[14] Perthometer S6P (Mahr, Göttingen, Germany).

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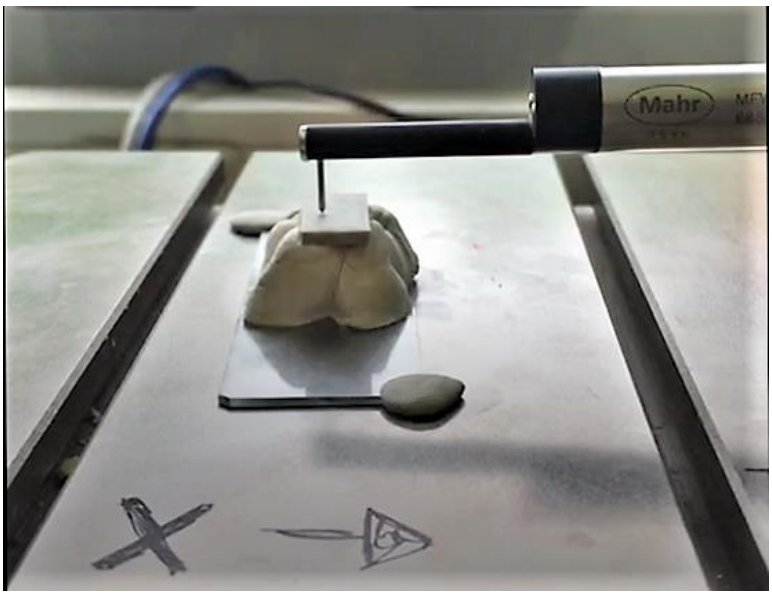

Figure (21) Perthometer (roughness measuring device)

3- Scan electron microscope[15]

The Surface topography of 3 specimens per each group was captured using scanning electron microscope (SEM). Figure (22)

Figure (22) scanning electron microscope device

[15] SEM Leo 1430 (Zeiss, Jena, Germany)

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4- Thermal cycling

All the specimens were tested for artificial aging by Thermocycler[16] which exposes the specimen to 5000 cycles of 30 seconds to 35 seconds in distilled water at (5 ± 1) °C and 30 seconds to 35 seconds in water at (55 ± 1) °C; figure (23).

Figure (23) thermal-cycling device

5- Macro-Shear bond strength measurements

Macro shear bond strength was tested by universal testing machine[17] which had a specimen holder through which specimens were firmly fixed throughout testing procedure. The force was applied by a chisel-shaped rod aligned parallel to the bond surface. The force was applied constantly at a distance of 0.5 ± 0.02 mm from the surface of the PEEK specimen with crosshead speed of 1 mm/min and starting from 0 newton load which increased gradually until fracture of the veneering composite. Then, the final maximum force at fracture was recorded; figures (24-26).

Macro shear bond strength was calculated according to the following equation S=F/A where S is the shear bond strength, F is the load applied in newtons, and A is the bonded area in mm^2. The shear bond strength was measured in megapascal (MPa).

[16] SD Mechatronik (Feldkirchen-Westerham, Germany)

[17] Z010 Zwick (Ulm, Germany)

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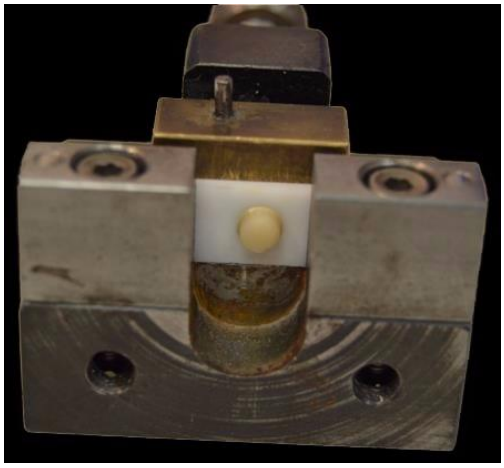

Figure (24) specimen's Holder

Figure (25) universal testing machine

Figure (26) Direction of force on specimen in universal testing machine

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6- STATISTICAL ANALYSIS

Statistical analysis was performed using SPSS software[18]. Data were represented as mean ± standard deviation. Normal distribution of data was examined using Kolmogorov-Smirnov test.

One-way ANOVA was used to compare the three studied variables in both groups. Post Hoc tests were used if ANOVA were significant. Independent sample t-test was used to compare the two studied groups. In all tests, results were considered statistically significant if the p-value was less than 0.05.

5. Results

Surface Roughness

In This study surface roughness (average roughness height, Ra) was evaluated in glass filled PEEK (group A) versus Ceramic filled PEEK (Group B) after each surface treatment. The results of this study are shown in tables (6-10) and illustrated in figures (36-40). The mean value is measured in micrometers (μm). Independent sample t-test was used to test the difference between two groups in non-related samples. One-way ANOVA was used to test the difference between more than two groups in non-related samples. The significance level was set at $P \leq 0.05$.

1- Effect of different surface treatment on surface roughness (Ra) within each type of PEEK

- **Effect of surface treatment on surface roughness of glass filled PEEK (group A)**

There was no statistically significant difference between (Control), (Sandblasting) and (plasma) groups where (p=0.184). The highest mean value of roughness was found in (Sandblasting) (6.23 ± 2.53) μm followed by (Plasma) (3.63 ± 0.18) μm, while the least roughness was found in (Control) (3.59 ± 1.62) μm. Table (1) - Figure (27).

- **Effect of surface treatment on surface roughness of ceramic filled PEEK (group B)**

There was no statistically significant difference between (Control), (Sand blasting) and (plasma) groups where (p=0.058). The highest mean value of roughness was found in (Sandblasting) (6.58 ± 2.41) μm followed by (Plasma) (3.38 ± 0.44) μm, while the least roughness was found in (Control) (3.32 ± 0.75) μm. Table (1) -Figure (27)

[18] Statistical package for the social sciences version 20 IBM corp, SPSS, Statistics, Armonk, NY, USA

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Table (1) Mean and standard deviation values of surface roughness within each type of PEEK, the unit of giving numbers is µm.

