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**The influence of different plasma treatment conditions
on the shear bond strength of three different
Polyaryletherketones (PAEKs) and veneering
composites**

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Dedication

I dedicate this dissertation with a deep feeling of gratitude to my dear parents, Salah Younis and Yousria Eissa, who have always loved and supported me unconditionally.

I also dedicate this work to my brother Abd-Elrahman and my sisters Rehab, Esraa, and Aya for their words of encouragement and constant support and push along the way.

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List of Abbreviations

PAEK	Polyaryletherketone
PEEK	Polyetheretherketone
UPEEK	Unfilled PEEK
CPEEK	Ceramic filled PEEK
CFRPEEK	Carbon fiber reinforced PEEK
PMMA	Polymethylmethacrylate
SBS	Shear Bond Strength
SEM	Scan Electron Microscope
Ra	Average Roughness Height
SD	Standard Deviation
TC	Thermocycling
°C	Celsius
STL	Standard Tessellation Language
ROS	Reactive Oxygen Species
RNS	Reactive Nitrogen Species
CT	Computed Tomography
MRI	Magnetic Resonance Imaging

1. Introduction

Plasma is a pervasive state of our universe composing almost 99% of it. Upon raising the temperature of a matter, it changes from the solid state into the liquid then the gas and finally the plasma state where the gas temperature increases to a sufficiently high degree so that the electrons can be stripped away from their atoms.¹ That is why plasma is also expressed in other words as the fourth state of matter.¹ The term “Plasma” was firstly introduced by the scientist Irving Langmuir describing in his article “Oscillations in Ionized Gases” that was published in 1928, a medium that contained different active components similar to blood plasma.² The applications of plasma are growing at an enormous rate in almost every field. In industry, plasma technology improves industrial manufacturing, cleaning, and adhesion of different products.^{1,3} Most affected industrial fields are aerospace, automotive, electronics, food, glass, optics, paints, papers, packings, plastics, and textiles.^{1,3}

In the middle of 1990s, much attention was directed toward possible future applications of plasma in the field of medical biology and clinical medicine.⁴ This field expanded very rapidly in a relatively short time and is well known today as “plasma medicine” which includes decontamination and sterilization of biomedical devices, plasma-assisted wound healing, other applications in the field of dermatology, pharmacology, and cancer therapy.⁴⁻⁷

While in dentistry, plasma was suggested as a method of cleaning and sterilization of dental instruments, root canal disinfection in endodontic treatments, teeth bleaching, and most recently as a method of surface treatment for different purposes.⁸ In restorative dentistry, research is still going on to create a better bonding between dentin and dental adhesives with the aid of plasma.⁸ Also, few studies tested possibilities to improve bonding between fiber or ceramic posts and root canal through plasma.⁸ In implantology, plasma trials have been made to enhance osseointegration of implant surfaces either by improving surface qualities or addition of surface coatings.⁸ In prosthodontics, different studies tried to use plasma as a method of surface treatment either as a solo treatment or in combination with other conventional methods of surface treatments like sandblasting and chemical etching to enhance bonding between prosthetic frameworks and their subsequent dental veneerings.^{8,9}

Conventional prosthetic frameworks are frequently made of metals because they showed good mechanical properties, high corrosion resistance, and long term survival rates. Nevertheless, they developed complications in the long term follow-ups as marginal discoloration, chipping, and fracture of its veneering.¹⁰ Therefore, zirconia frameworks were introduced as an esthetic substitute of metals and solution to their complications. Unfortunately, they are more expensive and also develop complications in the long run such as abrasion of remaining natural dentition and a higher rate of chipping and fracture of their veneering.¹⁰⁻¹³ Recently, a new family of polymers, named polyaryletherketone PAEK, has been introduced in prosthodontics as a replacement of metal and zirconium frameworks to overcome their problems.¹⁴ The most commonly used members of these polymers are polyetheretherketones (PEEKs) and polyetherketonketones (PEKKs), which show the ease of fabrication, high mechanical properties and can be constructed in thin sections without affecting their strength, thus producing lightweight restorations that subsequently more comforting to the patients.¹⁴ Although these polymers are more esthetically acceptable than metals and their low translucency is adequate in many dental situations, they should be veneered with composite resin in the anterior zones to create more esthetic restorations.¹⁴

The inherent challenge associated with polymers is that they possess inert hydrophobic surfaces which need to be treated before bonding to avoid chipping of the veneering material in clinical applications.¹⁴ Otherwise, this challenge will eliminate them as potential substitutes to metals or zirconia due to the increased need for repair and subsequently number of patient visits, besides the potential increase in the cost of the overall treatment and maintenance.¹⁵ Different sandblasting and chemical etching techniques were proposed as possible methods of surface treatments to improve the bonding of these polymers to veneering composites.^{16,17}

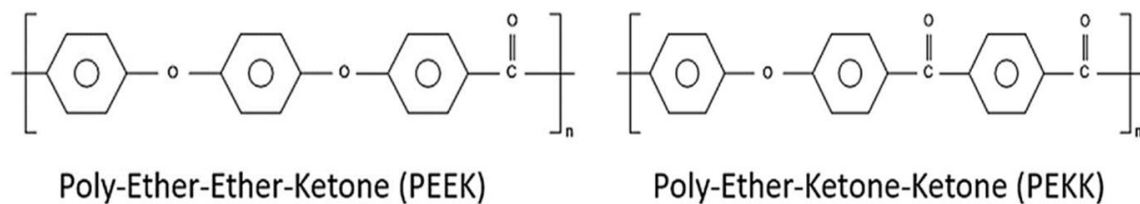
In the literature, very few articles studied the effect of plasma as a method of surface treatment on the bond strength of PEEK/PEKK to veneering resins.¹⁸⁻²⁰ Additionally, still little is known about the suitable gases and parameters settings which can widen the applications of plasma in the field of prosthodontics in the future. Therefore, the aim of this study was to probe the influence of different gaseous plasmas on the shear bond strength of different PAEK dental materials to a veneering composite resin.

1.2 Review of literature

1.2.1. Definition

Polyaryletherketone (PAEK) is a huge family of semi-crystalline polymers that in general consists of aromatic molecular chains as cornerstones interconnected alternately by functional groups of ether and ketone between aryl rings.²¹

In this family, two members are used popularly in the medical and dental field predominantly in prosthodontics. Polyetheretherketone (PEEK) which is the dominant member of the PAEK family and was prepared first by Rose and Staniland in 1982.²² The second member is Polyetherketoneketone (PEKK) which has a slightly different chemical structure of 2 ketone functional groups between aryl rings and was introduced by Bonner in 1962.²²



*Figure 1: Chemical structure of PEEK and PEKK*²²

1.2.2. Properties of PEEK and PEKK

Owing to their chemical structure, both polymers show excellent stability at elevated temperature degrees exceeding 300 °C. They can withstand the high corrosive environment and possess high resistance to radiation damage. Moreover, they are chemically inert and insoluble in nearly all organic and inorganic solvents at room temperature.^{14,23} They are characterized by high strength to weight ratio and high wear-resistance, which is greater than conventional polymethylmethacrylates (PMMA) and composite resins.²¹ PEEK can accept the addition of reinforcing agents such as glass fillers, carbon fillers, and ceramic fillers to further improve its mechanical and physical properties. While PEKK, as it has another ketone group instead of ether, shows already higher mechanical properties than PEEK with almost 80% higher compressive strength.^{21,24} Therefore, they are known in different industries as *high-performance thermoplastic polymers*.^{21,25,26} These polymers are nowadays highly attractive in medical and dental fields because of the following properties:

a. Biocompatibility

Both are bioinert materials and show a high degree of biocompatibility. They do not induce any adverse mutagenic or cytotoxic activities nor release any constituents to the human tissues, and also they resist degradation within living tissues.^{21,27,28}

b. Sterilization

The crystalline structure of both ensures high stability and resistance to hydrolysis even at elevated temperatures as PEEK and PEKK have glass temperatures at 143, 160 °C and melting temperatures at 341, 364 °C respectively.²⁴ Therefore, sterilization through pressurized steam like autoclaving is possible without degrading their properties.^{21,29} Besides, using gamma radiation or ethylene oxide for sterilization is also feasible without their deterioration because of their high resistance to gamma and electron radiation.^{21,29}

c. Medical imaging

Computer tomography (CT) and magnetic resonance imaging (MRI) show many scattering artifacts when metallic restorations are present in the area being scanned, which subsequently decreases the quality of the resultant images. Contrarily, both polymers are radiolucent in these imaging techniques which is beneficial in the follow-up of different implant surgeries.²¹

d. Solubility

Immersion of PEEK in different aging solutions as distilled water, sodium chloride, artificial saliva, and physiological saliva showed the lowest values of solubility and water absorption.³⁰ Furthermore, it was not damaged chemically by long term exposure to water up to a high temperature of 300 °C.²¹

1.2.3. Types of PEEK and PEKK used in medical and dental fields

PEEK can accept the addition of fillers to produce PEEK composites which have unique improved mechanical and biological properties that can cope better with various needs in industrial and biomedical applications.^{21,25,31} The most common examples of PEEK used in medicine and dentistry are:

I. Carbon fiber reinforced PEEK (CFR-PEEK), which is the first introduced PEEK composite. The addition of 20 - 30% carbon fibers provides an increase in the compressive strength, stiffness, wear-resistance, and load-carrying capability of PEEK. This grade also has better thermal conductivity than unreinforced PEEK, which is advantageous in increasing heat dissipation from load-bearing surfaces. Nowadays, CFR-PEEK biomaterials are applied in dental implants and medical implants for spine fusion and joint replacement surgeries.²¹

II. Glass Fiber Reinforced PEEK (GFR-PEEK), which shows increased strength and modulus of elasticity. In medical researches, glass fillers boosted the bioactivity of PEEK through increasing the proliferation of human osteoblastic cells and osteocalcin production.^{29,32}

III. Titanium oxide (ceramic) filled PEEK, which shows enhanced biomechanical properties and machinability of PEEK. Besides, it allows for the production of different white shade grades because the fillers act as white pigments.³¹ Therefore, this grade is more aesthetic than unfilled or carbon filled PEEK. Additionally, these fillers have fine granularity which is beneficial for the production of PEEK with high polishing properties, reduced plaque accumulation, and discoloration.³³

IV. Bioactive PEEK, which includes a wide range of bioactive fillers that can be added to unfilled or filled PEEK. Common examples of these fillers are hydroxyapatite, β -tricalcium phosphate, titanium, calcium silicate, strontium containing hydroxyapatite. Their purpose is to enhance the biological properties of medical and dental PEEK implants.^{21,25}

V. Radio-opaque PEEK or image contrast PEEK, where radio-opacifiers such as barium sulfate are incorporated into PEEK and its composites to be radiopaque, which allows for better visualization in different medical imaging techniques. This is beneficial for PEEK dental implants and spinal implants.²¹

Although for PEKK, there are still no composites with other fillers produced and documented in the literature, it is possible to obtain two different forms of PEKK; amorphous and crystalline forms during manufacturing. Quenching from the molten state produces quasi-amorphous PEKK, while slow cooling produces a semi-crystalline

type.^{24,34} Each type has different mechanical and physical properties.^{24,34} Worth mentioning that the melting point of PEKK, unlike PEEK, can be modulated according to manufacturing needs.^{24,34}

1.2.4. Processing of PEEK and PEKK

They can be prepared through one of the following approaches which offer flexibility in the manufacturing of different prosthetic frameworks.^{21,35} The first approach is injection molding, where PEEK and PEKK are supplied as pellets or granules, using a vacuum pressing device containing preheated muffle with a pressing plunger.²¹ The second approach is milling of pre-pressed blanks using computer-aided design and manufacturing technology (CAD/CAM).³⁶ While the third approach is three-dimensional printing technology using selective laser sintering (SLS), fused deposition modeling (FDM), and fused filament fabrication (FFF).^{28,37}

1.2.5. Applications of PEEK and PEKK

The global markets of PEEK and PEKK are supposed to grow tremendously owing to the increased demands of high-performance plastics instead of metals in the industrial field of automobiles and aerospace, biomechanics, electrical, and chemical industries.³⁸⁻⁴¹ In this section, the applications of these polymers in medical and dental fields are briefly discussed.

I. Medical field

Generally, they can be applied in every field where metals are materials of choice. PEEK was firstly proposed as biomedical implant material in April 1998 by a company called Invibio Ltd located in Thornton Cleveleys - United Kingdom.⁴² Ions release and significant mismatch in stiffness by a factor reaching to 20 times between titanium or metal alloys and cortical bone increased the need for new materials that are free from metals clinical complications. These complications can be allergy, infection, stress shielding, and bone resorption, which is the most significant as it leads to the reoccurrence of fracture. The bone in a healthy person or animal undergoes remodeling in response to the exposed loads, but if the loading on a bone decreases, the bone will become less dense and weaker and easily susceptible to fracture.⁴³ Hence, **stress shielding** can be defined as “reduction in bone density (osteopenia) as a result of removal of typical stresses from the

bone by an implant".⁴³ In comparison to metals, high-performance polymers offer bio-inertness, weight reduction and compatibility with different x-ray imaging techniques and better matching with bone stiffness.^{21,29,35,44} The most common examples of medical applications are compression bone plates, bone screws, intramedullary nails, hip prostheses, joint replacement systems, implants in spinal surgery, especially for cages used in vertebral fusion surgery.⁴⁵ As well as suture anchors in applications such as anterior cruciate ligament repair.²¹ Other future applications in the cardiovascular field are replacement of heart valves, pacemaker devices, and intracardiac pumps for minimally invasive surgery.^{29,46} Another applications are in craniofacial fields where patient-specific craniomaxillofacial implants as skull plates can be constructed through CAD/CAM technology which perfectly match the defected areas.⁴⁶⁻⁴⁸

II. Dental field

The need for highly aesthetic restorations increases over time, which revolutionizes the scope of non-metallic materials like PEEK and PEKK in implant and prosthetic dentistry.

1. Implantology

Till now, titanium implants are the most widely used with a survival rate reaching 98.8% and success rate of 97.0% in 10 years.⁴⁹ Nevertheless, marginal bone loss is one of its common complications, which is thought mainly due to the mismatch in modulus of elasticity between titanium dental implants (110 GPa) and cortical bone (18-30 GPa).^{14,25} This causes severe bone resorption, implant loosening, and failure over a considerable amount of time, especially in the presence of overloading.^{14,25} Other complications can occur in the presence of titanium implants as hypersensitivity, ion leakage, scattered radiation, and compromised esthetic, particularly in the presence of thin biotype gingiva showing a dark metallic hue.^{14,25} These reasons necessitated the search for alternative materials such as zirconium and PEEK.⁵⁰⁻⁵² Unlike unfilled PEEK, which has a very low modulus of elasticity (3-4 GPa), filled PEEK was suggested as an endosseous or subperiosteal dental implant material, because it showed modulus of elasticity near to that of human bone (18 GPa), plus being biocompatible with high mechanical properties.^{14,25,53,54} Up to date, there are no clinical trials in the literature that assess the application of PEEK as a potential implant material, and not all in-vitro studies showed conclusive results.⁵³

Sarot et al. studied the stress shielding of carbon fiber reinforced PEEK (CFR-PEEK) implants on peri-implant bone using finite element analysis (FEA). He designed four models with different implant abutment connections as follow: CFR-PEEK abutment with titanium implant, titanium abutment with CFR-PEEK implant, CFR-PEEK abutment with implant and titanium abutment with implant. The CFR-PEEK implants produced a high concentration of load in the cervical region, while titanium implants showed more homogenous stress distribution throughout the implant body. Abutment materials did not influence these results. The authors concluded that CFR-PEEK implant was not advantageous than the titanium implant regarding the effect of stress distribution concerning the peri-implant bone.⁵⁵

Lee et al. investigated whether the mechanical properties of carbon and glass modified PEEK could withstand the expected cyclic loading when simulating the clinical conditions in the patient's mouth. Additionally, he investigated through FEM analysis if PEEK could reduce the shielding effect upon application. From the results, he concluded that PEEK implants could withstand static and cyclic loading, and they may decrease stress shielding and induce bone deposition in the cervical area.⁵⁶

Schwitalla et al. followed the study done by Sarot et al. and tested a stronger carbon filled PEEK with 60% carbon fibers filled PEEK in addition to titanium that served as control. The aim of that study was to explore whether a stronger carbon filled PEEK could produce fewer stress peaks at implant-bone interfacial zone due to reduced elastic deformation. Through finite element analysis, he reached the conclusion that 60% carbon filled PEEK had a stress distribution almost near to that of titanium.⁴² Schwitalla et al. also studied the elastic behavior and long term dimensional stability of 11 different dental implant PEEK materials using cyclic loading tests to imitate oral mastication. The results showed that all specimens exceeded the required minimum elastic limit and could be used for fabrication of dental implants with the smallest possible diameter of 4mm. Once more, carbon fiber showed the highest stability of all used materials.⁵⁷

Regarding bioactivity, PEEK showed inadequate bioactivity and osteoconductivity because of the bio-inertness and hydrophobicity of its surface.⁵⁸ The bioactivity could be improved through 3 different approaches which could be done separately or in combination with each other.