Variables	**Surface roughness [µm]**								
	Group A		**95% confidence interval for mean**		**Group B**		**95% confidence interval for mean**		**P-value**
	Mean	**SD**	**Lower bound**	**Upper bound**	**Mean**	**SD**	**Lower bound**	**Upper bound**	
Control	3.59 aA	1.62	-0.42	7.61	3.32 aA	0.75	1.45	5.19	**0.804ns**
Sandblasting	6.23 aA	2.53	-0.06	12.52	6.58 aA	2.41	0.59	12.57	**0.871ns**
Plasma	3.63 aA	0.18	3.19	4.07	3.38 aA	0.44	2.29	4.47	**0.418ns**
P-value	**0.184 ns**				**0.058 ns**				

Different letters in the same column indicate statistically significant difference

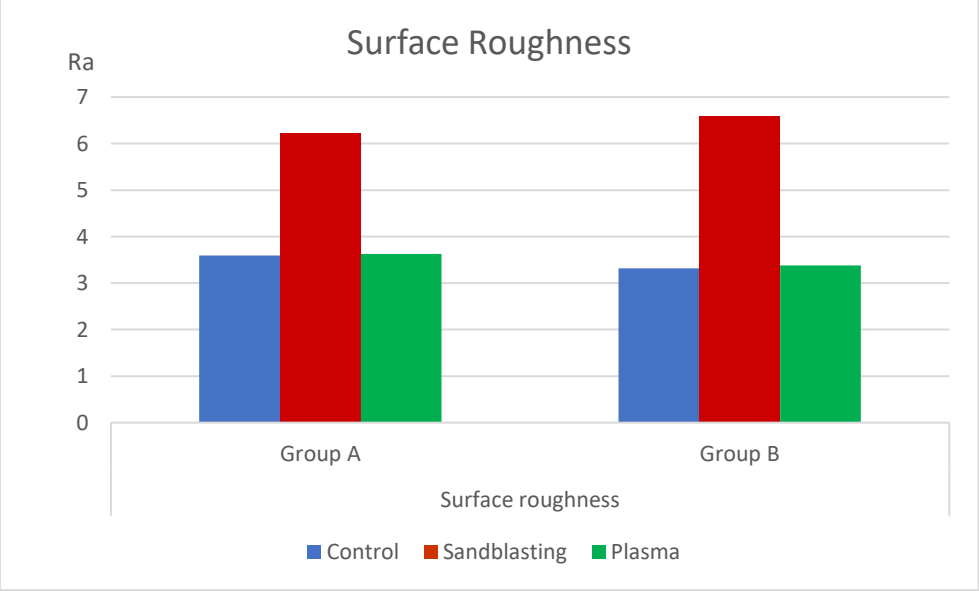

Figure (27) Column chart for mean of surface roughness in µm within each type of PEEK

2- Effect of each surface treatment on both groups (A, B)

- **Regarding control groups**

There was no statistically significant difference (p-value 0.15) between Group A (glass filled) with a mean value of 3.59 µm and Group B with a mean value 3.32 µm (ceramic filled) groups where (p=0.804). Table (2) Figure (28)

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- **Regarding the sandblasting groups**

There was no statistically significant difference (p-value 0.871) between Group A (glass filled) with a mean value of 6.23 µm and Group B with a mean value 6.58 µm (ceramic filled) groups. Table (2) - Figure (28)

- **Regarding the plasma group Table**

There was no statistically significant difference (p-value 0.418) between Group A (glass filled) with a mean value of 3.63 µm and Group B with a mean value 3.38 µm (ceramic filled) groups. The unit of giving numbers is µm. Table (2) - Figure (28)

Surface treatment	Groups	N	Mean	Std. Deviation	P- Value
Control	Group A	3	3.59	1.62	0.15
Sandblasting	Group A	3	6.23	2.53	0.871
Plasma	Group A	3	3.63	0.18	0.418

Table (2) Mean, standard deviation (SD), and p value of surface roughness values in control, sandblasting, plasma groups between glass and Ceramic filled PEEK.

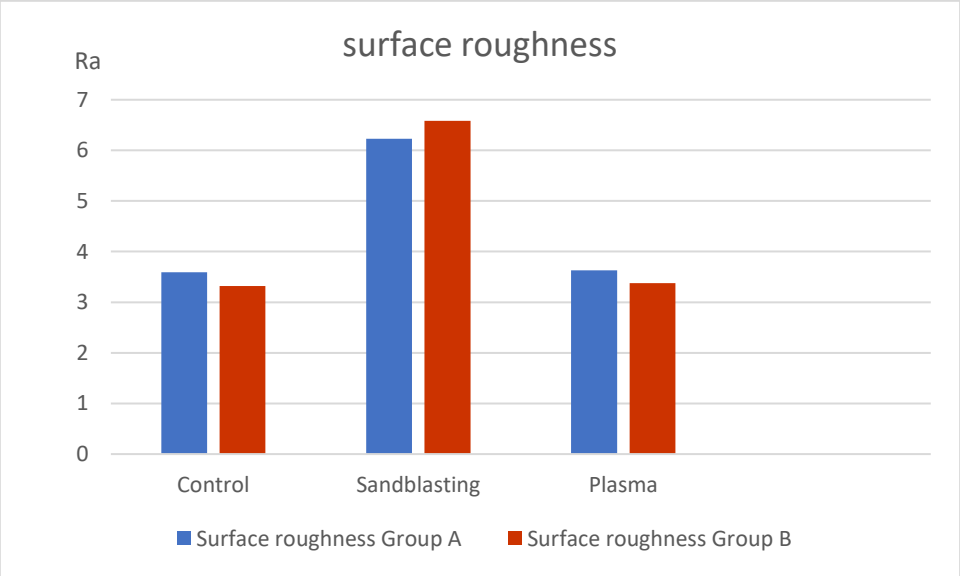

Figure (28) Column chart for mean of surface roughness in µm between control, sandblasting, plasm Groups of glass (A) and Ceramic PEEK (B)

3- Effect of surface treatment methods on surface roughness regardless type of PEEK

There was a statistically significant difference between (Control), (Sand blasting) and (plasma) groups where (p=0.004). A statistically significant difference was found between Sand blasting group with highest mean value of 6.41 µm than each of Control (p-value 0.008, mean 3.46 µm) and plasma (p-value 0.009, mean 3.51 µm). No statistically significant difference was found between (Control) and (plasma) groups where (p=0.998). Table (3) figure (29)

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Table (3) Mean and standard deviation values of surface treatment methods on surface roughness regardless of groups, the unit of giving numbers is µm.