I. Physical surface treatment, which could be done by exposing PEEK's surfaces into chemical acids in a process known as wet chemistry. This method aimed to change the chemistry of PEEK implants in a positive way rendering them bioactive. Common examples were amination, nitration, sulfonation and fluorination that could form chemical groups on the PEEK surface as PEEK-ONa, PEEK-OH, PEEK-F, and PEEK-NH₂, PEEK-NCO, and SPEEK-W. With the aid of these groups, PEEK surfaces showed lower values of water contact angle and improved adhesion and growth of cells, which means better bioactivity of PEEK.⁵⁹ Another method was by exposing PEEK surface into plasma using different gases like oxygen, nitrogen, ammonia, and argon.^{14,59-61} This will be discussed in detail in the section of surface treatments.

II. Surface coating, which could be done through different techniques mostly incorporating plasma technology as vacuum plasma spraying, radiofrequency magnetron sputtering, cold spray technique, physical vapor deposition, spin coating techniques, aerosol deposition, ionic plasma deposition, plasma immersion ion implantation and deposition, electron beam deposition, and arc ion plating.⁵⁹

III. Impregnating bioactive fillers into the PEEK matrix to produce different composites of bioactive PEEK.^{50,62,63} This could stimulate cell attachment and protein absorption that could improve the wound healing capacity and osseointegration.^{21,64-66}

Johansson et al. conducted his study on rabbits using PEEK implants with nanocoating of hydroxyapatite of 20–40 nm thickness. After three months, he made histological sections that showed osseointegration of PEEK implants with high bone-implant contact values in comparison to uncoated PEEK implant.⁶⁷

Deng et al. investigated the osseointegration of PEEK implants modified with carbon fillers to improve its mechanical properties, and with nanohydroxyapatites to also enhance the bioactivity. He placed his implants in dogs, and after two months, the implants were well osseointegrated with no evidence of bone resorption around them.⁶⁸

Khonsari et al. reported failure of osseointegration and infection at the sites of placement of PEEK dental implant in 3 different clinical cases. He attributed the reasons for these complications to failure of osseointegration and lack of clinical data needed to deal with the future complications of PEEK implants.⁶⁹

Dental implants made of PEEK are theoretically promising mainly because of its mechanical properties. Yet, the bioactivity of its surface should be further investigated and improved to have predictable osseointegration with human bones. In addition, up till now, no clinical trials have been done to prove that PEEK implants will be more clinically successful than titanium. Lastly but not least, PEEK implants should show homogenous stress distribution throughout the implant body as the mentioned finite element analysis studies proved that this has to be improved in the near future. In conclusion, there is still a gap in the literature because of few numbers of human or even animal studies regarding using PEEK as dental implants in addition to the need for further investigation to improve the biomechanics of this material to suit more its application as a dental implant. At the moment, it is difficult to give recommendations for using dental implants made of PEEK clinically.⁷⁰

2. Prosthodontics

The original first suggestion of PEEK as a future dental material was made by **Wada et al. in 1984** based on their computer simulation of different plastic materials that could function as denture base material instead of metals.⁷¹ In prosthodontics, conventional polymers as Polymethylmethacrylates (PMMA) must be fabricated bulky to withstand mastication forces and resist fracture while PEEK and PEKK are lighter in weight and can be designed in thinner sections without framework's weakening. That is why patients feel more comfortable with these new materials. In case of material's milling, these polymers provide perfect balance between metals and ceramics as the milling process is relatively shorter than metals and not technique sensitive as with ceramics.¹⁴ Additionally, a study showed that PEEK had the lowest discoloration in different coloring media as compared to PMMA and composite which is beneficial for long-term serviceability.⁷² Another study showed that PEEK offered long-term dimensional stability under cyclic loading tests that replicate the mastication process.⁵⁷ Consequently, in the literature, a large scope of PEEK and PEKK applications exists because of the mentioned advantages.

In removable prosthodontics, they are used as a framework in removable dentures either through CAD/CAM systems or vacuum pressing technique.^{14,73-75} During construction of telescopic prostheses, it is possible to construct primary or secondary crowns from PEEK or PEKK.⁷⁶⁻⁷⁸

In fixed prosthodontics, both PEEK and PEKK were reported as a substructure in single crowns or bridges.⁷⁹⁻⁸¹ The milled PEEK fixed dentures showed a fracture resistance higher than lithium disilicate glass ceramics, alumina, and zirconia.¹⁴ Moreover, PEEK manifested comparatively high abrasive resistance like metals.⁸²

In implant prosthodontics, both were materials of choice for construction of implant superstructures as abutments, implant bars, telescopic implant bridges, implants crowns and bridges, fixed implants prostheses, removable implant prostheses.^{14,83} As for healing abutments, a study found that there was no change in oral microbial flora attachment formed around PEEK abutments in comparison to other materials like titanium, zirconia, and PMMA abutments.⁸⁴ Moreover, two studies investigated the effect of using PEEK healing abutments on marginal bone loss and soft tissue recession during healing and did not find any detrimental effect or increased risk of marginal bone loss or soft tissue recession.^{85,86} For the construction of temporary abutments, unfilled PEEK could be used as it was cheap and easily modified and strong enough to support an interim prosthesis delivered at the time of implant placement.^{87,88} As final abutments, filled PEEK or PEKK could be individualized using CAD/CAM or pressing techniques and then cemented to titanium base.⁸⁹⁻⁹¹ With regard to abutment screws, a study examined the tensile strength of PEEK abutment screws and compared them to the mechanical requirements needed for abutment screws to be suitable for final fastening of screw-retained restorations on dental implants. The results showed that only 50% carbon filled PEEK could be used for 1.6 mm diameter abutment screw.⁹² Another study compared the fracture resistance of abutment retention screws made of titanium, PEEK and 30% carbon filled PEEK and the results showed that titanium abutment screws had higher fracture resistance than PEEK and with 30% carbon fiber reinforced PEEK abutment screws.⁹³ Therefore, more researches are still needed to have a clear conclusion for its application as a tightening screw.

With respect to retention clips and clasps, PEEK showed low retention characteristics, but a clinical trial revealed that it is applicable for very old patients with low neuromuscular control or in the initial adaptation of patients to implant-retained removable dentures.⁹⁴ Another study reported the applicability of PEEK as retentive clasps, which provided adequate retention that could be maintained for a considerable time.^{73,95}

In Maxillofacial Prosthodontics, custom made implants can be fabricated via CAD/CAM milling or 3D printing to suit different maxillofacial defects, especially if they are large and complex. In these cases, they allow for intraoperative modifications and are good options for patients who do not prefer taking autogenous bone grafts to rebuild the defected areas and restore facial skeleton.⁹⁶ For intraoral defects, a case report showed the possibility of constructing an obturator's frameworks from PEEK and PEKK.^{97,98}

As mentioned before, the only drawback of PEEK/PEKK that they are naturally opaque and grayish, which is problematic when restoring anterior teeth. To solve this problem, composite resins should be added to PEEK/PEKK frameworks in a layering manner. However, another problem with bonding to these veneers arises as PEEK has a chemically inert and hydrophobic surface with low surface energy. Different surface treatments were proposed in the literature to overcome the hydrophobic nature of PEEK/PEKK surfaces and achieve strong, durable bonding with composite resins.

3. Orthodontics

A study showed that orthodontic wires could be made of PEEK as it offers high bending strength, creep resistance, reasonable esthetics and produces orthodontic forces comparable to Ni-Ti wire of $0.40 \times 0.55 \text{ mm}^2$ cross section.⁹⁹

4. Restorative dentistry

A study reported the possibility of using ceramic filled PEEK to fabricate an endocrown to restore a badly decayed upper first molar tooth after endodontic treatment. After 22 months following up, the restoration was still sound with good retention and esthetics, and no sign of recurrent decay.¹⁰⁰

1.2.6. Surface treatments of PEEK and PEKK in prosthodontics

The surface treatment is an applied process to alter the surface of a material aiming to achieve a desired property such as an improved wettability and increased surface energy. In the literature, different surface treatments were suggested to improve PEEK and PEKK surfaces making them more suitable for their applications in prosthodontics. Surface treatments can be classified 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).

I. Chemical etching

It is a process of applying different chemical solutions, either strong acids or alkalis on a material's surface. Therefore, it can be classified into oxidizing and reducing treatments depending on the type of solution used. These solutions can change the physical and the chemical characteristics of a surface for improved adhesion. The aim is to increase surface roughness, which consequently enlarges the surface area accessible for micromechanical bonding beside the possibility of creation of new chemical functional groups on the surface.²¹ In restorative dentistry, 30 - 40% phosphoric acids are commonly used for etching enamel and dentin before bonding to composite resins. While in prosthodontics, because PEEK and PEKK surfaces are highly chemical resistant, strong acids are used for effective etching. These acids are toxic, environmentally unfriendly, and need high laboratory skills during handling. The resultant effects by etching depend mainly on the duration of etching, acid's type, and concentration. Sulfuric, hydrofluoric and piranha acids are the most commonly used for etching PEEK and PEKK in the literature.^{16,22,101-104} The surface topography and degree of roughness vary accordingly which ultimately change the bonding characteristics.¹⁰⁵

II. Sandblasting

It is the process of compulsorily pushing a stream of abrasive particles at high pressure against a surface with the aim of roughening a smooth surface and/or removing surface contaminants.¹⁰⁶ Sandblasting is the most popular method for preparing surfaces of metals, ceramics, and polymers before adhesive bonding. It increases the surface area available for micromechanical interlocking by roughening the surface.¹⁰⁶ The device projects abrasive particles with irregular shapes and sizes at a high velocity to produce pitting at the surface or to remove surface contaminants. Different ways of processing can be achieved by varying the device parameters as projection time, particle size, and pressure.¹⁰⁶ Different types of particles can be applied as metals or glass beads depending on the desired amount of abrasiveness. In dentistry, alumina particles (Al_2O_3) are widely used and supplied from dental manufacturers in three different particle sizes 50 μm , 110 μm , and 250 μm .¹⁰⁶ Ideally, the surfaces to be treated should be first cleaned to remove any pre-existing contaminants on the surface as well as after abrasion to remove the abrasive debris from the surface.¹⁰⁶

Sandblasting is considered fast, cheap, and convenient in comparison to other surface treatments. Unfortunately, it is highly operator dependent which makes the treatment inconsistent from the surface to surface and from an operator to another.¹⁰⁶

III. Laser

The term "laser" is an abbreviation for light amplification by stimulated emission of radiation. According to the kind of lasing medium used, different types of laser exist as solid-state lasers (e.g. neodymium-YAG laser), gas lasers (e.g. CO₂ laser), excimer lasers (a mixture of reactive gas as chlorine and inert gas as argon), dye lasers (using organic dyes in liquid solution as lasing media) and finally diode lasers (they are based on semiconductor media and called semiconductor lasers).¹⁰⁷

Laser was investigated as a physical surface treatment to roughen the surfaces and improve the adhesion to the treated surface.¹⁰⁸ It can modify surface topography, chemical composition, and microstructure of material; thus, improving surface characteristics.¹⁰⁸ The process is generally simple, clean, quicker, and relatively cheaper than other surface treatments.¹⁰⁹ In addition, laser parameters as intensity, area of irradiation, and affected material depth are controllable. This is why it becomes attractive as the properties of the bulk of the material will not be affected.¹⁰⁸

Excimer laser showed that it is capable of improving surface properties of PEEK for better adhesion. It increases the wettability of PEEK firstly by cleaning and removing of weak boundary layers then modification of surface chemistry by forming polar and reactive chemical groups on the treated surfaces and finally increases the surface roughness via laser ablation.^{109–113}

IV. Plasma

Plasma is an ionized gas consisting of an equal density of free mobile positive ions and free electrons, resulting in no overall electric charge.¹ This phenomenon can exist either at low temperature and pressures (e.g., fluorescent lamps) or very high temperatures and pressures (e.g., stars).¹

The plasma state is reached by supplying a gas with energy over a given time to break the bonds in an atomic scale and eventually releasing of positively charged ions, negatively charged ions, neutral particles, free radicals and ultraviolet radiation from the atoms.¹

A. Types of Plasma

Plasma is classified into two main categories. Hot (thermal or high temperature) plasma which exists at temperatures ranging from 100 electron volt to 30 kiloelectron volts and cold (non-thermal or low temperature) plasma which occurs at temperatures below 100 electron volts.¹

Hot plasma is distinguished by an equilibrium state between electrons, ions, and neutrals within the plasma. The most common examples are plasma torches and microwave-based plasma.¹ They are mainly used for sterilization of waste products and deposition of relatively thick bioactive coatings as calcium phosphate and hydroxyapatite on metallic implants to improve cellular adhesion.^{1,21} They are not used with polymers because the high temperatures of plasma treatment cause melting of polymers.^{1,21}

Cold plasma is in general plasma discharges with no absolute equilibrium state as in case of thermal plasmas. Most common examples are plasma jets and plasma pencils. They are mainly used for food sanitation, antimicrobial treatments, and surface treatment through surface's etching and deposition of reactive species or thin coating for better bonding of treated surface. Different surfaces, including chemically inert ones, can be modified without affecting the properties of the bulk material. Cold plasma can easily and effectively be applied to polymers, ceramics, and metals.²¹ In general, several factors affect plasma treatment like vacuum chamber geometry, gas pressure, type of feeding gas, gas flow rate, the distance between the discharge electrode and material surface, substrate surface properties and electromagnetic parameters input power.¹

B. Mechanisms of surface reactions of cold plasma

Two main reactions occur during plasma treatment. Firstly, physical reactions which are governed by ionic activity. Gas atoms start to split into positive and negative ions, and these ions gain kinetic energy from the electrical field generated from the electrode. As they are directed toward the surface to be treated, the bombardment will cause the removal of weak boundary layer and surface contaminants plus increasing roughness of the surface. Secondly, chemical reactions which are controlled by the number of free radicals created on the material surface during plasma discharge. Thus, plasma can change the surface properties of a material without changing its bulk properties.¹

Five principal effects exist as a result of the mentioned surface reactions. These effects occur together but also to varying degrees depending on processing conditions like reactor design, gas chemistry, substrate type.^{1,114}

(1) Surface cleaning

All surfaces suffer from the presence of low molecular weight organic contaminants in the form of residues, antioxidants, mold release agents, and several other organic compounds. These contaminations can be naturally formed, technically formed or both. Although they are attached to surface with weak C-H bonds, they remain after any cleaning process that ends with a liquid rinse.¹¹¹ Therefore, their presence is problematic and accounted for hindering optimal adhesion. During plasma treatment, reactive species (e.g., monatomic oxygen in oxygen plasma) chemically react with surface contaminants causing their volatilization and removal from the plasma treatment zone. Hyperclean surfaces can be then achieved which offer stronger reproducible bonds than normally cleaned surfaces.^{1,115}

(2) Surface Ablation

After removal of low molecular weight organic compounds from the surface, the continuous bombardment of free radicals, electrons, and ions on the substrate surface breaks the covalent bonds of the polymer backbone producing smaller and shorter molecular chains. Afterward, the reactive particles are adsorbed on the surface (adsorption), then they bond with other molecular chains (chemisorption) forming new molecules at the surface which are removed away from the plasma reaction zone with exhaust (desorption).¹ This step is called micro-etching or dry etching as it leaves rougher surface with higher surface area available for micromechanical bonding.¹ The micro-etching produced by cold plasmas is more chemical in nature than physical, and it is limited only to a very superficial layer of the material reaching up to 10 nanometers.¹ Therefore, it does not affect the mechanical properties of the bulk material of the film and can increase surface adhesion. Argon is the most powerful gas in producing high ablation of the material surface.^{1,115}

(3) Surface crosslinking

This effect is manifested only in polymers when noble gases like helium and argon are used during plasma treatment. Energetic particles of these gases have enough power to split C–H bonds of polymer chains and produce free radicals on the polymer surface.¹ In the absence of free radical's scavengers as oxygen, these free radicals because of their high reactivity migrate across polymer chains to react with other species of free radicals present on the surface.^{115,116} This recombination of free radicals causes branching and interconnection of polymer molecular chains on the surface, which is known as crosslinking.¹¹⁵ Crosslinking leaves polar functional groups on polymer surfaces which provides strong covalent bonding between the substrate and its interface (e.g., coatings, adhesive agents).¹¹⁵ Additionally, it enhances shear resistance, heat resistance, and cohesive strength of the surface due to the formation of three-dimensional networks of crosslinked molecular chains which act as barrier layer hindering diffusion across this interphase. Noble gas plasmas are considered most effective in creating free radicals and therefore known as crosslinking plasmas.^{1,115,116}

(4) Surface activation

The next step to surface cleaning and ablation is activation of the surface through the deposition of chemical functional groups as carboxyl and hydroxyl groups on the treated surface. A plasma-treated surface can exhibit now a stronger attraction to adhesive's molecules, which means increased surface energy and wettability. This helps adhesives to wet the treated surface without voids formation in the bond interface, which results in improved bonding quality.^{115,117} Another advantage is the possibility of polar functional groups at the surface to react with chemical groups of adhesives which provide durable, strong chemical bonding than just micromechanical interlocking.¹ In medical and dental implant applications, surface activation is important to increase cells adhesion and improve osseointegration.⁶⁴

(5) Surface coating

Under certain plasma conditions and utilizing special gases (e.g., acetylene), thin coatings can be formed on the substrate surface through a process known as plasma polymerization. These coatings can exhibit different properties depending on selected gas and other process parameters.¹ Plasma coating can widen the applications of polymers

through the formation of anti-scratch biocompatible coatings useful for biomedical devices.¹¹⁸ Furthermore, it can enhance the adhesion of polymers to metals.¹¹⁸

C. Influence of the feeding gas

Principally, each feeding gas shows different effects during plasma treatment. These effects can be categorized according to the feeding gas used. Noble gases as argon or helium generate free radicals on the surfaces and promote for crosslinking.¹¹⁵ Active gases as NH_3 precipitates functional groups (amino groups) on the surfaces that bind covalently with adhesives.¹¹⁵ Oxidizing gases like oxygen, air are scavenger as they remove organics by oxidation and deposit oxygens on the polymer surfaces which promote adhesion by creating hyperclean surfaces.¹¹⁵ Reducing gases like H_2 are used to remove organics from surfaces that are sensitive to oxidation.¹¹⁵

D. Applications of plasma

(1) Plasma medicine

Plasma medicine indicates the direct application of non-thermal plasma in the human body for therapeutic purposes.¹¹⁹ Plasma was suggested to be used in medicine for the first time roughly two decades ago. As some studies in the middle 1990s were conducted on non-thermal plasma and showed that low-temperature atmospheric pressure plasmas (LTP) could inactivate a broad spectrum of microorganisms, including resistant ones.¹¹⁹ This sparked the medical and plasma physics communities to search for the possible applications of non-thermal plasmas in medicine.