Variables	**Surface roughness**	
	Mean	**SD**
Control	3.46 [b]	1.14
Sandblasting	6.41 [a]	2.22
Plasma	3.51 [b]	0.33
P-value	**0.004***	

Different letters in the same column indicate statistically significant difference

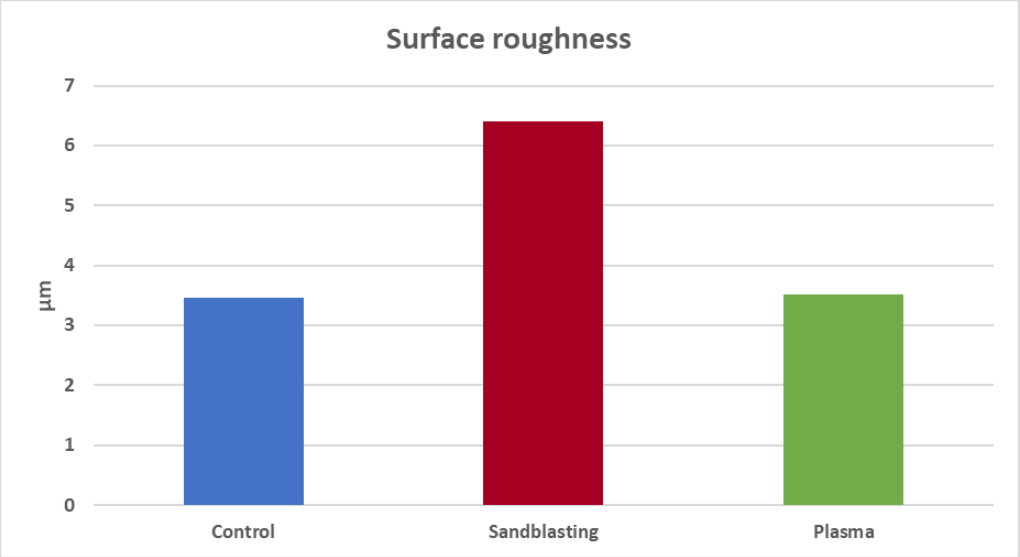

Figure (29) Column chart of mean values of surface treatment methods on surface roughness in µm regardless type of PEEK.

Scan Electron Microscope

1- Glass filled PEEK

Analysis of untreated and plasma specimens under scan electron microscope showed smooth surface with very few irregularities on the surface. While sandblasted specimen showed a considerable roughness in its surface. Figure (30-32)

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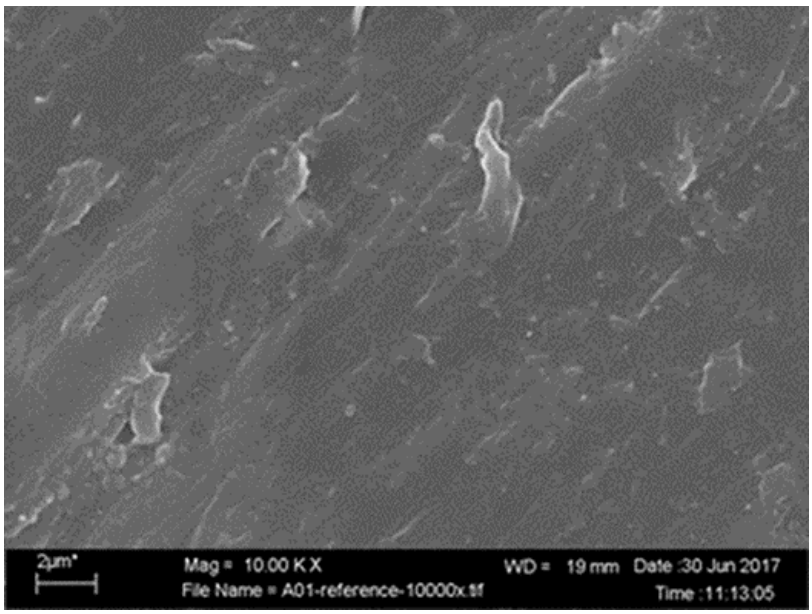