Firstly, plasma was applied to sterilize biomedical devices and disinfect skin wounds.⁵ Over time, some studies discovered that plasma could interact with biologic cells positively and produce many favorable outcomes as stimulating cell proliferation and angiogenesis, in addition to promoting tissue regeneration.¹¹⁹ This expanded the applications of plasma from only disinfection of skin wounds to the healing of skin wounds through activation of fibroblasts proliferation, in addition to its applicability in skin cosmetics.¹¹⁹ Recently, plasma has been introduced into the field of oncology, as it could penetrate more than 1 mm in the biological tissues and selectively increased intracellular reactive oxygen and nitrogen species (ROS, RNS) which were generated in liquid phases within cells that induced finally apoptosis (programmed cell death).^{5,119}

In addition to ROS and RNS, plasma parameters like ultraviolet radiations and electrical fields were also important to produce different biological responses within cells.¹²⁰ Dielectric barrier discharge (DBD) and atmospheric pressure plasma jets (APPJ) are CE certified medical devices since 2013 for clinical applications like chronic wounds, pathogen based skin diseases and electrosurgical applications (e.g., argon plasma coagulation), in addition being big research spot at present.^{4,119} DBD devices use the human body as a counter electrode, and it has the advantage of the production of homogenous plasma with more generation of active species. While its disadvantage is that it requires a constant distance from the body, which is difficult to achieve due to body curves and folds that limits the size of the area to be treated.⁶ APPJ devices generate a plasma between 2 electrodes present inside the device, and the plasma is then directed to the target area.⁶ The main benefits of this device are that it allows the usage and mixing of different gases for the production of active species and can treat a larger surface area of the human body than DBD devices.⁶ Unfortunately, because of device geometry and design, only lower quantities of active components reach the target in comparison to DPD devices.⁶ Plasma medicine is still at introduction state and needs further development, more researches, and clinical trials to confirm its practicality as a treatment of choice in different medical fields in the near future.¹¹⁹

(2) Plasma dentistry

As in the medical field, plasma was first introduced to dentistry as a possible approach to treat dental caries after it became known that it had a bactericidal effect on streptococcus mutants (the most significant bacteria in developing dental caries).^{8,121} Plasma applications extended into field of endodontics where a study, done on extracted teeth infected with *Enterococcus Faecalis* (the main bacterial in persistent endodontic infections), found that plasma can effectively disinfect root canal systems after treatment duration longer than 6 minutes better than conventional irrigation therapy with 7 days Ca(OH)_2 temporary dressings. Moreover, another study found that the combination of chemical irrigation with sodium hypochlorite solution plus plasma application was more effective in decontaminating *Enterococcus Faecalis* than doing one of both methods alone.^{8,121} In restorative dentistry, plasma was also proposed as a surface treatment to improve bonding qualities to dentin, which is up till now the most challenging step when restoring teeth with composite restorations. It could increase the surface energy of dentin,

thus improving infiltration of adhesive into dentinal tubules, which allowed the creation of longer resin tags that bond micromechanically better to dentin.^{8,121} Same principles were applied to posts cementation during the reconstruction of badly destroyed teeth.⁸ Lastly but not least, plasma was also suggested to be used for polymerization of self-etch adhesive and replacement of light source in dental bleaching.⁸

In prosthodontics, plasma was attributed to many applications. Firstly, bonding dental ceramics to tooth structures instead of using hydrofluoric acid and silane coupling agent. A study stated that with cold atmospheric pressure plasma, carboxyl groups could be formed on the ceramic surface, and better hydrophilicity could be achieved.⁸ Other studies tried to overcome the difficulties that arise during bonding of zirconia using plasma for better bonding with resin cements.⁸ Secondly, a study found that it was possible to apply plasma on elastomeric dental impressions to clean it from residues of saliva and improve the wettability of impression material which is fundamental for accurate reproduction of intraoral structure after their pouring.⁸ Lastly, a study showed that it was advantageous to use plasma as adjunctive therapy to treat denture wearer who suffered from fungal infections because signs of infection like erythema were rapidly reduced after plasma treatment.¹²² In implantology, two main roles for plasma were proposed. Firstly, the modification of implant surfaces for better protein adsorption, cell adhesion, and osseointegration.^{8,121} Plasma could be used either to increase surface energy, wettability or to coat implant surface with bioactive coatings without changing the bulk properties of the implant through plasma spraying. This was applied to implant materials with low bioactivities like PEEK and zirconia implants, and it is still a big research spot nowadays. Secondly, the treatment of peri-implantitis due to its bactericidal effect in addition to its ability to accelerate gingival wound healing through stimulating fibroblasts proliferation and migration to the wound site.^{8,121}

Finally, plasma could be used in patients with oral cancers and prospective studies showed the palliative effects of using plasma on patients suffering from squamous cell carcinomas.^{123,124} Under plasma treatment, patients showed fewer demands to pain medications, and disinfection of cancer ulcers was evident with a decreased foul odor, besides, decreased the overall size of tumor surface without observation of severe side effects.^{123,124}

1.2.7. Bond strength testing

One of the criteria to predict the clinical success of dental restorations particularly composite restorations and veneered prosthetic frameworks (e.g., porcelain fused to metal or zirconia frameworks and recently PAEK frameworks with veneering composites) is their adhesion competence. This is important to be analyzed for prevention of future complications such as discoloration, recurrent caries associated with direct composite restorations, chipping, and fracture of composite restorations or different veneerings in prosthetic restorations.

Bond strength tests are used for this purpose and can be defined as “mechanical tests designed to measure the stress required to disrupt the bond between two materials” according to dental vocabulary in ISO 1942.¹²⁵ To date, in-vitro bond strength tests are used to evaluate adhesion capabilities and predict their clinical performance as well. Over time, clinicians and dental technicians rely more and more on these laboratory tests to choose the appropriate adhesion protocol and adhesive system in their daily practice.

Bond strength tests are classified into laboratory tests and clinical trials. Clinical trials are the most reliable methods for assessing the effectiveness of dental restorations.¹²⁶ Unfortunately, most of the time, it is difficult to identify the exact reasons for failure because of the presence of multiple confounders within the oral cavity.¹²⁶ Contrarily, laboratory studies are successful in gathering data efficiently on a chosen property by keeping at the same time all other confounders constant.¹²⁶ In this way, laboratory tests can collect data about the properties of dental material and somehow anticipate the clinical behavior of this material in the oral cavity.

Laboratory tests are classified into qualitative tests that analyze bond failures and quantitative tests that focus on bond capacity and longevity of bonding. Moreover, they can be further classified into static or dynamic tests. In static tests, specimens are standing still during application of load while in dynamic tests, the specimens are moving actively upon testing.¹²⁶ According to the size of bonding, static bond tests are classified further into micro tests when bonding area is smaller than 3 mm² and macro tests when the bonding area is larger than 3 mm².¹²⁶ According to means of loading at the interface of the bonding area, static tests are additionally classified into shear, tensile and pushout tests.¹²⁶

I. Static tests

A. Shear bond tests (Macro/Micro)

Following bonding, the specimens are placed in a universal testing machine where force is applied in shear approach until a fracture occurs. In this test, the preparation of specimens is uncomplicated and fast, in addition testing can be done directly after the bonding step. Therefore, shear tests are the most used tests for bond-strength testing in the literature.¹²⁶ Various tools can be used for force application as a single-edged chisel, flat-ended rod, wire loop, and metal tape. The test starts with crosshead speed ranges from 0.5 mm/min to 5.0 mm/min. Upon contacting the specimen, the force of crosshead rises from 0 newtons gradually to a nominal value where the fracture occurs. The final force at fracture is recorded by a load transducer connected to the crosshead.¹²⁷ In the micro shear test, the bonded area is of 3 mm² or less. Micro-tests have the advantages of effortless manipulation and the ability to create and test several specimens from a single tooth. Worth mentioning that shear tests produce uneven stress distribution at the bonding interphase which is more pronounced with micro tests than macro tests.¹²⁸

Parameters affecting shear bond strength measurements:

1. The configuration of the loading tool has a significant effect on stress concentration and distribution at the bonding interface and ultimately, bond results. For instances, wire loop provides homogenous distribution of the forces on the adhesive interface, unlike chisels which develop higher stresses at the area of force application.¹²⁹
2. The location of the loading tool from the bonding interface during force application affects the amount and the type of stresses produced at the bonding interface. Upon loading, typically shear and tensile stresses develop at bonding interface which is responsible for crack initiation and finally debonding or fracture. Loading at an increased distance from the interface creates more tensile stresses because of a bending moment developed in the composite cylinder.¹²⁹
3. The matching of the elastic modulus between the composite and the substrate, the higher the mismatch, the higher concentration of the stresses at the interface which produces false lower values of bond strength.¹³⁰

4. Other critical factors that should be considered as a type of substrate and veneering, bonding area, specimen's storage, artificial aging, test design, sensitivity of the test and operator skills.¹³⁰

B. Tensile bond tests (Macro/Micro)

In this test, the specimens can be gripped actively or passively, and the force should be applied on either side of the test specimen with perpendicular alignment to the bonded interface to avoid bending stresses. Unlike shear testing, stress distribution in tensile tests is more uniform and homogenous.¹²⁶ Therefore, it gives a more accurate estimation of the stress level that initiated debonding. Unfortunately, specimens preparation is more difficult and time-consuming in comparison to shear bond tests.¹²⁶ Tensile tests are mainly used to evaluate the bond strength of different dental cements and compare them to each other.¹³⁰

Micro tensile tests are the most common micro bond tests where specimens have very small bonding area of approximately 1mm^2 .¹³⁰ This test produces the most homogenous stress distribution at the interface and it is more economical as multiple micro specimens originating from one tooth can be made.¹³⁰ In comparison to macro tensile test, specimen preparation is more difficult, time-consuming, technique sensitive because specimen's preparation starts after the bonding step and requires an experienced operator to avoid the creation of flaws at the interface that results in crack initiation and propagation which finally resulted in low bond strength values. Moreover, specimens could be easily damaged or fracture after bond testing.¹³⁰

C. Push-out bond tests (Macro/Micro)

Pushout tests are shear tests which are adapted to measure retention of different posts in addition to adhesion of different endodontic sealers. Through the universal testing machine, the force is applied using a mounted plunger that covers completely the tested post or sealer without contacting the inner walls of root canals. This test is also time-consuming and more difficult in specimen preparation than shear bond testing.^{126,130}

Micro push out tests require a specimen thickness of 1mm^2 or less. it imitates the clinical conditions better as the shear forces are created parallel to the cement/dentin and cement/post interfaces.¹²⁸

II. Dynamic tests

In these tests, specimens are exposed to cyclic loadings as produced during chewing.¹²⁶ For more clinical relevance of in-vitro studies, dynamic tests should be done in conjunction with static bond tests because alone they cannot examine growing fatigue in the bonded materials that occur intraorally.¹²⁶ Available tests in the literature are micro tensile fatigue test, micro-rotary fatigue test macro/micro shear fatigue, point-bend fatigue test, and macro/micro push-out fatigue test.¹²⁶

III. Durability tests

Testing of bond durability is important to measure and predict the effectiveness of bonding under a more clinically relevant environment. Water storage and thermocycling are the most common artificial aging methods that test bond durability.¹³⁰ Thermal cycling involves repeatedly cycling a specimen between two extreme temperatures (usually 5 and 55 °C) with enough resting time in between to ensure the thermal adjustment of the specimen before exposing it to another extreme thermal stress. This process creates stresses at the bonding interphase due to the 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 correspond to approximately 4-5 years period in vivo.^{130,131}

1.2.8. Review of studies that have investigated the impact of different surface treatments on bond strength between different PAEK and resin materials

Schmidlin et al. (2010) explored the effect of chemical etching and different sandblasting techniques on shear bond strength between unfilled PEEK and two composite resin materials. The applied surface treatments were etching using 98% sulfuric acid for 1 minute, sandblasting using alumina 50 µm, sandblasting using alumina 110 µm and sandblasting using Rocatec system. The selected veneering protocols were 3M universal composite resin cement and Hybrid composite resin after application of Heliobond adhesive. After bonding, the specimens were stored in distilled water at 37 °C for 24 hours. Results showed higher bond strength with sulfuric acid etching using both composites materials. Moreover, no adhesion was established with resin cement with all

different sandblasting treatments, and high bond strength measurements were obtained only after adhesive applications following sandblasting using alumina 50 µm or Rocatec system.¹⁶

Kern et al. (2012) investigated the ability of air abrasion to affect the tensile bond strength and bond durability between PEEK and provisional resins. Chair-side air abrasion was done through 110 µm alumina particles (Rocatec-Pre) alone or with tribochemically silica-coated particles (Rocatec-Plus). The applied adhesive agents were (Luxatemp-Glaze & Bond, Ecusit composite repair, Clearfil Ceramic, and 3M ESPE Sil). PEEK specimens were veneered with Luxatemp Fluorescence provisional resins. For artificial aging, specimens were either kept in distilled water at 37 °C for three days without thermocycling or for 150 days with added 37,500 thermal cycles at 5 and 55 °C. The results showed that strong and durable bonds were obtained in case of application of Luxatemp-Glaze & Bond adhesive after air abrasion using alumina 110 µm (Rocatec-Pre).¹³²

Hallmann et al. (2012) probed the impact of combining chemical etching and air abrasion on the tensile bond strength of PEEK to resin cement. PEEK specimens were distributed into six groups; no treatment group, etching with piranha acid, air abrasion using 50 µm alumina followed by piranha etching, air abrasion using 110 µm alumina then piranha etching, air abrasion using 30 µm silica-coated alumina then piranha etching, and air abrasion using 110 µm silica-coated alumina then piranha etching. The applied adhesives were Clearfil Ceramic and Heliobond while Rely-X-Unicem used as veneering resins. After bonding, immersion in distilled water at 37 °C for three days followed by tensile bonding testing was done. The results revealed that air abrasion using 50 µm alumina and etching with piranha solution in addition to Heliobond adhesive provided the highest bond strength. Moreover, PEEK in the control group could not bond with resin cements, also silica coated and etched PEEK did not show improved bonding.¹⁷

Stawarczyk et al. (2013) investigated how different adhesives can influence the tensile bond strength of one type of PEEK and different brands of veneering composites. The tested PEEK was ceramic filled PEEK. Multiple adhesives including Visiolink, Z-Prime Plus, Monobond Plus, Ambarino P60, Signum PEEK Bond were tested in addition to the non-treated control group. Three composite resins were applied 3M Sinfony, VITA VM

LC, and GC GRADIA. Surface abrasion using 50 µm alumina was done at first then conditioning with different adhesive agents. In each group, half of the specimens were only kept in distilled water at 37 °C for 24 hours, and the second half was additionally exposed to 10,000 thermal cycles at 5 and 55 °C. The highest bond values between PEEK and all tested veneering composites were present in groups conditioned with Visiolink and Signum PEEK Bond adhesives.¹³³

Stawarczyk et al. (2013) studied the influence of plasma on the shear bond strength of PEEK to 2 self-adhesive resin cements. Ceramic filled PEEK specimens were distributed into two groups; group treated with helium plasma and untreated control group. In this study, 3 different adhesives were tested Visiolink, Signum PEEK Bond and Ambarino P60. The used resin cements were Rely-X-Unicem and Clearfil SA. Subsequent to bonding; specimens were immersed in water for 24 hours at 37 °C. Afterwards, 2 groups were additionally exposed to thermocycling for 5,000 and 10,000 cycles. From the results, plasma treatment couldn't enhance bond strength with and without application of adhesive agent.¹³⁴

Sproesser et al. (2014) studied the influence of prolonged etching durations with sulfuric acid on shear bond strength of PEEK to different luting resin cements. Specimens of ceramic filled PEEK were polished then etched using sulfuric acid at different durations (0 (control), 5 seconds, 15 seconds, 30 seconds, 60 seconds, 90 seconds, 120 seconds, and 300 seconds). After ultrasonic cleaning, bonding started with the following resin cements Clearfil SA, Rely-X-ARC, Variolink II. Then, specimens were kept in distilled water at 37 °C for 28 days. Shear bond testing were done first then scan electron microscopy. The high bond strength measurements were found in 3 resin cements groups at etching durations reaching up to 120 seconds. Moreover, etching duration of more than 120 seconds showed detrimental effects on bond strength measurements. Specimens of the non-etched control group didn't bond to resin cements. This study demonstrated that sulfuric acid etching could enhance bond strength of resin cements to PEEK surfaces. However, chemical treatment using sulfuric acids is hazardous and not recommended for use in dental clinics.¹⁰¹

Stawarczyk et al. (2014) studied the effect of two different etchants (sulfuric acid and piranha acid) on the tensile bond strength of PEEK to different veneering resins. The

materials used were 20% ceramic filled PEEK, 2 adhesive agents Visiolink and Signum PEEK Bond and 2 veneering composites 3M Sinfony and VITA VM LC. Sulfuric acid groups were etched for 60 seconds while piranha groups were etched for 30 seconds. After treatment, surface energy and roughness were calculated. Artificial aging was done through immersion in distilled water at 37 °C for two different durations (24 hours and 60 days) before bond testing. The results showed high bond strength generally after adhesive application in addition to 3M Sinfony as veneering resin but this improvement in bond strength compared to untreated groups was not significant.¹⁰²

Fuhrmann et al. (2014) probed the impact of different techniques of air abrasion and adhesives on the tensile bond strength of 3 different PAEK to resin cements. Three types of PAEK were used glass filled PEEK, crystalline PEKK and amorphous PEKK. Air abrasion was done by alumina particles (Rocatec-PRE) and tribochemical silica-coating (Rocatec SOFT). 2 adhesive agents were applied Universal Monobond Plus and Luxatemp Glaze & Bond. Specimens were then bonded using Multilink Automix to MultiCore Flow through Plexiglas tubes. Artificial aging for 3, 30 and 150 days in water at 37 °C including thermal cycling at 5 and 55 °C for 10,000 times or for 37,500 times was done before tensile bond strength test. Results showed that glass filled PEEK had higher bond strength than both types of PEKK throughout all groups.²⁴

Rosentritt et al. (2014) probed the impact of different chemical etching and sandblasting techniques on shear bond strength of unfilled PEEK to veneering composites. Different 18 groups were created according to methods of treatment and surface conditioning used. The surfaces of PEEK specimens were exposed to chemical etching using sulfuric acid 98% for 1 min or piranha acid for 30 seconds, air abrasion with alumina 50 or 120 µm, air abrasion using Rocatec silica modified alumina 30 µm or 110 µm and finally untreated control group. After each treatment surface roughness (Ra) of each group was calculated. Next, different dental surface conditionings were used including ESPE Sil, Signum connector, Solidex Solibond, GC Composite Primer, 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 and 2. Additionally, standard and flowable opaquer were used. Artificial aging was done in distilled water for a full day and for 90 days in addition to thermal cycling for 12000 cycles. Results showed that highest bond strength could be achieved after sandblasting

through 50 μm alumina particles then using Signum Connector adhesive and addition of opaquer.¹³⁵

Keul et al. (2014) tested the influence of chemical etching and air abrasion on tensile bond strength between PEEK and veneering composites. Ceramic filled PEEK specimens were either air abraded through 50 μm alumina particles, etched with piranha acid, air abraded followed by piranha etching or left untreated. Surface energy and surface roughness were measured after each treatment. Different adhesives were probed including Heliobond, Visiolink, Clearfil Ceramic Primer and Signum PEEK Bond. 2 composite resins were also tested Signum composite and Signum Ceramis. Following bonding, specimens were immersed in water for 60 days at 37°C then thermocycled for 5000 cycles at 5°C/55°C with dwell time of 20 seconds. The results manifested high surface energy and roughness with air abrasion group then air abrasion/piranha acid etching group. Among adhesives, Visiolink, Heliobond showed the highest bond strength measurements. Among surface treatments, combining the air abrasion and chemical treatment showed highest bond strength measurements.¹³⁶

Zhou et al. (2014) examined the impact of 3 surface treatments sandblasting, plasma treatment and chemical treatment on shear bond strength of PEEK to 2 different composite resins. Silica filled PEEK specimens were treated either with sulfuric acid etching, hydrofluoric acid etching, argon plasma, 50 μm alumina air abrasion or left untreated as control group. Bonding of the specimens were done either through using Rely-X-Unicem resin cement or Clearfil composite following application of Clearfil SE adhesive. After bonding, all specimens were immersed in distilled water at 37 °C for 24 hours. The results showed that the highest bonding of PEEK to both resin materials occurred after chemical surface treatment with sulfuric acid. Moreover, high bond strength was achieved using Clearfil SE adhesive and composite resin system rather than direct application of resin cement when surface treatment was kept constant.¹⁰³

Silthampitag et al. (2016) investigated the influence of four different surface treatments on the bond strength between PEEK and composite resin. Specimens of ceramic filled PEEK were exposed to one of the following groups; etching with 98% sulfuric acid, etching with piranha solution, sandblasting using 50 μm alumina and control untreated group. After each treatment, surface roughness was measured in addition to surface

analysis using scan electron microscope and Fourier transform infrared spectroscopy. The applied adhesive in each group was Heliobond and the veneering resin was Z350xt flowable composite from 3M. In each group of surface treatment, bonding steps were made with and without adhesive. The results showed that both sandblasting and surface etching had comparable high surface roughness measurements in comparison to other groups. Chemical etching through sulfuric acid followed by Heliobond application produced the highest bond strength measurements.¹³⁷

Schmidlin et al. (2016) probed the influence of glycine application after helium plasma treatment on tensile bond strength of PEEK to two resin cements. Ceramic filled PEEK specimens were air abraded with alumina 50 μm then cleaned in ultrasonic device. Following, the specimens were distributed into 2 main groups; plasma treated and non-plasma treated. Further, in each group the specimens were conditioned using different adhesive agents which were either mixed with glycine powder or directly applied to the specimens. The used adhesive agents were Soft Liner Liquid, Visiolink, Ambarino P60. Two different resin cements were used Rely-X-Unicem and Clearfil SA. For artificial aging, all the specimens after bonding were stored in distilled water at 37 °C. Afterwards, the tensile bond testing was done directly to half of the specimens whereas the other half was additionally aged for extra 14 days and thermocycled for another 10,000 cycles. The results showed that without addition of glycine there was no effect of helium plasma on tensile bond strength. While mixing glycine with Soft Liner Liquid or Ambarino P60 showed significantly higher initial tensile bond measurements which couldn't survive thermocycling tests afterwards. Without application of plasma nor addition of glycine, all groups conditioned with Visiolink adhesive showed the highest tensile bond strength measurements.²⁰

Stawarczyk et al. (2017) investigated the influence of different protocols of sandblasting (particle size and sandblasting pressure) on the tensile bond strength of PEEK to composite resin. Unfilled PEEK specimens were tested with five different sandblasting protocols including 50 μm alumina at 0.05 MPa, 50 μm alumina at 0.35 MPa, 110 μm alumina at 0.05 MPa, 110 μm alumina at 0.35MPa and Rocatec 110 μm at 0.28 MPa. The applied adhesive agents were Visiolink, Monobond Plus/Heliobond, Scotchbond Universal, Dialog Bonding Fluid. The veneering composite used was Dialog Occlusal. After bonding, artificial aging was done by immersing the specimens in distilled water at

37 °C for 28 days followed by thermocycling for 20,000 cycles at 5/55 °C. Regarding type of adhesive, Visiolink had the highest bond strength results even following thermocycling and independently to the surface treatment method. The grain size of powder used in sandblasting didn't affect the bond strength while sandblasting pressure and type of adhesive did.¹³⁸

Schwitalla et al. (2017) explored the influence of cold low pressure plasma mixture of argon/oxygen gases on the shear bond strength of PEEK to veneering composite. Four groups were designed untreated, argon/oxygen plasma, sandblasting and sandblasting followed by argon/oxygen plasma. The materials used in his study were 3 types of PEEK (unfilled PEEK, ceramic filled PEEK and pigment powder filled PEEK), veneering composite (Vita VM LC) and adhesive (Visiolink). Before and after each treatment surface roughness and contact angle measurements were calculated. Then the specimens were stored in distilled water for 24 hours before bond testing. The results manifested a significant reduction in the contact angle after plasma treatment while sandblasting caused significant high contact angle measurements. Plasma reduced surface roughness while sandblasting increased it in comparison to control group. The group of combined treatments (sandblasting followed by plasma) had the highest bond strength. Unfilled PEEK exhibited the highest bond strength in comparison to the other two PEEK materials.¹⁸

Stawarczyk et al. (2017) studied the impact of different surface treatments and adhesive agents on tensile bond strength of PEKK to either polymethylmethacrylate (PMMA) or composite resins. Specimens of PEKK (Pekkton ivory) were first sandblasted using 100 µm alumina then cleaned with distilled water in ultrasonic device. Following, they were allocated to one of the following treatments; Visiolink, Visiolink plus opaquer, Pekkbond, Pekkbond plus opaquer, plasma, plasma plus opaquer, plasma followed by Visiolink then opaquer and finally plasma then Pekkbond and opaquer. The plasma treatment used oxygen as a feeding gas. Surface roughness was measured after adhesive and opaquer application. After conditioning the specimens were bonded either to PMMA, packable and flowable composite resins. Afterwards, specimens were stored in distilled water for 24 hours at 37 °C. In addition, 20 specimens of each subgroup were exposed further to thermocycling for 10,000 cycles between 5 and 55 °C. The results showed that opaquer increased the surface roughness and bond strength when applied. Visiolink showed higher

bond strength than Pekkbond. Plasma alone couldn't establish bonding to PEKK specimens while after combination with Visiolink, highest bond strength could be achieved. PMMA bonded better on PEKK than composite resins. Flowable composite showed significantly higher bonding than packable material.¹³⁹

Lee et al. (2017) studied the impact of different surface treatments on shear bond strength of PEKK to veneering composite resins. The applied surface treatments were 95% sulfuric acid etching, sandblasting through 50 µm alumina and sandblasting through 110 µm silica-coating alumina. After each treatment, measurements of surface roughness and contact angles were done. Additionally, quality surface analysis was made using scanning electron microscopy. Five different bonding agents were applied in this study; Luxatemp Glaze & Bond, Visiolink, Single Bond Universal, All Bond Universal, and Monobond Plus with Heliobond. The results showed that sandblasting with either particle sizes had significantly higher values of shear bonding strength than chemical treatment. Regarding bonding agents, Single Bond Universal and Visiolink showed the highest shear bond strength irrespective to the applied surface treatment.¹⁰⁴

Lümkemann et al. (2018) studied the effect of different sandblasting pressures and adhesive agents on tensile bond strength of PEEK to self-adhesive resin cement. The materials used were ceramic filled PEEK and Clearfil SA resin cement. The sandblasting pressure was varied into 0.05, 0.2 and 0.4 MPa. Different primers were applied Scotchbond Universal, Clearfil Universal Bond, Futurabond U, Adhese Universal, G-Premio Bond, Pekkbond, Visiolink. After bonding, thermal cycling of 5,000 cycles were done then tensile bond strength was measured. Additionally, surface roughness after each pressure parameter was measured. The results showed that conditioning primers had a significant impact on tensile bond strength where Visiolink showed the highest values of tensile bond strength in all sandblasting pressure groups. Although sandblasting pressure had an impact on surface roughness, it did not affect the tensile bond strength.¹⁴⁰

Henriques et al. (2018) tried to roughen three different PEEK materials (unfilled PEEK, 30% glass filled PEEK and 30% carbon filled PEEK) with carbon dioxide laser by creating small holes of 200 µm diameter spaced apart at 400 µm in the first group and 600 µm in the second group. While the third group PEEK specimens were additionally treated with acid etching after laser treatment with 200 µm sized holes spaced apart at

400 µm. The fourth group was acid etching without previous laser treatment. These holes were created in laser ablation through removing part of PEEK material via melting through laser pulses with the aim to provide anchorage for the resin cement. Shear bond strength was made following artificial aging in distilled water storage at 37 °C for 24 hours. The results showed that no evidence of improvement of bond strength of PEEK to resin cement after laser treatment. The author recommended testing different laser ablation parameters to find the best conditions needed for durable strong bond with composite resins.¹⁰⁸

Sakihara et al. (2018) probed the impact of chemical etching on shear bond strength of PEKK to veneering composite. PEKK specimens (pekkton ivory) were etched either with sulfuric acid or vinyl sulfonic acid. 3 concentrations of sulfuric acid 80, 90, or 98% and two concentrations of vinyl sulfonic acid 90 or 95% were tested. Additionally, both acids were tested at three different durations 5, 30, and 60 seconds. Two control groups were created (unetched/unprimed) and (unetched/primed). Following each treatment, surface analysis through scan electron microscope was carried on. Afterwards, adhesive agent (Metal Z Primer) was applied followed by veneering composite (Gc Gradia Opaque then Gc Gradia Body). Artificial aging was done by immersing the specimens in distilled water at 37 °C for 24 hours plus thermocycling for 20.000 cycles at 4 and 60 °C. The results showed that highest bond strength values could be achieved only following etching with 90% sulfuric acid for 5 seconds or 95% vinyl sulfonic acid for 30 seconds.²²

Bötel et al. (2018) studied the impact of different plasma parameters on shear bond strength of PEEK to veneering composites. Three PEEK materials were used; unfilled PEEK, ceramic filled PEEK, ceramic filled PEEK with pigments. All specimens were first polished then air abraded with alumina 110 µm followed by ultrasonic cleaning. The applied treatments were control without plasma, O₂ plasma for 3 minutes, O₂ plasma for 35 minutes, Ar/O₂ plasma for 3 minutes, Ar/O₂ plasma for 35 minutes. Surface roughness and water contact angles were measured before and after each plasma treatment. The chosen adhesive was visiolink while three veneering composites (Vita VM LC, Gc Gradia and GC Gradia Flo) were tested. The specimens were then immersed in distilled water at 37 °C for 24 hours before shear bond testing. The results showed that the highest bond strength values occurred when two ceramic filled PEEK compounds treated with O₂ plasma for 35 minutes and veneered with GC Gradia Flo.¹⁴¹

1.2.9. Aim of the study

The aim of this study was to examine the shear bond strength between veneering resin and three different types of PAEK (unfilled PEEK, filled PEEK and PEKK) after plasma surface treatment with different gases. The main objective was to probe the best method of achieving high and durable bond strength of PAEK to veneering resins which can solve the chipping and fracture of veneering resins from surface of these polymers in clinical practice.

The null hypothesis: all plasma treatments will not improve bond strength in comparison to untreated surfaces.

Research question: Can plasma surface treatment improve bonding between PAEKs and veneering composite resins?

Clinical relevance

PEEK and PEKK are introduced as a replacement of metal and zirconium substructure in prosthodontics because they offer many advantages as already stated. Unluckily, reliable guidelines to modify PEEK/PEKK surfaces for better bonding with veneering composites are missing. This can affect their long-term serviceability intra-orally with a high possibility of chipping and fracture of veneering resins. Consequently, increased demand for repair and the number of patient visits will be evident, which also increases the overall cost of treatment and maintenance.