Figure (30) SEM-picture of glass filled PEEK - Control group

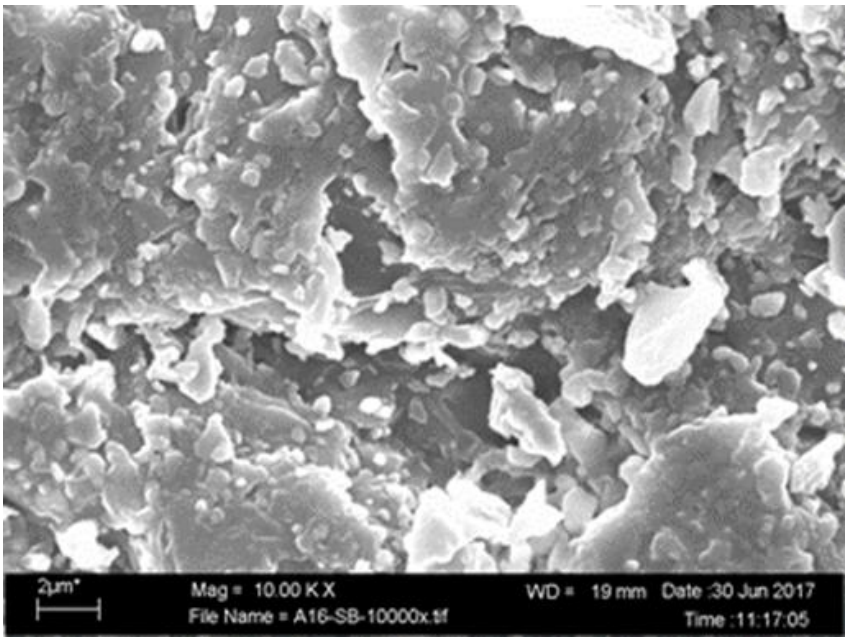

Figure (31) SEM-picture of glass filled PEEK - Air abrasion group

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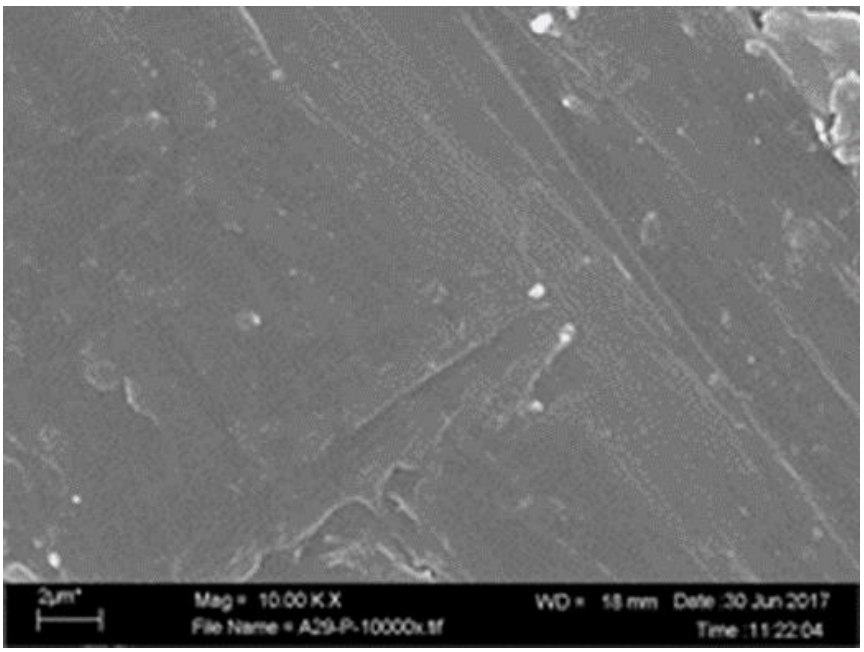

Figure (32) SEM-picture of glass filled PEEK - Plasma group

2- Ceramic filled PEEK

Analysis of untreated and plasma specimens under scan electron microscope showed smooth surface with very few irregularities and patches on the surface. While sandblasted specimen showed a high roughness with more pronounced irregularities and sharp streaks and flaws. Figure (33-35)

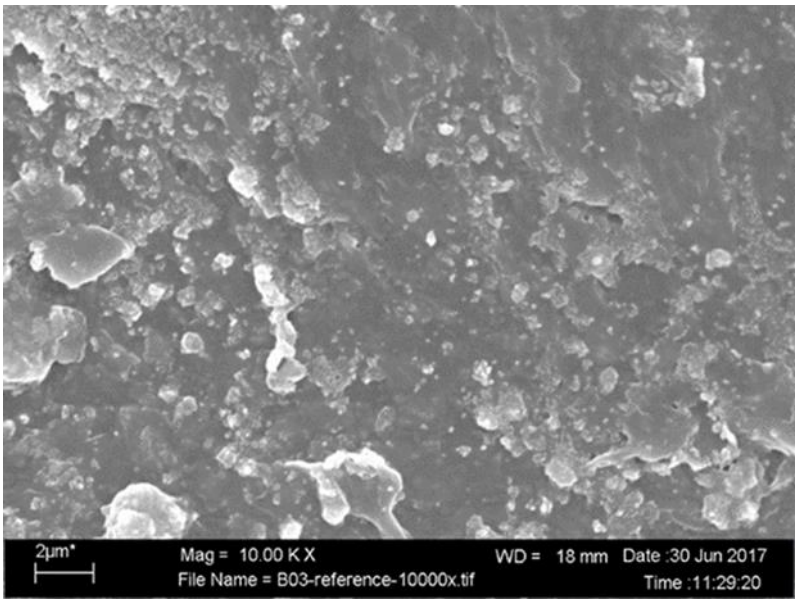

Figure (33) SEM-picture of Ceramic filled PEEK – control group

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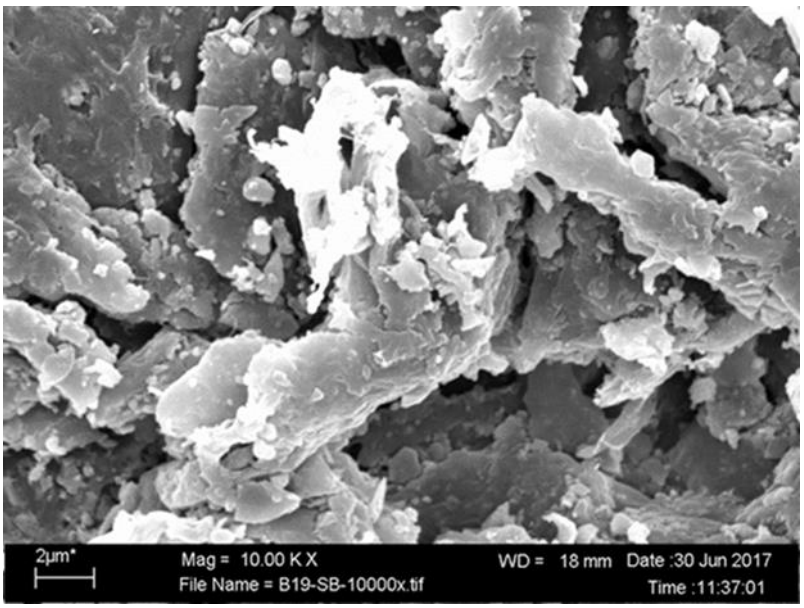

Figure (34) SEM-picture of Ceramic filled PEEK - Air abrasion group

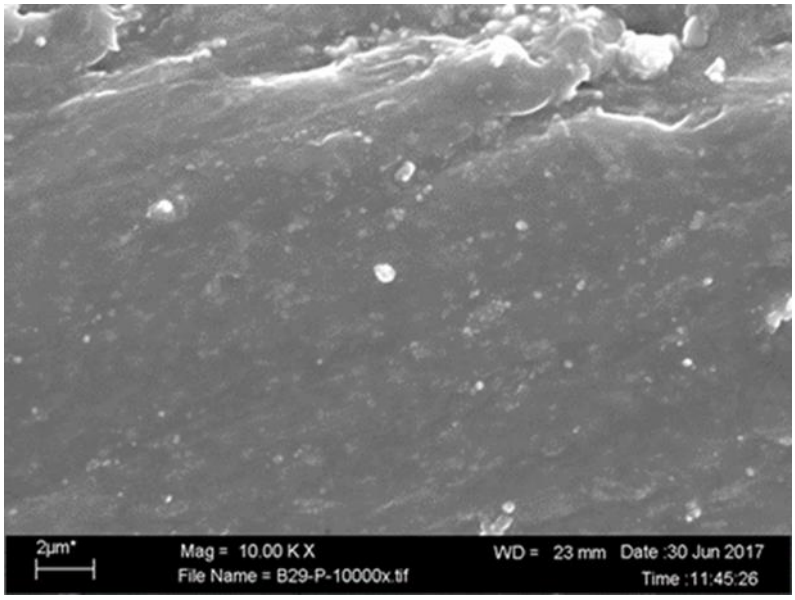

Figure (35) SEM-picture of Ceramic filled PEEK - Plasma group

Shear Bond Strength

The present study evaluated the shear bond strength between glass filled PEEK and veneering resin (group A) versus Ceramic filled PEEK and veneering resins (Group B). The results of this study are shown in tables (1-5) and illustrated in figures (31-36). The mean value is measured in megapascal (MPa). Testing for the significance was carried out using ONE-WAY ANOVA test. Probability value (p-value) ≤ 0.05 was considered statistically significant in this result. Additionally, multiple comparison between different surface treatments of both groups (A, B) were done using POST HOC Tamhane.

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1- Effect of different surface treatment on shear bond strength (SBS) between veneering resin and PEEK

- ***Within glass filled PEEK (group A)***

The highest mean value of shear bond strength between glass PEEK and veneering resin was after surface treatment with sandblasting 10.78 MPa and this result was statistically significant (p-value 0.001) in comparison to control (mean = 5.68 MPa) and plasma treatment (mean = 5.83 MPa) groups. While plasma surface treatment improved SBS (5.82 MPa) very little with mean difference 0.14 MPa to control group (5.68 MPa) and its effect was statistically insignificant (p-value 0,996). Table (4) - Figure (36).

Table (4) Descriptive statistics including mean, mean difference (MD), standard deviation (SD), and 95% confidence interval for shear bond strength (SBS) values with the different surface pretreatment within glass filled PEEK, the unit of giving numbers is MPa.

Mean	(I) Group A	(J) Group A	Mean Difference (I- J)	Std. Error	Sig. P-Value	95% Confidence Interval	
						Lower Bound	Upper Bound
Without	Without	Sandblasting	-5.10	0.59	.001	-6.69	-3.52
5.68		Plasma	-0.14	0.72	.996	-2.03	1.74
Sandblasting	Sandblasting	Without	5.10	0.59	.001	3.52	6.69
10.78		Plasma	4.96	0.61	.001	3.31	6.61
Plasma	Plasma	Without	0.14	0.72	.996	-1.74	2.03
5.83		Sandblasting	-4.96	0.61	.001	-6.61	-3.31

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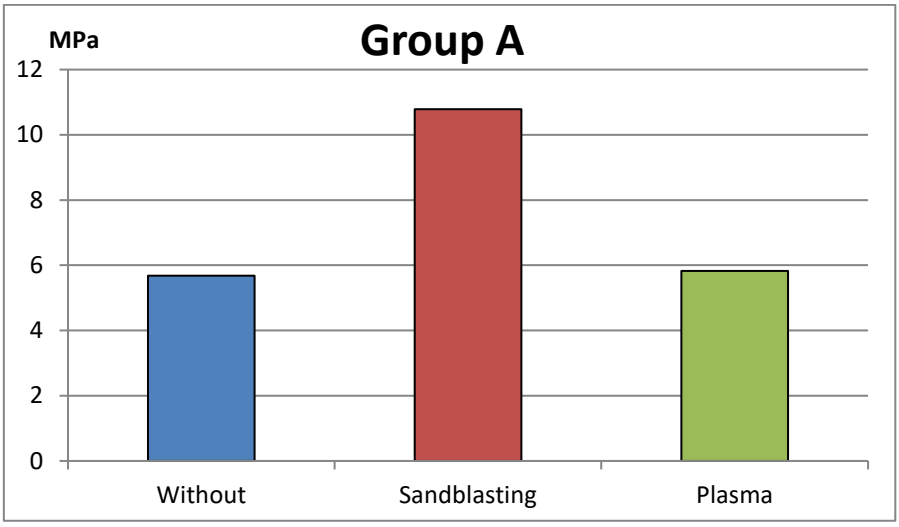

Figure (36): Column chart for the mean of SBS of different surface treatments within glass PEEK

- **Within Ceramic filled PEEK (group B)**

The highest mean value of shear bond strength between Ceramic PEEK and veneering resin was after surface treatment with sandblasting 12.85 MPa and this result was statistically significant (p-value 0.001) in comparison to control (mean = 3.55 MPa) and plasma treatment (mean = 3.92 MPa) groups. On other hand, plasma surface treatment improved SBS very little with mean difference 0.16 MPa and its effect was statistically insignificant (p-value 0,998). Table (5) Figure (37)

Table (5) Descriptive statistics including mean, standard deviation (SD), and 95% confidence interval for shear bond strength values (in MPa) with the different pretreatment within Ceramic filled PEEK,

Mean	(I) Group B	(J) Group B	Mean Difference (I- J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Without	Without	Sandblasting	-8.66	1.08	.001	-11.51	-5.80
3.56		Plasma	-.16	0.94	.998	-2.67	2.34
Sandblasting	Sandblasting	Without	8.66	1.08	.001	5.80	11.51
12.85		Plasma	8.49	1.14	.001	5.48	11.51
Plasma	Plasma	Without	0.16	0.94	.998	-2.34	2.67
3.93		Sandblasting	-8.49	1.14	.001	-11.51	-5.48