2. Materials and Methods

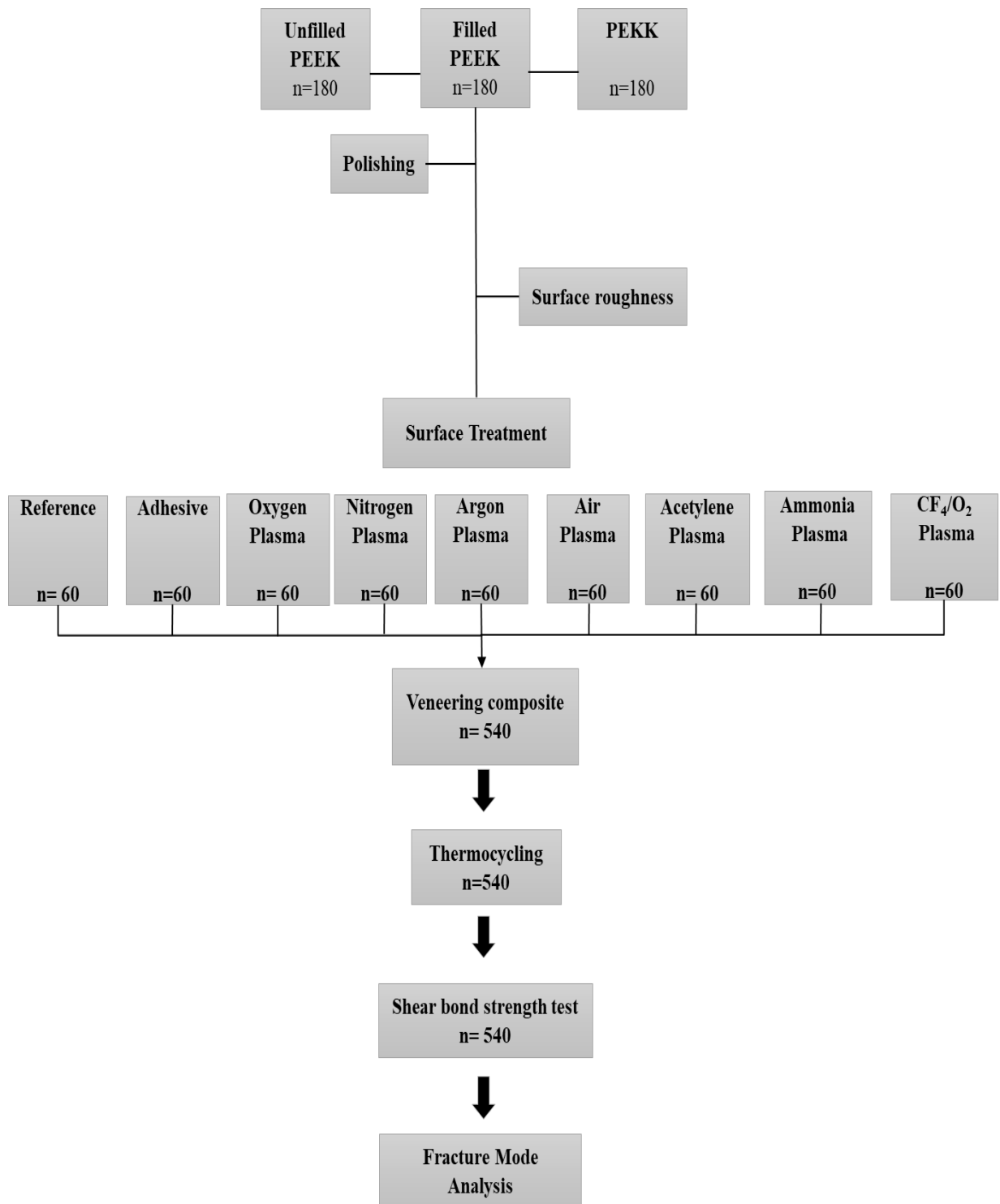


Figure 2: Flow chart of research study following ISO 10477 guidelines

Table 1: Applied materials in the study

Material	Composition	Manufacture	LOT
Optima PEEK	Unfilled PEEK	(Juvora Ltd., Lancastershire, UK)	J000009
Bre.CAM. BioHPP dentine shade 2	Ceramic filled (30%) PEEK	Bredent, Senden, Germany	450449
Pekkton Ivory	PEKK	Cendres+Métaux, Biel-Bienne, Switzerland	NA
CarbiMet	Abrasive Papers with different grit P180 up to P1200	Buehler UK LTD, Coventry, England	36-12-0180 30-12-0320 36-12-0360 36-12-0600
Ethanol	70% ethanol	Liquid production GmbH (Rosenheim-Germany)	20180517
Visiolink	MMA, PETIA, dimethacrylates, photoinitiators	Bredent; Senden, Germany	161628
Sinfony opaquer	Powder: Silane treated quartz, Calcium Fluoride, Titanium Dioxide, Isobutylmalonyl-N,N'-Dicyclohexylsulfamide, Lauroyl Peroxide, Silane treated silica, C.I. pigment yellow 42, Iron hydroxide oxide Liquid: Dicyclopentyl dimethylene diacrylate, Methyl methacrylate, Monoacrylateacetate, Vinyl acetate polymer, Phosphine oxide, N,n - dibutylphenylethylamine hydrochloride.	3M ESPE AG, Seefeld, Germany	3331717
Sinfony composite paste A3	Silane-treated glass powder, diurethane dimethacrylate, dicyclopentyl dimethylene diacrylate, substituted dimethacrylate, silane treated silica, glass ionomer filler, HEMA	3M ESPE AG, Seefeld, Germany	3331717

2.1. Specimen preparations

2.1.1. Milling

In this study, three different PAEK materials were used unfilled PEEK, ceramic filled PEEK and PEKK. The specimen's geometry and dimensions were designed through Solidworks software (Solidworks Corp, Massachusetts, USA) with following dimensions 20 mm x 10 mm x 2 mm³ then exported as STL file to mill 180 specimens from each material through CAD/CAM system.

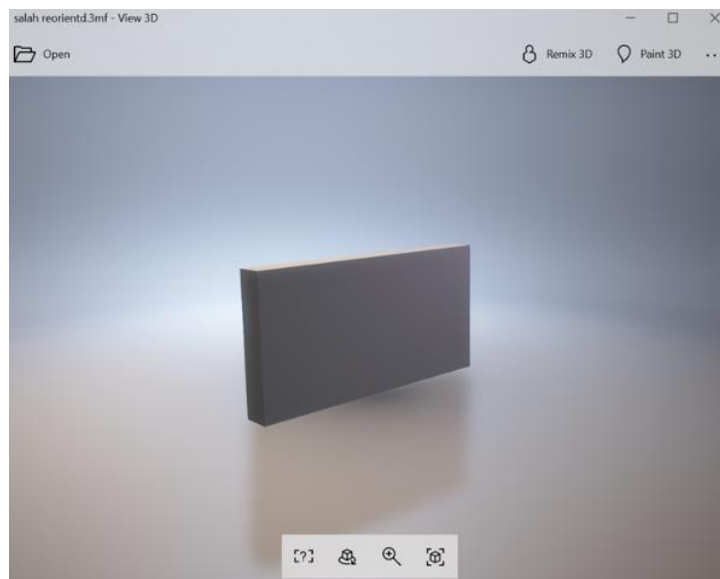


Figure 3: 3D view of the specimen's dimension exported as STL file.

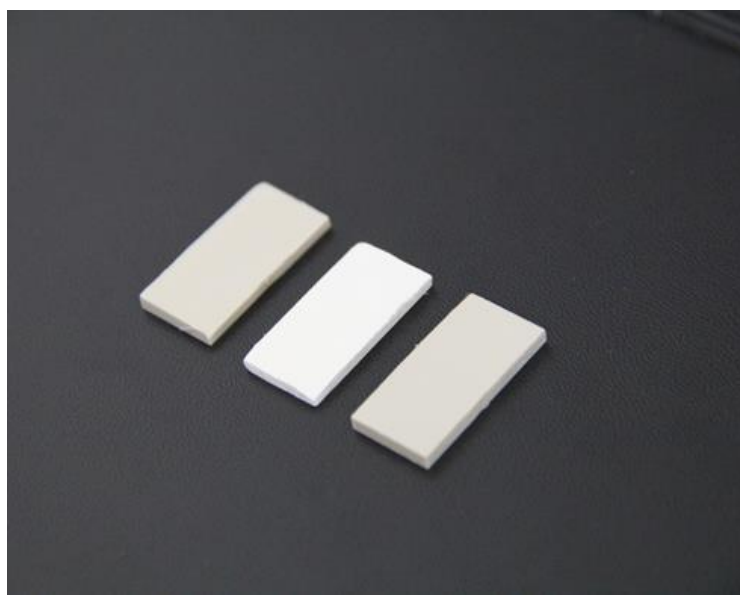


Figure 4: From left to right, milled specimens of unfilled PEEK, ceramic filled PEEK and PEKK.

2.1.2. Polishing

Firstly, 40 specimens of ceramic filled PEEK were polished with four different abrasive papers: P180, P320, P600, P1200. 10 specimens were used for each abrasive paper. In P180, specimens were polished directly while with other abrasive papers the polishing procedure was done in sequence (i.e., to polish specimens with P1200, they were firstly polished with P180 then P320 then P600 and finally P1200). The polishing machine used was Metaserv Motopol 12 (Buehler UK LTD, Coventry, England) and polishing step was done under standardized conditions where silicon carbide paper (SIC) was rotating at 150 RPM under constant water. Each specimen was painted with black color and polishing was done until complete disappearance of the painting.

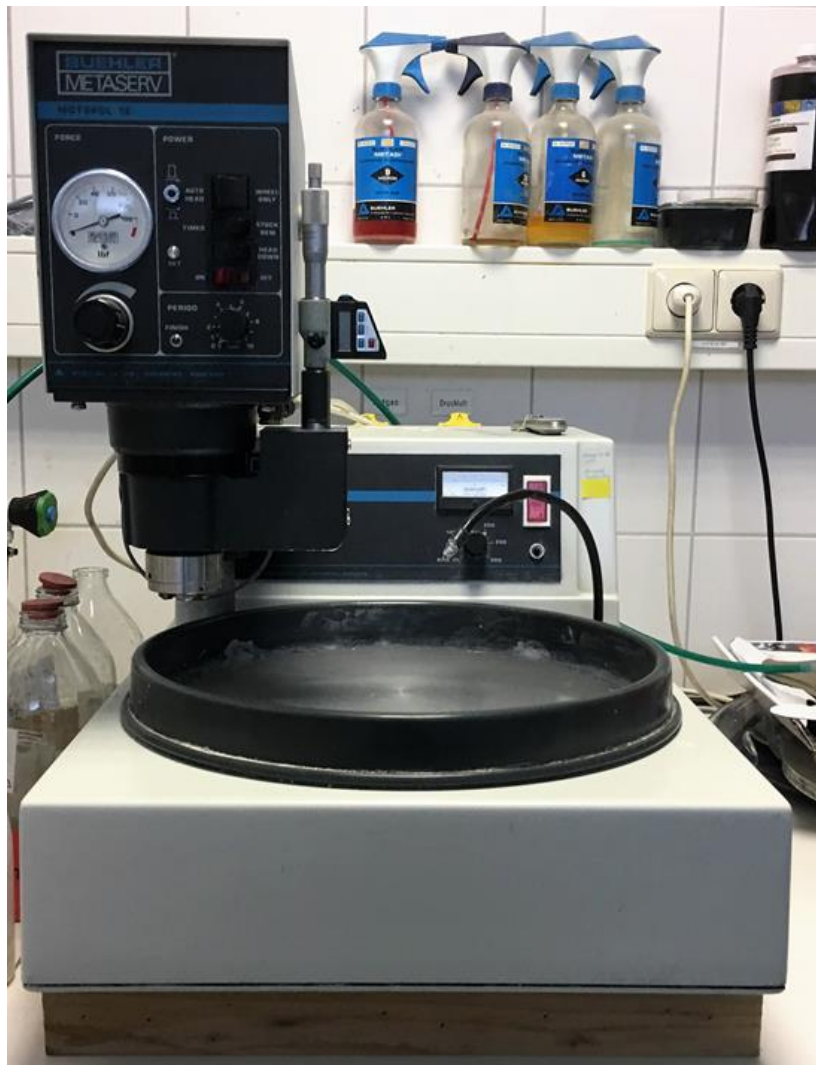


Figure 5: Automatic polishing machine used to standardize surface roughness of the specimens



Figure 6: Different types of polishing discs used to standardize the surface roughness of the specimens

2.1.3. Surface roughness

The surface roughness of the 40 pre-polished PEEK specimens was measured using Perthometer Perthen (Mahr, Göttingen, Germany). This device was equipped with a needle that had a 2 μm diamond tip which allowed two-dimensional tracing of a given surface. The stylus traversed the center of each specimen surface at a constant speed of 0.5 mm/s in an area of 3 mm length and width. 121 measurement lines with 25 μm distance between the lines were performed and through analyzing software; MountainsMap Universal 7.2 (Digital Surf, Besancon-France) surface roughness could be calculated in Ra (average roughness height). After comparing the Ra results with the study done by Rosentritt et al.¹³⁵, all test specimens were polished by using abrasive papers P180 followed by P320.

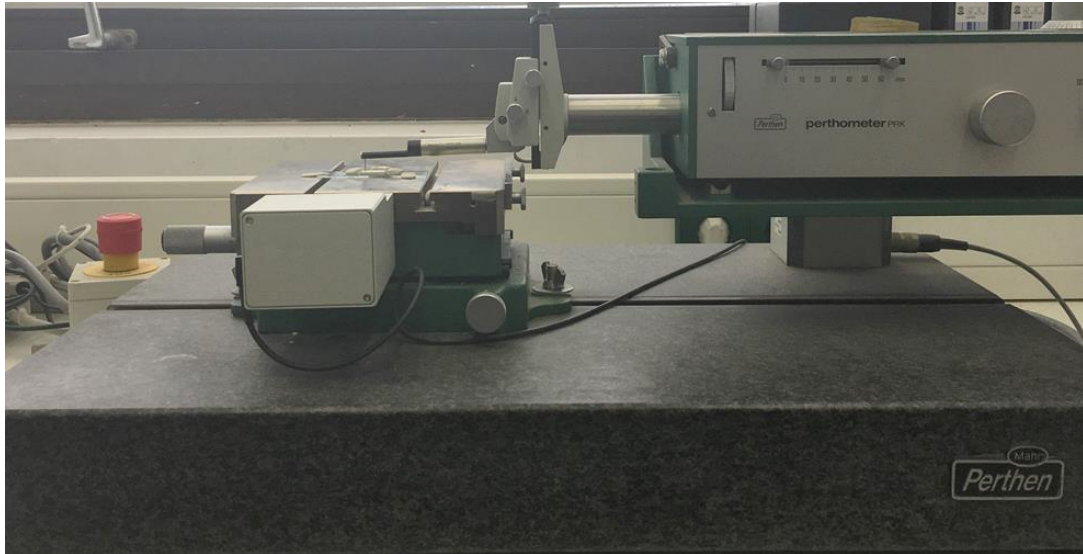


Figure 7: Surface roughness measuring machine (Perthometer)

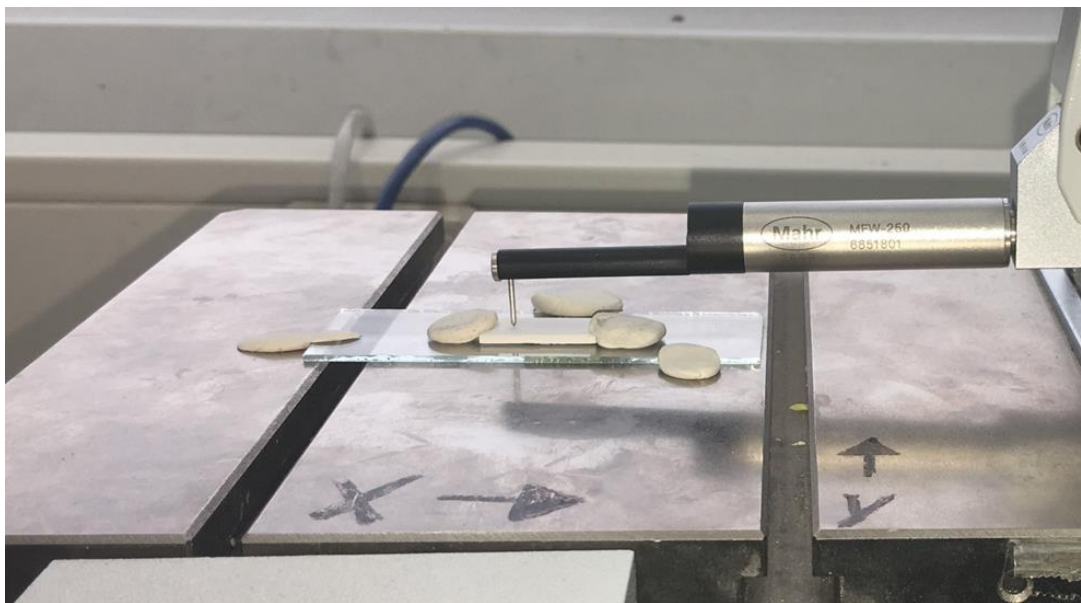


Figure 8: A close photo of Perthometer while measuring the roughness of the specimen's surface

2.1.4. Surface Cleaning

After polishing, all specimens were cleaned in an ultrasonic bath containing 70% ethanol for 20 minutes using an ultrasonic machine (Sonorex, Bandelin, Berlin-Germany) then left to dry in the air before surface treatment. Finally, the specimens of each type of PAEK were then numbered and randomly allocated to different surface treatment groups.



Figure 9: Ultrasonic cleaning of specimens via Sonorex device

2.1.5. Surface treatment

In each material, 9 different groups were created. Each group consisted of 20 specimens. The groups were control (untreated surface), adhesive (application of adhesive without prior plasma treatment), and 7 different gaseous cold plasma treatment groups. 2 low-pressure cold plasma systems were used. The first one was Denta Plas Pc (Diener electronic GmbH, Ebhausen, Germany) where surface treatments using the following gases air, argon, oxygen, nitrogen, acetylene were done.

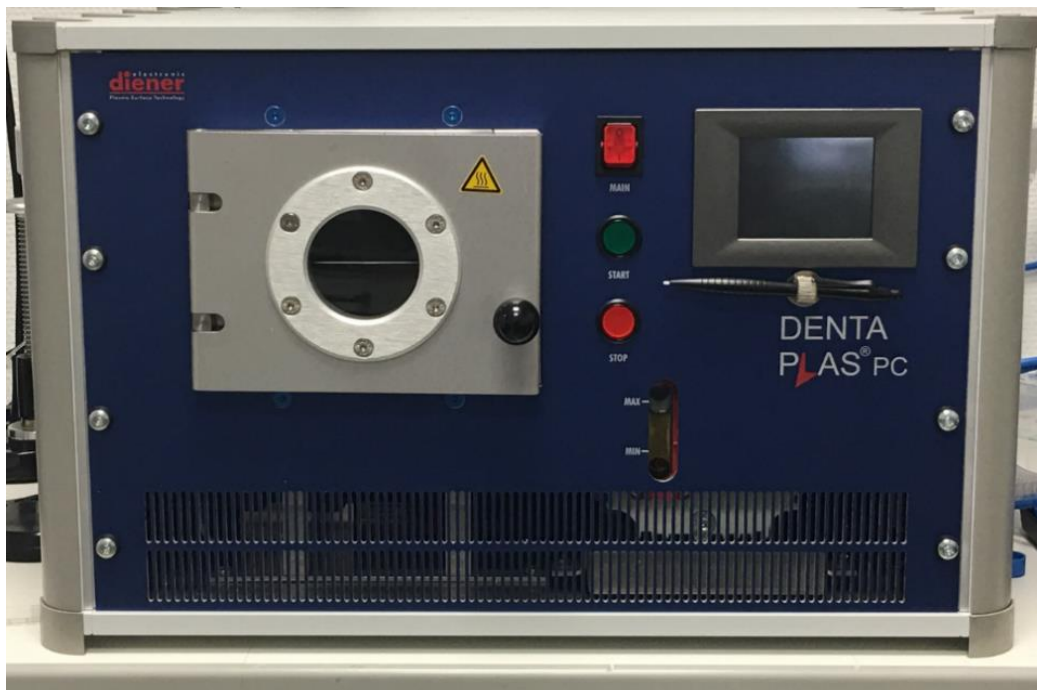


Figure 10: Denta Plas Pc plasma device

The second device was Tetra 30 plasma (Diener electronic GmbH, Ebhausen, Germany) where surface treatments using ammonia and a mixture of tetrafluoromethane with oxygen gases were done. According to manufacturer recommendations. The settings of surface treatment were; 10 minutes treatment duration at a pressure of 0.3 mbar, a temperature of 20 °C, frequency of 40kHz and power output of 100 Watt



Figure 11: Tetra 30 plasma device

2.2. Bonding of specimens with veneering composites

Before bonding, special jigs (seating and bonding jigs) were designed using CAD software; Siemens NX 10.0 (Siemens PLM, Texas- USA). It consisted of two parts. A part where specimens were seated on and another part with dimensions 20 mm x 10 mm x 2.5 mm³ where bonding steps were made through a hole in the center with a diameter of 5 mm. After designing both parts were exported as STL file.

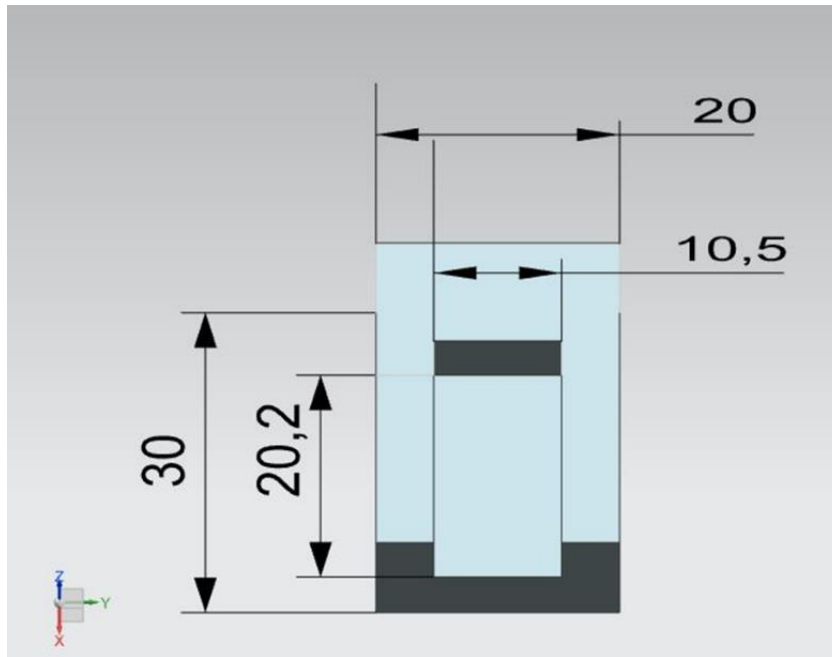


Figure 12: 3D view of designed seating jig. (millimeter was the unit of the linear measurements)

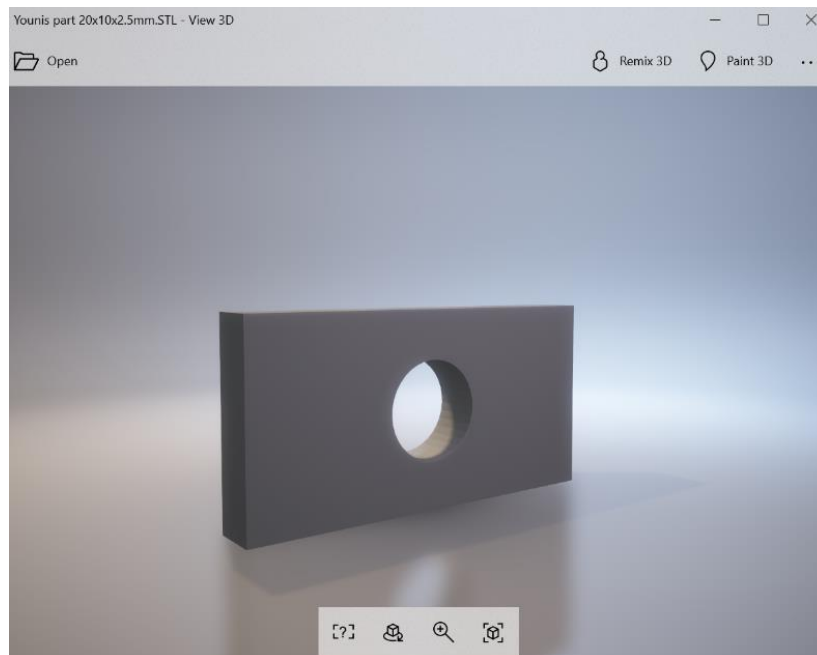


Figure 13: 3D view of the bonding jig

The seating jigs were printed with help of a printing software (MakerBot Print, MakerBot Stratasys, Newyork-USA), a 3D printer based on fused filament fabrication technology (MakerBot replicator, MakerBot Industries, Newyork-USA) and the printing material (filament polylactic acid) from the same company.



Figure 14: Makerbot 3D printer

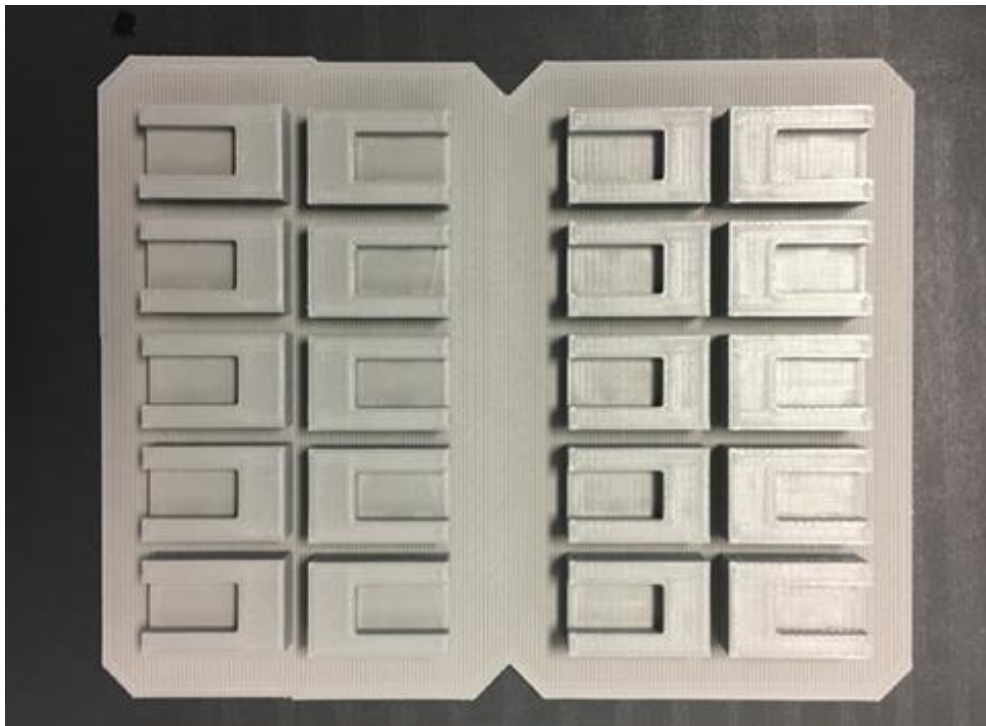


Figure 15: Printed seating jigs through MakerBot printer

The bonding jigs were 3D printed based on stereolithography technology (SLA) using form2 printer (Formlabs, Massachusetts - USA) and the printing material was grey resins from the same company.

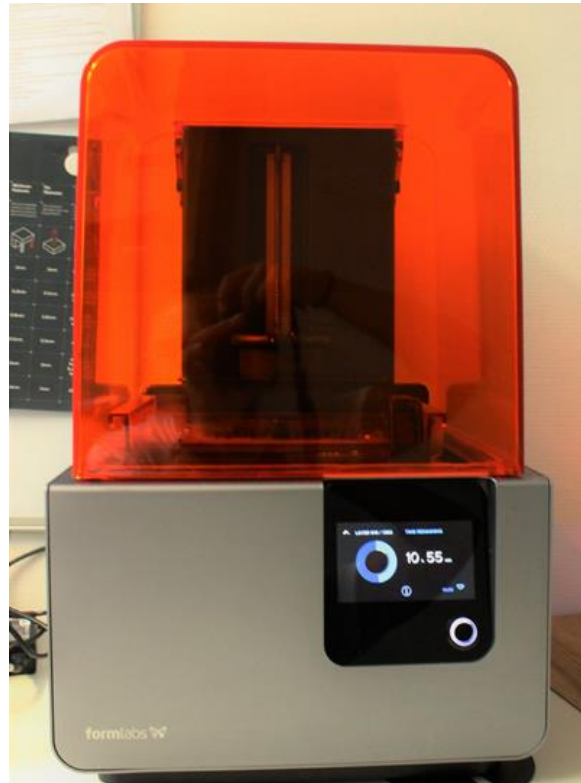


Figure 16: Form2 Printer



Figure 17: 3D printed bonding jigs

Directly before starting bonding procedures, the inner wall of the hole of bonding jig was painted with a separating medium (Vaseline) using micro-brush (Omnibrush Eco, Omnident dental-handelsgesellschaft mbh, Rodgau, Hesse-Germany) for easier

separation after final curing of the composite resin. The reference group was a control group, so bonding steps started after ultrasonic cleaning of the specimens. While in the adhesive group, the bonding started with the application of Visiolink primer followed by Sinfony opaquer and veneering composite. All other plasma treatment groups bonding steps started after completing plasma treatment by application of Sinfony opaquer and composite.

Table 2: Bonding steps of adhesive and Sinfony veneering composite.

Material	Application steps	The used device
Visiolink	<p>According to manufacturer instructions, single application of Visiolink adhesive primer using a micro brush on the surface of specimens through the hole present in the 3D printed jig was done.</p> <p>The specimens were immediately cured in the light-curing unit with wavelengths ranging from 320 to 550 nm for 90 seconds</p>	<p>SPEED Labolight HAGER and WERKEN GmbH and Co.KG, Duisburg-Germany</p>
Sinfony Opaquer	<p>Mixing powder and liquid at ration 1:1 using a plastic spatula for 45 seconds.</p> <p>Applying a layer of opaquer that covered totally specimens surface using clean disposable brushes then light curing for 10 seconds using a halogen curing unit that produced blue light of 400 – 515 nm wavelength</p>	<p>Elipar Trilight (3M ESPE, Seefeld-Germany)</p> <p>The device was set at medium mode</p>
Sinfony Composite	<p>Apply a paste layer of 1 mm directly from the dispenser then light curing for 5 seconds.</p> <p>Application of another layer until the jig’s hole was filled then light curing for 5 seconds.</p>	<p>Intermediate Curing: Elipar Trilight at medium mode</p>

	<p>Subsequently careful separation of the specimen from the jig and final curing in vacuum light-curing unit in a P1 mode (1 minute of light exposure without vacuum plus 14 minutes light curing with vacuum)</p>	<p>(3M ESPE, Seefeld-Germany) Final Curing: Visio Beta Vario (3M ESPE, Seefeld-Germany)</p>
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Figure 18: Light curing unit for opaquer and veneering composite



Figure 19: Light curing unit of Visiolink primer



Figure 20: Light curing unit for final curing of veneering composite

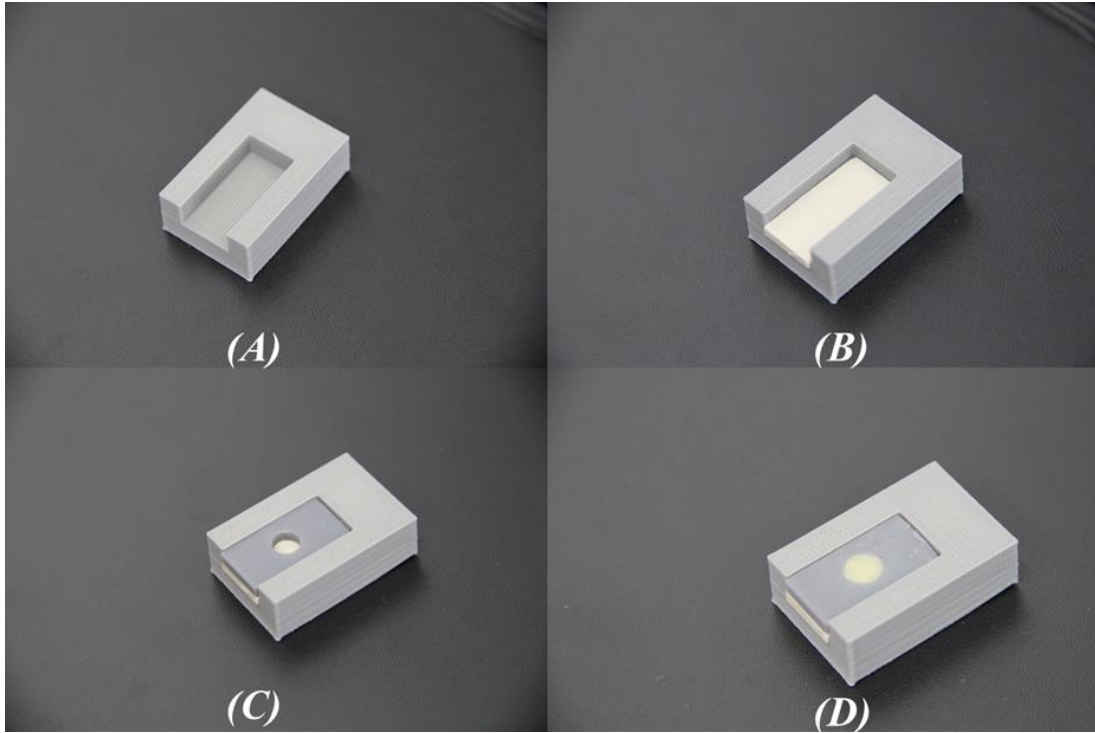


Figure 21: A-D pictures show using of jigs during bonding

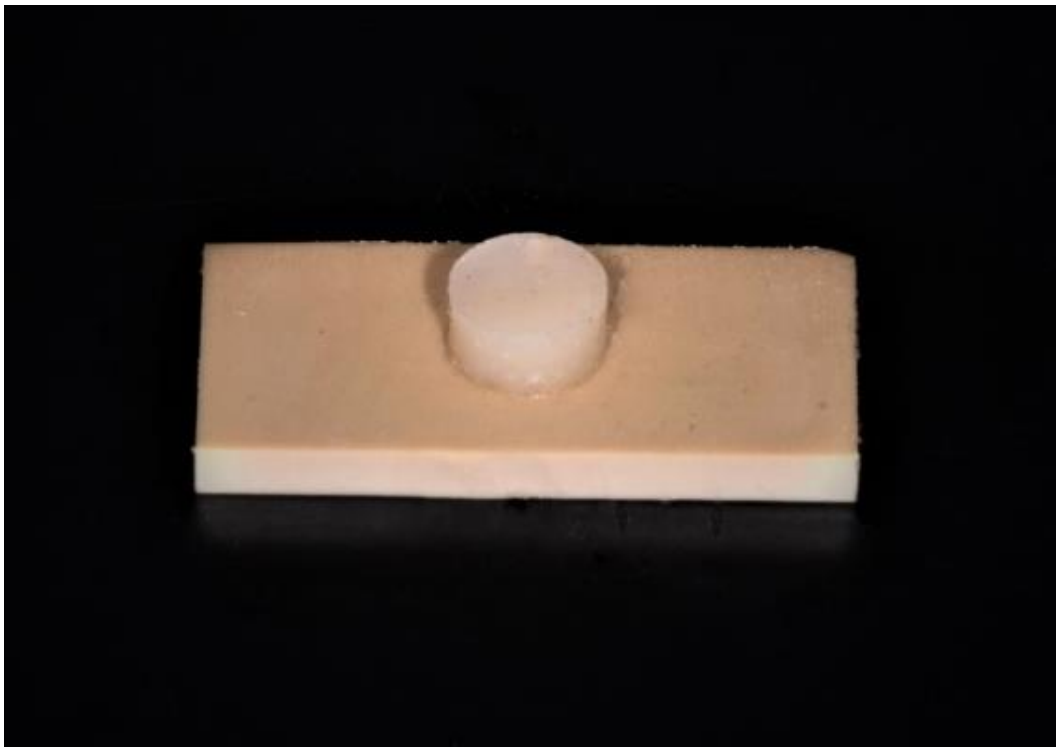


Figure 22: Finished Specimen (unfilled PEEK after Acetylene treatment)

2.3. Surface area calculation

After bonding, the surface area of veneering composite in all specimens was calculated through taking a picture of the veneered area under microscope Wild M400 photomicroscope (Wild Heerbrugg, Gais - Switzerland). Measuring the surface area was made by the software Datinf measure software (Datinf GmbH, Tübingen- Germany) and the veneered area was measured 3 times per each sample then the mean surface area was calculated.