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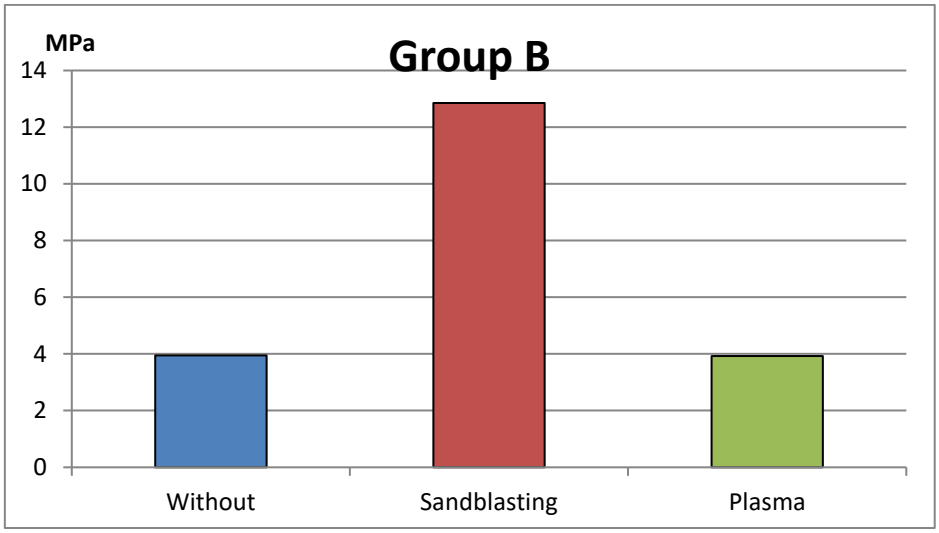

Figure (37) Column chart for the mean of SBS of different surface treatments within glass filled PEEK

2- Effect of each surface treatment on both groups (A, B)

I. Regarding control groups

Without surface treatment, glass filled PEEK showed a mean value of shear bond strength to veneering resins equals 5.68 MPa which is higher statistical significant difference than Ceramic filled PEEK that showed a mean value of 3.55 MPa (p-value .015). Table (6) - Figure (38)

Table (6) Mean, standard deviation (SD), for shear bond strength values in MPa between control groups of glass and Ceramic filled PEEK, the unit of giving numbers is MPa.

Without treatment (control group)	N	Mean	Std. Deviation	*Std. Error Mean*	*P- Value*
Group A	10	5.68	1.57	0.49	.015
Group B	10	3.56	1.93	0.61	

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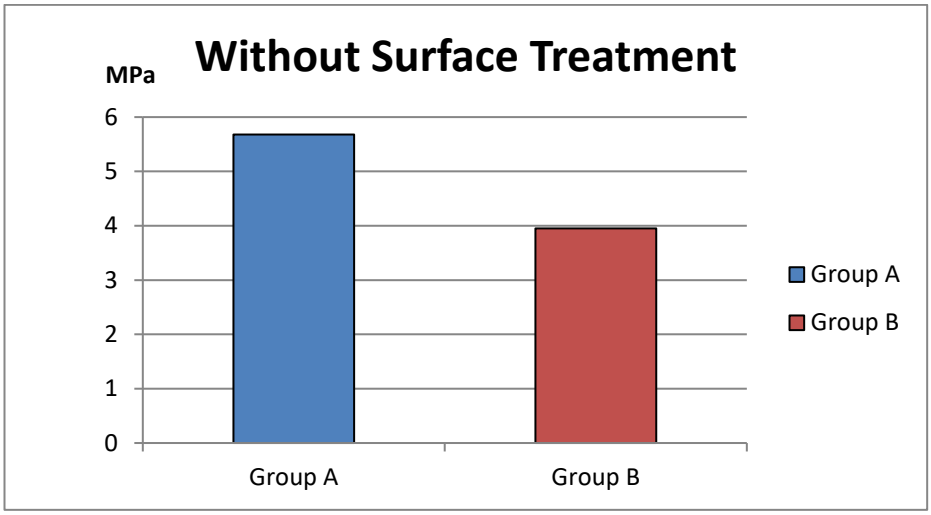

Figure (38) Column chart for the mean of SBS value between control groups of glass (A) and Ceramic PEEK (B)

II. Regarding the sandblasting groups

After sandblasting, Ceramic filled PEEK showed a mean value of shear bond strength to veneering resins equals 12.85 MPa which showed higher statistically significant difference than glass filled PEEK that showed a mean value of 10.79 MPa (p-value 0.017). Table (7) - Figure (39)

Table (7) Mean, standard deviation (SD), and for shear bond strength valuesin MPa between control groups of glass & ceramic filled PEEK,the unit of giving numbers is MPa.

Sandblasting	N	Mean	Std. Deviation	Std. Error Mean	P-Value
Group A	10	10.78	1.04	0.33	.017
Group B	10	12.85	2.16	0.68	

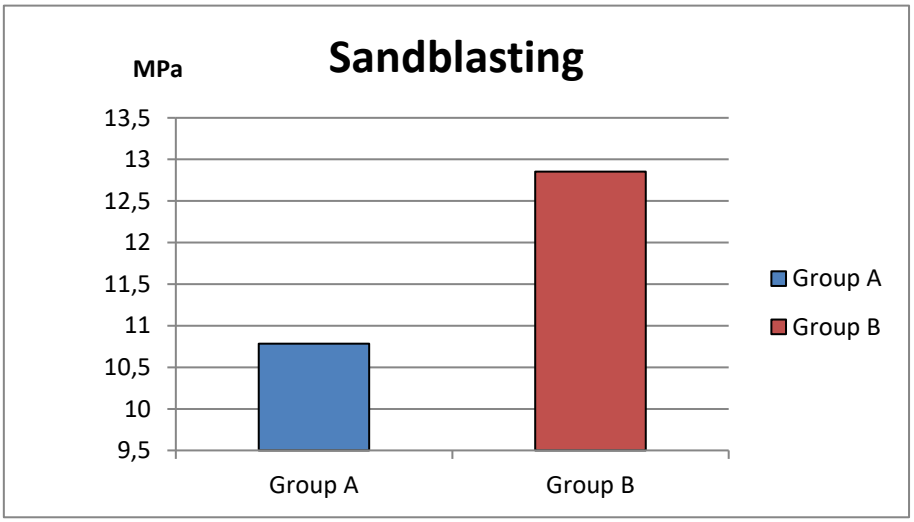

Figure (39) Column chart for the mean of SBS value between Sandblasting groups of glass (A) & Ceramic PEEK (B)

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III. Regarding the plasma group