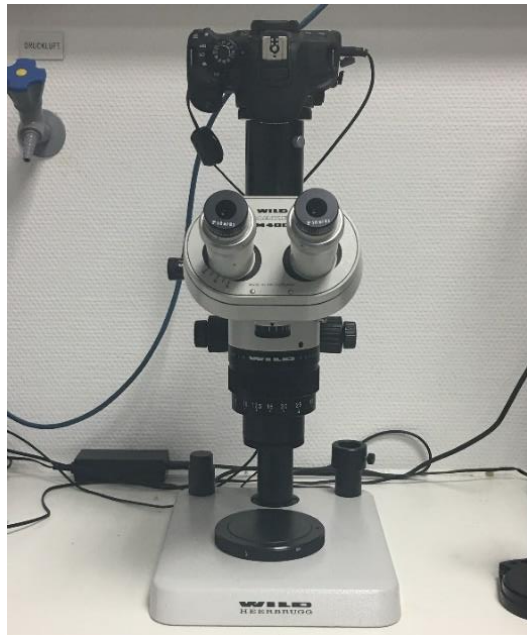


Figure 23: photomicroscope

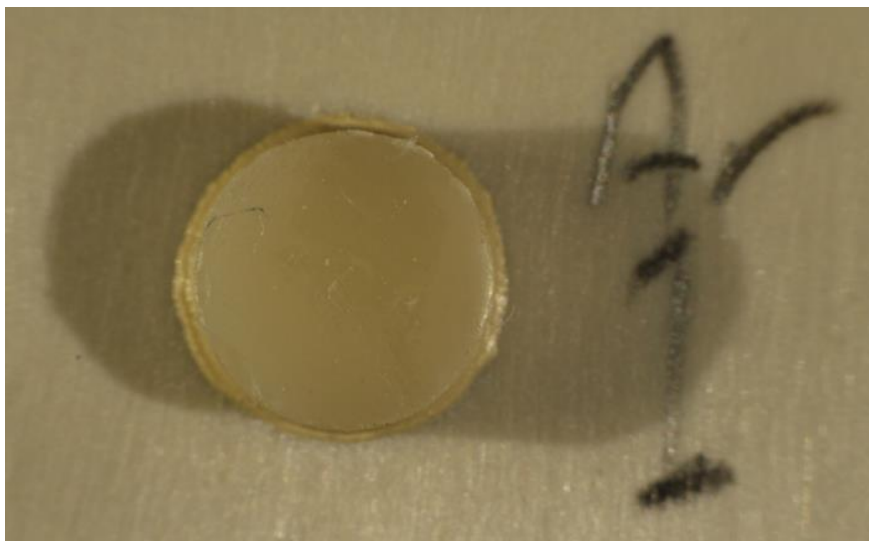


Figure 24: Imaging each specimen via macroscope to calculate the surface area of veneered composite



Figure 25: Surface area calculation via Datinf measure software

2.4. Thermal cycling

Artificial aging for all specimens using thermocycler (SD Mechatronik, Feldkirchen-Westerham, Germany) was done. The device exposed the specimens to thermal stresses by immersing in distilled water for 5.000 cycles at two extreme temperatures 5°C (± 1) and 55°C (± 1). The specimens stayed immersed in water at each degree for 30 seconds with a dwell time of 20 seconds in between both temperatures.



Figure 26: Thermocycler

2.5. Shear bond strength testing

Macro shear bond strength using a universal testing machine (1120 Zwicki, Zwick - Ulm, Germany) was made. For shear testing, a customized specimen holder was made through which specimens were firmly fixed throughout the testing procedure. A chisel-shaped rod applied force constantly parallel to the bond surface at a distance of 0.5 ± 0.02 mm from the surface of the PEEK specimen with 1 mm/min speed of crosshead and starting from a 0-newton load which increased gradually until fracture of the veneering composite. Then, the maximum force at fracture was recorded. Shear bond strength could be calculated according to the equation $S=F/A$ where S was the shear bond strength, F was the load applied in newtons, and A was the bonded area in mm^2 . The unit of shear bond strength was measured in megapascal (MPa). Specimens which did not survive artificial aging and showed premature debonding of veneering composites during thermocycling were assigned 0 MPa shear bond strength and considered as pre-failures.



Figure 27: Universal testing machine

2.6. Analyses of failure types

Following shear bond testing, all specimens were examined under microscope Wild M400 photomicroscope (Wild Heerbrugg, Gais - Switzerland) to determine the type of failure. Three failure types were defined and determined as follows:

1. Adhesive failure, where no resin remnants were left on the PEEK surface.
2. Cohesive failure, where the failure was in the bulk layer of the resin.
3. Mixed where resin remnants partially left on PEEK and PEEK surface exposed.

2.7. Statistical analysis

(a) Testing for normal distribution:

To test whether the data were normally distributed or not, the Shapiro-Wilk test was used, which allowed selecting the proper comparative analysis tests.

(b) Descriptive analyses:

Shear bond strength was described in terms of mean, median, standard deviation (SD) and range according to each group surface treatments. Bar charts representing means and standard deviations were used to graphically illustrate comparisons between surface treatments within each group.

(c) Comparative analysis:

To assess overall differences in shear bond strength of surface treatments within each group, the non-parametric Kruskal-Wallis test was performed. Multiple pairwise comparisons using post-hoc tests according to Conover (or Conover's test) to assess differences in shear bond strength of pairs of surface treatments within each group were done.

(d) The significance level:

It was verified at $p \leq 0.05$. The results were considered to be statistically significant if the p-value was less than 0.05.

(e) The statistical package used for this study:

R statistical package version 3.3.1 (R Core Team 2016, R: A language and environment for statistical computing, R Foundation for Statistical Computing, Vienna, Austria) [Reference: <https://www.R-project.org>].

3. Results

3.1. Surface Roughness

Before plasma surface treatment, the surface roughness of ceramic filled PEEK was evaluated (average roughness height, Ra) and the results were compared with the study done by Rosentritt et al.¹³⁵

Table 3: The mean and standard deviation of surface roughness values in comparison to Rosentritt et al. study.¹³⁵

Pre-treatment	Average of Ra (µm)	The standard deviation of Ra (µm)	Data category
Polishing disc with 180 Grit (P180)	2.470178632	0.493178261	Roughness data of the current thesis
Polishing disc with 280 Grit (P320)	0.929099863	0.397606538	
Polishing disc with 360 Grit (P600)	0.737344398	0.166412009	
Polishing disc with 600 Grit (P1200)	0.155969972	0.025236046	
Sandblasting with Rocatec Pre/Plus system	1.49	0.11	Roughness data of the study of Rosentritt et al
Sandblasting with Alumina (Al₂O₃—50 µm/2 bar)	0.96	0.07	
Sandblasting with Alumina (Al₂O₃—120 µm/2.8 bar)	1.84	0.16	
Control untreated group	0.06	0.03	
Etching with H₂SO₄ 98% 1 min	6.76	1.11	
Etching with H₂O₂/H₂SO₄ 1:1 30 s	0.04	0.01	

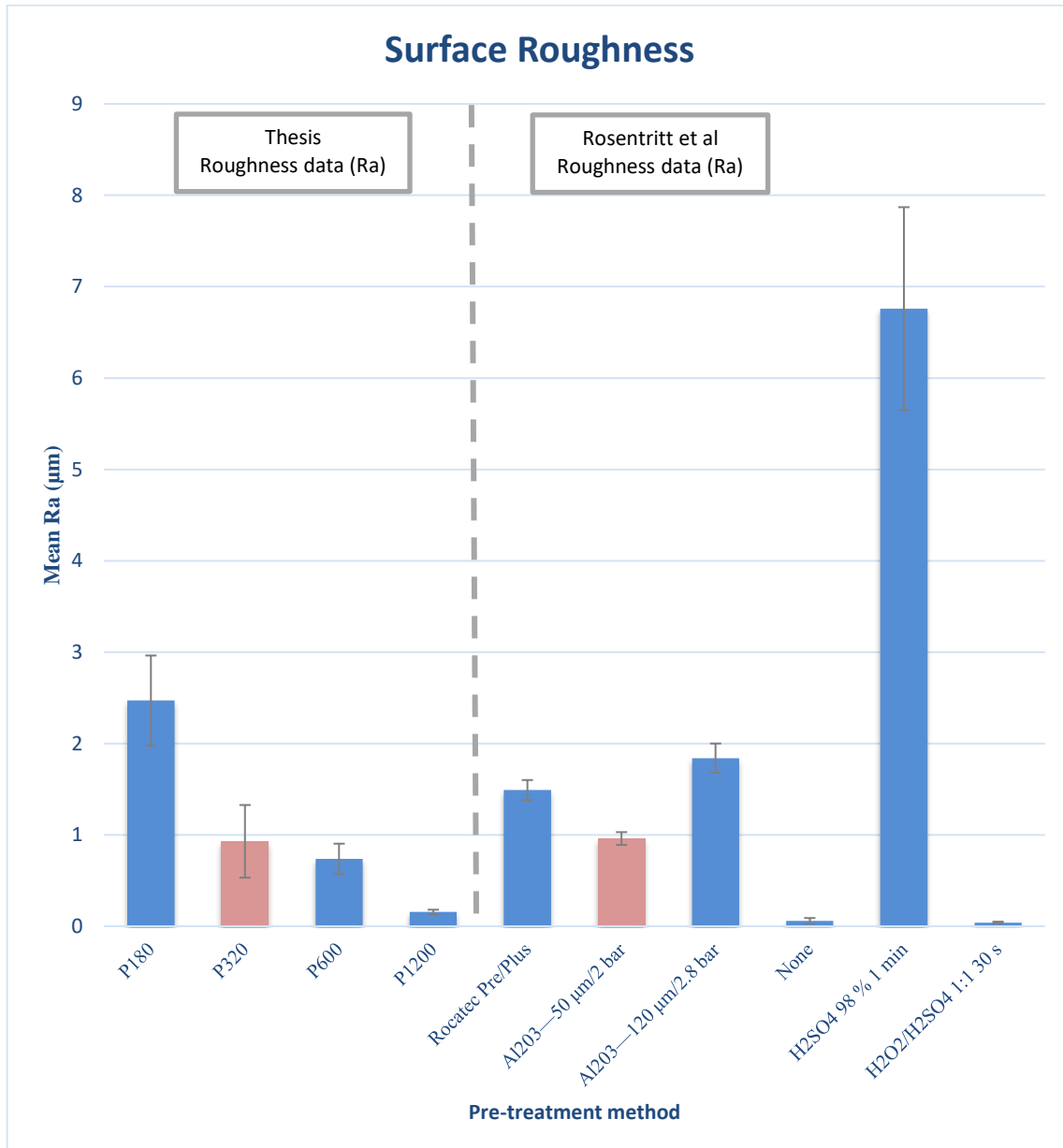


Figure 28: Column chart of surface roughness average (Ra) and standard deviations in comparison with Rosentritt study¹³⁵

3.2. Shear Bond Strength

The present study evaluated the shear bond strength between different PAEK and veneering composites. The results of each statistical analysis (test for normality, descriptive analysis, and comparative analysis) were listed in tables and column charts figures as follow:

I. Testing for normality

Table 4: Shapiro-Wilk test for normality of shear bond strength in all groups:

Variable		Shapiro-Wilk	Interpretation
		p-value*	
CPEEK	Reference	0.0783	Data were Normally distributed
	Adhesive	0.6878	Data were Normally distributed
	Argon	0.1055	Data were Normally distributed
	Oxygen	0.1451	Data were Normally distributed
	Nitrogen	0.0075	<i>Data were Not Normally Distributed</i>
	Air	0.0600	Data were Normally distributed
	Acetylene	0.2411	Data were Normally distributed
	Ammonia	0.4962	Data were Normally distributed
	Cf ₄ /O ₂	0.2609	Data were Normally distributed
UPEEK	Reference	0.2443	Data were Normally distributed
	Adhesive	0.761	Data were Normally distributed
	Argon	0.5987	Data were Normally distributed
	Oxygen	0.9312	Data were Normally distributed
	Nitrogen	0.0195	Data were Normally distributed
	Air	0.5242	Data were Normally distributed
	Acetylene	0.0079	<i>Data were Not Normally Distributed</i>
	Ammonia	0.0056	<i>Data were Not Normally Distributed</i>
	Cf ₄ /O ₂	0.0008	<i>Data were Not Normally Distributed</i>
PEKK	Reference	0.6309	Data were Normally distributed
	Adhesive	0.3528	Data were Normally distributed
	Argon	0.7787	Data were Normally distributed
	Oxygen	0.2363	Data were Normally distributed
	Nitrogen	0.7577	Data were Normally distributed
	Air	0.9237	Data were Normally distributed
	Acetylene	0.0078	<i>Data were Not Normally Distributed</i>
	Ammonia	0.0062	<i>Data were Not Normally Distributed</i>
	Cf ₄ /O ₂	0.0131	Data were Normally distributed

*Significance level at p-value ≤ 0.01 .

II. Descriptive analysis

Table 5: Descriptive analysis of shear bond strength (MPa) and results of the Kruskal Wallis test for comparing between groups:

Group	Surface treatment	Mean	SD	Median	Range		Kruskal-Wallis test	
					Min	Max	p-value*	Interpretation
CPEEK	Reference	8.41	1.16	8.61	6.82	10.20	<0.0001	Statistically significant difference
	Adhesive	13.41	2.23	13.66	9.68	17.54		
	Argon	8.77	2.52	8.55	5.35	14.45		
	Oxygen	6.98	1.19	6.96	4.73	10.32		
	Nitrogen	8.13	1.82	7.61	5.67	12.42		
	Air	8.88	2.42	8.17	5.72	15.26		
	Acetylene	10.15	3.03	9.87	6.04	15.52		
	Ammonia	4.90	1.59	5.28	0.75	7.78		
	Cf4/O2	3.82	1.62	3.97	0.21	6.30		
UPEEK	Reference	5.38	2.90	5.64	0.50	9.41	<0.0001	Statistically significant difference
	Adhesive	9.23	1.34	8.96	6.83	11.98		
	Argon	9.56	1.35	9.27	7.28	12.07		
	Oxygen	8.59	1.64	8.51	5.97	12.16		
	Nitrogen	10.04	1.84	9.98	7.42	14.63		
	Air	9.27	1.33	9.44	6.27	12.32		
	Acetylene	10.75	2.65	10.11	7.95	18.31		
	Ammonia	2.46	2.47	1.19	0.07	8.07		
	Cf4/O2	1.93	2.14	0.54	0.09	6.02		
PEKK	Reference	4.71	1.54	4.81	1.48	8.66	<0.0001	Statistically significant difference
	Adhesive	9.16	1.48	8.87	7.08	12.05		
	Argon	7.54	1.52	7.52	4.90	10.38		
	Oxygen	5.69	1.59	5.31	2.60	8.88		
	Nitrogen	7.03	1.48	7.03	4.36	9.43		
	Air	7.09	1.99	7.03	2.83	10.53		
	Acetylene	9.89	3.08	8.79	5.44	17.36		
	Ammonia	3.12	2.39	3.71	0.12	6.37		
	Cf4/O2	2.26	2.01	1.85	0.08	5.80		

*Significance level at $p\text{-value} \leq 0.05$.

III. Comparative analysis

A. Comparison between surface treatments within each PAEK Material

(1) Unfilled PEEK material

Acetylene surface treatment had the highest mean shear bond strength of 10.75 (\pm 2.65) MPa, followed by nitrogen treatment (10.04 \pm 1.84 MPa), then argon treatment (9.56 \pm 1.35 MPa). Generally, between groups, differences were statistically significant (p-value $<$ 0.0001). Multiple pairwise comparisons using post-hoc tests, according to Conover, were made to assess differences in shear bond strength of different surface treatments in unfilled PEEK group. The following results showing p-value*:

Table 6: Multiple Pairwise comparisons using post-hoc tests according to Conover of surface treatments within unfilled PEEK

UPEEK	Reference	Adhesive	Argon	Oxygen	Nitrogen	Air	Acetylene	Ammonia	Cf ₄ /O ₂
Reference	-								
Adhesive	<0.0001	-							
Argon	<0.0001	1	-						
Oxygen	0.0031	1	0.9699	-					
Nitrogen	<0.0001	1	1	0.1189	-				
Air	<0.0001	1	1	1	1	-			
Acetylene	<0.0001	1	1	0.0125	1	1	-		
Ammonia	0.284	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	-	
Cf ₄ /O ₂	0.1076	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	1	-

*Significance level at p-value \leq 0.05.