After Plasma treatment, glass filled PEEK showed a mean value of shear bond strength to veneering resins equals 5.826085 MPa which showed higher statistically significant difference than Ceramic filled PEEK that showed a mean value of 3.925803 MPa (p-value .039). Table (8) - Figure (40)

Table (8) Mean, standard deviation (SD), and for shear bond strength values between Plasma groups of glass & Ceramic filled PEEK

Plasma	N	Mean	Std. Deviation	Std.Error Mean	P-Value
Group A	10	5.83	1.64	0.52	.039
Group B	10	3.93	2.13	0.67	

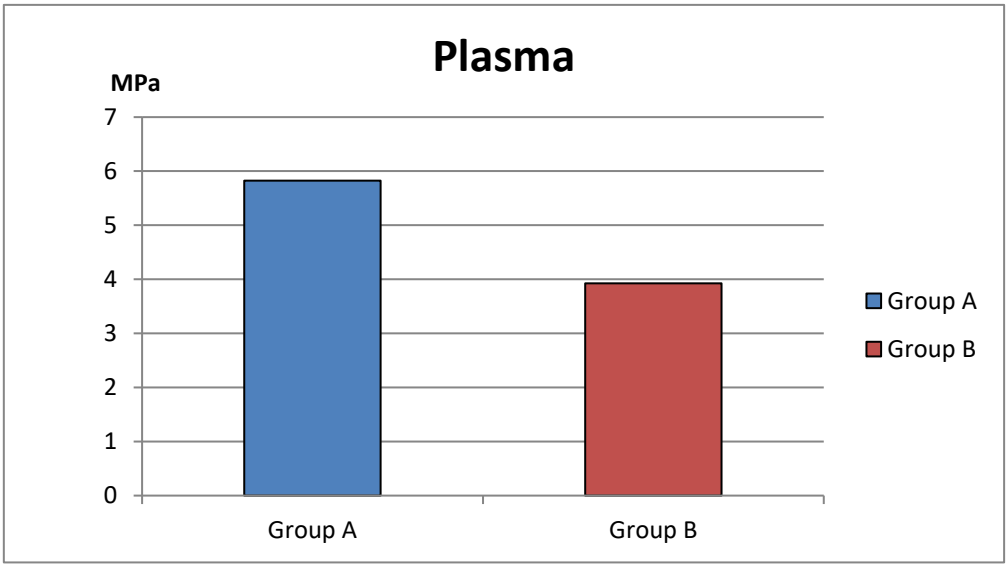

Figure (40) Column chart for mean of SBS between Plasma Groups of glass (A) and Ceramic PEEK (B)

5. Discussion

The present study investigated the effect of two different surface treatments Sandblasting and Plasma surface treatment on the bond strength between veneering composite resins and two different PEEK materials ceramic filled PEEK and glass filled PEEK.

- **Discussion of materials & methods**

Despite the fact that invitro studies can't reproduce clinical conditions in detail with all individual factors, they are important to assess the quality of adhesion and provide information on the reliability of bonding in different dental restoration. Through invitro studies a specific parameter or property can be individually tested which is difficult in case of clinical studies where diverse stresses can act simultaneously on dental restorations. Following the laboratory studies, a clinical studies with controlled and standardized parameters should be performed to evaluate clinical performance [85], [93], [98].

CAD/CAM technology was used to prepare the specimens from PEEK blanks because of its ease of preparation, speed and precision. Ultrasonic cleaning with ethanol was done to remove any debris or particles remaining after specimens machining [100]. Putty jig was made to allow seating

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aluminum jig on the PEEK specimen accurately during bonding procedures which standardize the specimens [101]. In order to prevent intrusion of any potential bias, the specimens were numbered randomly by clerical staff then through computer generated sequence the specimens were assigned to one of surface treatment groups [102].

Sandblasting surface treatment can increase the surface roughness and consequently increase the surface area for micromechanical bonding. Moreover, conditioning of the surface with MMA-containing adhesive systems as Visiolink was of paramount importance to improve the bonding characteristics of PEEK.

Following instruction of PEEK & adhesive manufacturers, the air abrasion treatment was done by110 μm alumina at pressure of 2.5 bar and the duration of sandblasting range from 45 seconds to 90 seconds. Although more recent study investigated the effect of grain size of aluminum oxide on the bond strength between PEEK and resin and found no statistical difference [83]. After sandblasting the specimens was cleaned with dry brush. to remove any remnants of Alumina particles before bonding.

In respect to plasma treatment, it has the potential to solve many drawbacks that are associated with air abrasion as the generation of dust during treatment and the inconsistency of the surface preparation which is highly dependent on the operator. Plasma not only increases surface roughness for micromechanical bonding but can also enhance the bonding by increasing surface energy and wettability of polymer surface plus adding chemical functional groups which interact and bind with the adhesives [103]–[105].

In this study PEEK specimens were treated with atmospheric plasma because atmospheric plasma treatment does not require a special chamber and there is no contamination expected. It can treat complex shapes and can be applied to the specific areas of the substrate to be bonded rather than performing the treatment on the entire structure. In addition, the device doesn't contact the treated surface, requires minimal operator intervention. Another important advantage of this treatment is that the modifications are confined to a depth of a few nanometers without affecting bulk of PEEK [103], [104].

In addition, other plasma treatments need a special chamber to control the gas source and pressure. The atmospheric plasma device is more environmental friendly to be used in the clinic or in the lab because it uses the air as process gas under atmospheric pressure to produce plasma. This allows to precipitate oxygen and hydroxyl functional groups on the surface which can form covalent bonds with the adhesive [104], [106].

Up till now, data of plasma treatment on PEEK in the field of prosthetic dentistry is still little and the guidelines about the accurate selection of plasma devices and treatment conditions are still absent [89].

The adhesive of choice was visiolink and steps of its application was done following manufacture instructions. Visiolink was chosen because it contains methyl-methacrylate monomer which improves bonding to PEEK [69], [79], [80], [83], [85].

Moreover, In the reported studies different adhesives were used for conditioning PEEK surfaces prior to bonding of composite, high bonding values were found after the use of visiolink as conditioner on different pretreated PEEK surfaces [69], [79], [81], [85].

The opaquer was applied to all PEEK specimens for two reasons. Firstly it was reported that conditioning of PEEK's surface with adhesive in combination with opaque application improved the shear bond strength [87]. Secondly, glass filled PEEK specimens have unaesthetic opaque grey color.

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Consequently, to resemble clinical application of this material an opaquer was applied after conditioning with visiolink adhesive. The opaquer was added to both glass & ceramic PEEK specimens to standardize the bonding procedures in this study [101], [107].

The veneering composite was light cured in two layers as the instructions of manufacturer recommended that the maximum thickness of composite to be cured is 2 mm and the total height of the composite bonded PEEK specimen through aluminum jig was 2.5 mm.

Thermal cycling was performed to simulate as much as possible the oral conditions and clinical relevant situations. It allows also to investigate long term durability of the bonding method used [80].

Shear bond strength was determined because the stresses that act between framework & veneering materials are mainly shear stresses [108]. These stresses causes one surface of material to displace or delaminate with respect to the opposite bonded surface.[108] shear bond strength test was done according to international organization of standardization "**ISO 10477"** to standardize the methods of bond strength testing and the results are reproducible.[101] Therefore, it is appropriate for evaluating bond strength between veneering composite and different PEEK materials. The type of bond test is macro shear bond test because the area of bonded veneering composite resin to PEEK specimen is larger than $3mm^2$. According to ISO 10477, values of shear bond strength higher than 5 Mpa is considered acceptable [101].

- **Discussion of the Results**

In this study, the results revealed that sandblasting could establish a significant improvement of shear bond strength while plasma showed insignificant improvement regarding the shear bond strength. Therefore, the null hypothesis was rejected.

Regardless the type of PEEK, sandblasting had the highest impact on the bond strength between PEEK and veneering composite in comparison to untreated & plasma treated groups. This can be attributed to increased roughness on the surface which in turn increase surface area available for micromechanical interlocking with adhesives that ultimately increase bond strength [69], [79], [80], [83], [85].

In both glass & ceramic filled PEEK, the pictures of scan electron microscope showed that sandblasting produced irregular fissured and rougher surface than control or plasma group. In respect to sandblasting, ceramic filled PEEK showed higher bond strength values than glass filled PEEK which might be due to the erosion caused by sandblasting on the surface of Ceramic filled PEEK which was higher than that on the surface of glass filled PEEK. Thus, Sandblasting caused 4-fold increase in the SBS of veneering composite to the ceramic filled peek sample. On the other hand, it caused almost doubling of the SBS of veneering composite to the glass fiber filled sample. The variation of the reaction of the two types of PEEK to sandblasting might be related to the structure of both composites. In the ceramic filled PEEK probably the sandblasting could easily displace the ceramic filler content from the PEEK matrix leaving evident micro roughness pores which increased the chance for better bond with the veneering composite. For the glass fiber filled material the structure of the composite block might be less affected by the sandblasting procedure with less tendency to abrasion and loss of surface particles under the effect of the sandblasting material.

In control groups where, direct application of adhesive without surface treatment was done. Glass filled PEEK showed higher bond strength than ceramic one. Although surface roughness analysis showed slightly higher mean value of glass PEEK than ceramic PEEK the difference is statistically not significant. It seems that different incorporated fillers had different effect on shear bond strength. The precise influence of these fillers on surface characteristics and shear bond strength should be further evaluated [92].

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Regarding plasma treatment, A non-significant improvement of shear bond strength after plasma treatment in both glass and ceramic filled PEEK in comparison to control group was found. There is no difference in surface roughness between plasma & untreated control groups which might be due to the fact that the treatment was done in room temperature at atmospheric pressure which is not enough to produce significant micro mechanical roughness [92],[109]. while the slight improvement might be due to the decrease in contact angle and consequently the increase in wettability plus increasing surface energy and formation of oxygen and hydroxyl functional group at the surface [92].

5. Summary

In this study, shear bond strength between two different filled PEEKS and veneering composite after application of two different surface treatments. 30 samples of glass filled PEEK and 30 samples of ceramic filled PEEK were prepared in this study. Samples of each type of PEEK were allocated in 3 different surface treatment groups; untreated (control), sandblasting and plasma treatments.

In control group, bonding protocol started directly without any surface treatment. Adhesive bonding was added and cured followed by application of one layer of opaquer then cured and lastly addition of veneering composite resins and its curing. In sandblasted group, surface of PEEK specimens was treated with 110 μm alumina particles followed by bonding of veneering composite the same way as control group. In plasma treated group, surface of PEEK specimens was treated with atmospheric plasma treatment at room temperature followed by bonding of veneering composite the same way as control group.

Surface roughness measurements and scan electron microscope were done in each group. Then thermocycling test was done through a repeated cycling between two temperatures (5 and 55 °C) and in between an adequate dwell time for 20 seconds to ensure the thermal adjustment of the specimens before exposure to another extreme thermal stress. After thermalcycling, macroshear bond strength testing was done to all specimens using universal testing machine.

- **The results showed that**

1- Sandblasting produced a statistically significant increase in surface roughness regardless the type of PEEK used.
2- Sandblasting showed a statistically significant increase in shear bond strength within each type of PEEK.
3- In sandblasting group, ceramic filled PEEK showed statistically significant higher shear bond strength than glass filled PEEK.
4- Within each type of PEEK, plasma treatment showed a statistically insignificant improvement in shear bond strength compared to untreated control group.
5- In untreated and plasma group, glass filled PEEK showed statistically significant higher shear bond strength than ceramic filled PEEK**.**

6. Conclusions

Within the limitations of this in-vitro study, it could be concluded that:

1. Sandblasting is still the best method to provide good bonding of PEEK composites to veneering resins where micromechanical interlocking by surface roughness appears to have high impact on the adhesion between PEEK and resin materials than wettability & surface energy produced by plasma treatment.

2. Ceramic filled PEEK yielded higher bond strength than glass filled PEEK after sandblasting.

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3. The effect of atmospheric plasma treatment on bond strength between PEEK and veneering resins was not sufficient to replace the current protocol of micromechanical roughening for PEEK surfaces by sandblasting

Recommendations

1. More studies on plasma deposition methods are required to find the best possible protocol regarding plasma parameters such as process duration, process gas, temperature and pressure. This will open other possibilities to establish successful improvement of bonding between the PEEK substrate and resin materials

2. Further studies are required to study the combined effect of sandblasting followed by plasma treatment of different PEEK samples

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