As shown in table (6), pairwise comparisons which were statistically insignificant:

- Reference with ammonia, CF₄/O₂ surface treatments
- Adhesive with argon, oxygen, nitrogen, air, acetylene surface treatments
- Argon with oxygen, nitrogen, air, acetylene surface treatments
- Oxygen with nitrogen, air surface treatments
- Nitrogen with air, acetylene surface treatments
- Air with acetylene surface treatment
- Ammonia with CF₄/O₂

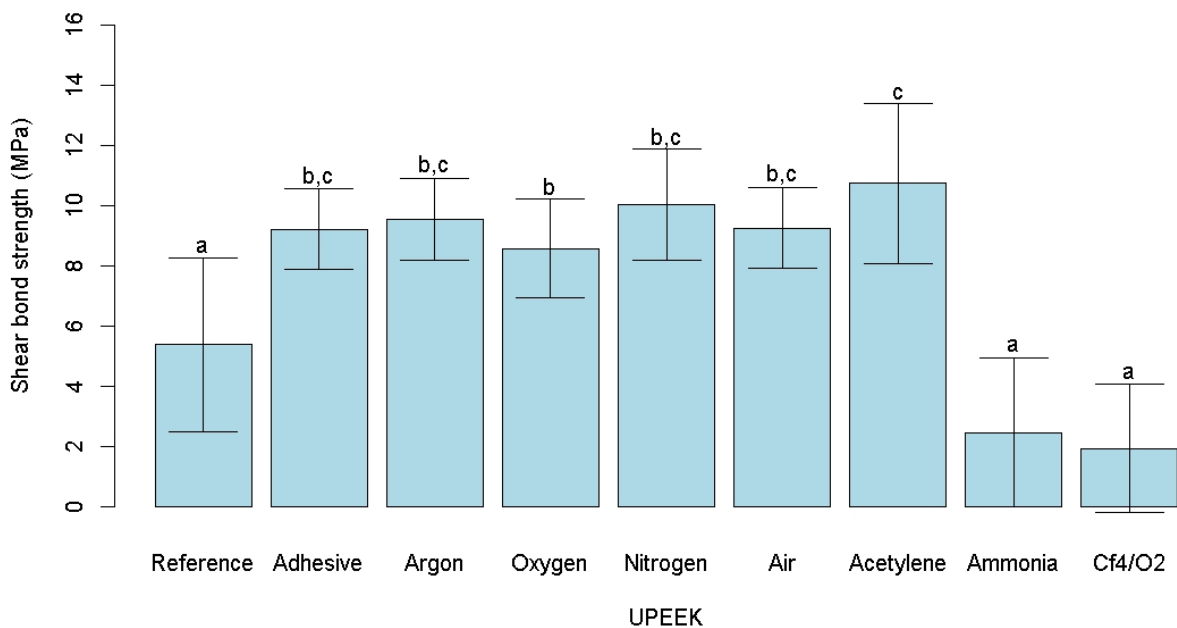


Figure 29: Comparison between different surface treatments within unfilled PEEK regarding means and standard deviations of shear bond strength

(2) Ceramic filled PEEK material

Adhesive surface treatment had the highest mean shear bond strength of $13.41 (\pm 2.23)$ MPa, followed by acetylene treatment (10.15 ± 3.03 MPa), then air treatment (8.88 ± 2.42 MPa). Generally, between groups, the differences were statistically significant (p -value < 0.0001). Multiple pairwise comparisons using post-hoc tests, according to Conover, were made to assess the differences in shear bond strength values of different treatments in the ceramic filled PEEK group. The following results showing p -value*:

Table 7: Multiple Pairwise comparisons using post-hoc tests according to Conover of surface treatments within ceramic filled PEEK.

CPEEK	Reference	Adhesive	Argon	Oxygen	Nitrogen	Air	Acetylene	Ammonia	Cf₄/O₂
Reference	-								
Adhesive	<0.0001	-							
Argon	1	<0.0001	-						
Oxygen	0.0272	<0.0001	0.0371	-					
Nitrogen	1	<0.0001	1	0.5347	-				
Air	1	<0.0001	1	0.0152	1	-			
Acetylene	1	0.0023	1	<0.0001	0.3534	1	-		
Ammonia	<0.0001	<0.0001	<0.0001	0.0041	<0.0001	<0.0001	<0.0001	-	
Cf₄/O₂	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	1	-

*Significance level at p-value ≤ 0.05 .

- As shown in table (7), pairwise comparisons which were statistically insignificant:
 - Reference with argon, nitrogen, air, acetylene
 - Argon with nitrogen, air, acetylene
 - Nitrogen with oxygen, air, acetylene
 - Air with acetylene
 - Ammonia and CF₄/O₂ surface treatments

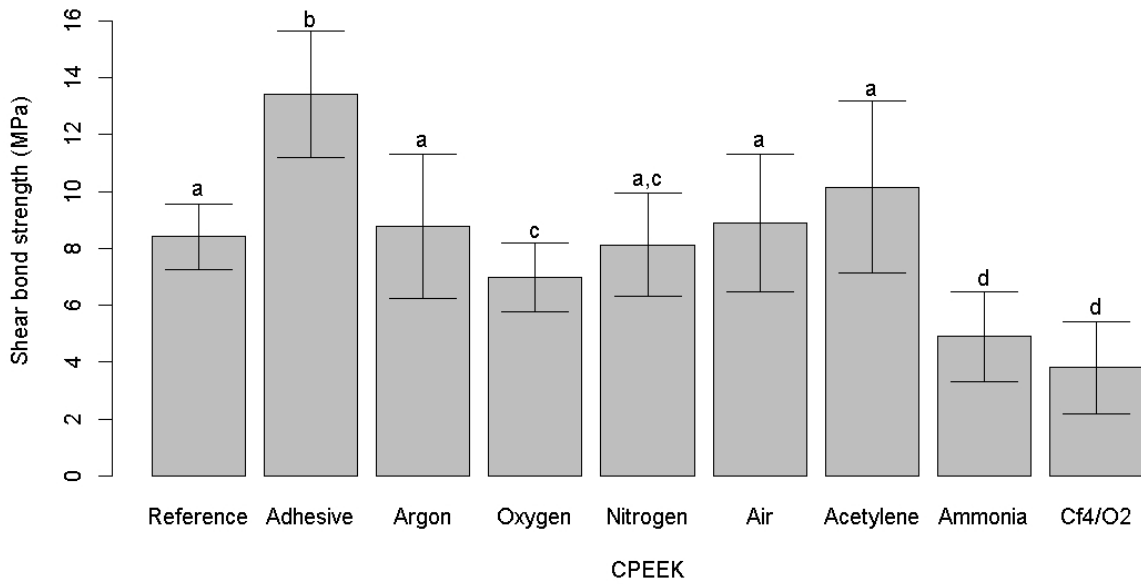


Figure 30: Comparison between different surface treatments within ceramic filled PEEK regarding means and standard deviations of shear bond strength

(3) PEKK material

Acetylene surface treatment had the highest mean shear bond strength of $9.89 (\pm 3.08)$ MPa, followed by adhesive treatment (9.16 ± 1.48 MPa), then argon treatment (7.54 ± 1.52 MPa). Generally, between-groups differences were statistically significant (p -value < 0.0001). Multiple pairwise comparisons using post-hoc tests, according to Conover, to assess differences in shear bond strength of different treatments in the PEKK group. The following results showing p -value*:

Table 8: Multiple Pairwise comparisons using post-hoc tests according to Conover of surface treatments within PEKK.

PEKK	Reference	Adhesive	Argon	Oxygen	Nitrogen	Air	Acetylene	Ammonia	Cf ₄ /O ₂
Reference	-								
Adhesive	<0.0001	-							
Argon	<0.0001	0.0914	-						
Oxygen	1	<0.0001	0.0017	-					
Nitrogen	<0.0001	0.0021	1	0.0767	-				
Air	<0.0001	0.0028	1	0.0592	1	-			

Acetylene	<0.0001	1	0.1139	<0.0001	0.0027	0.0037	-		
Ammonia	1	<0.0001	<0.0001	0.0167	<0.0001	<0.0001	<0.0001	-	
Cf4/O2	0.1194	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	1	-

*Significance level at $p\text{-value} \leq 0.05$.

- As shown in table (8), most pairwise comparisons were statistically significant, except comparisons between:
 - Reference with Oxygen, Ammonia, CF4/O2 surface treatments
 - Adhesive with argon, acetylene surface treatments
 - Argon with nitrogen, air, acetylene surface treatments
 - Oxygen with nitrogen, air surface treatments
 - Nitrogen with air surface treatments
 - Ammonia with CF4/O2

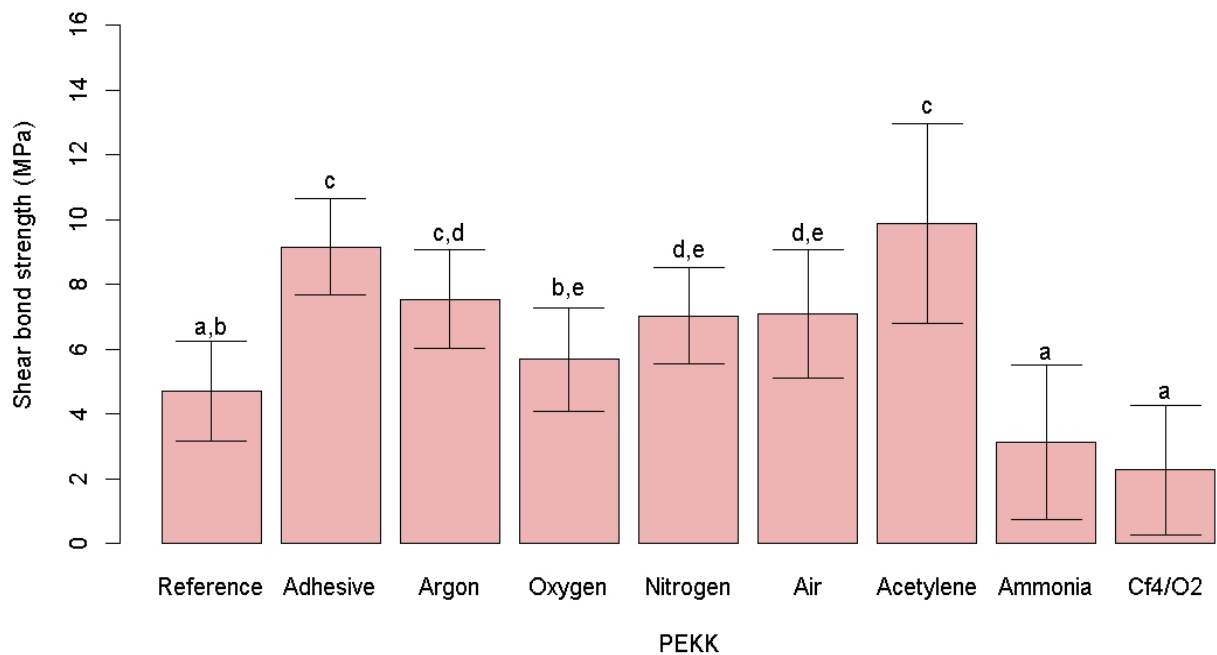


Figure 31: Comparison between different surface treatments within PEKK regarding means and standard deviations of shear bond strength

B. Comparison between PAEK Materials within each surface treatment

Table 9: Comparison between materials regarding each surface treatment - results of the One-Way ANOVA showing p-value:*

Surface treatment	One-Way ANOVA	
	p-value*	Interpretation
Reference	<0.0001	Statistically significant difference
Adhesive	<0.0001	Statistically significant difference
Argon	0.0046	Statistically significant difference
Oxygen	<0.0001	Statistically significant difference
Nitrogen	<0.0001**	Statistically significant difference
Air	0.0019	Statistically significant difference
Acetylene	0.3495**	Statistically insignificant difference
Ammonia	0.0043**	Statistically significant difference
Cf₄/O₂	0.0198**	Statistically significant difference

*Significance level at p-value ≤ 0.05 .
test

**Results of the non-parametric Kruskal-Wallis

- The results showed that all surface treatments were statistically significant across all groups except for acetylene surface treatment.

(1) Reference group

Table 10: Multiple pairwise comparisons using post-hoc Tukey’s test to assess pairwise differences in shear bond strength across different materials regarding reference surface treatment - results showing p-value:*

Reference	CPEEK	UPEEK	PEKK
CPEEK	-		
UPEEK	<0.0001	-	
PEKK	<0.0001	0.5426	-

*Significance level at $p\text{-value} \leq 0.05$.

- The differences between shear bond strength of the CPEEK and both UPEEK and PEKK groups were statistically significant. While the difference between UPEEK and PEKK was insignificant.

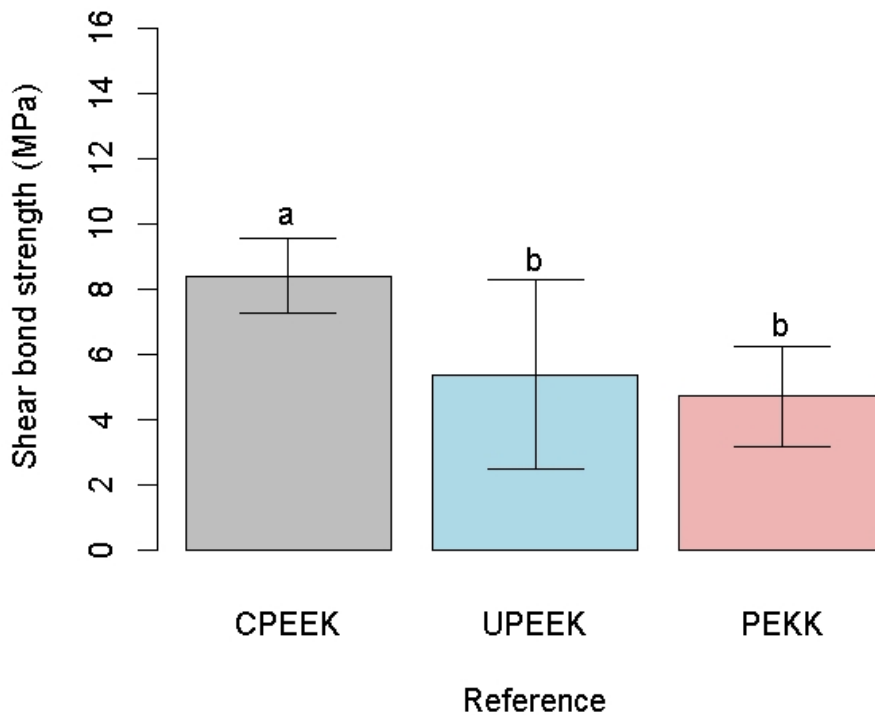


Figure 32: Comparison between means and standard deviations of shear bond strength of different PAEK materials within reference groups

(2) Adhesive group

*Table 11: Multiple pairwise comparisons using post-hoc Tukey’s test to assess pairwise differences in shear bond strength across different materials regarding adhesive surface treatment - results showing p-value**

Adhesive	CPEEK	UPEEK	PEKK
CPEEK	-		
UPEEK	<0.0001	-	
PEKK	<0.0001	0.9905	-

*Significance level at $p\text{-value} \leq 0.05$.

- The differences between shear bond strength of the CPEEK and both UPEEK and PEKK groups were statistically significant. While the difference between UPEEK and PEKK was insignificant.

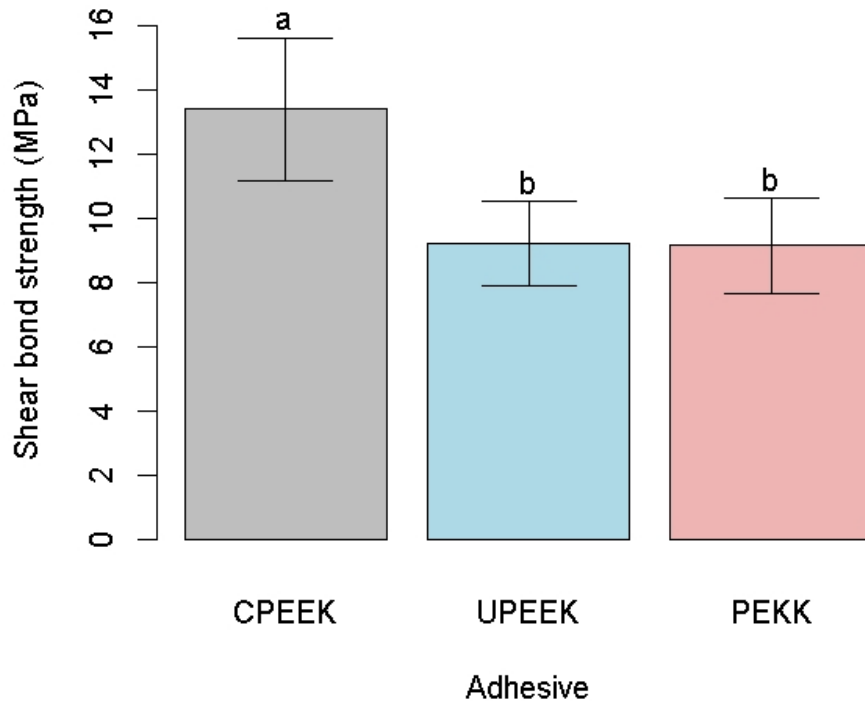


Figure 33 Comparison between means and standard deviations of shear bond strength of different PAEK materials within adhesive groups

(3) Argon group

*Table 12: Multiple pairwise comparisons using post-hoc Tukey’s test to assess pairwise differences in shear bond strength across different materials regarding argon surface treatment - results showing p-value**

Argon	CPEEK	UPEEK	PEKK
CPEEK	-		
UPEEK	0.3838	-	
PEKK	0.1026	0.0034	-

*Significance level at $p\text{-value} \leq 0.05$.

- The differences between shear bond strength of the CPEEK and both UPEEK and PEKK groups were statistically insignificant. While the difference between UPEEK and PEKK was significant.

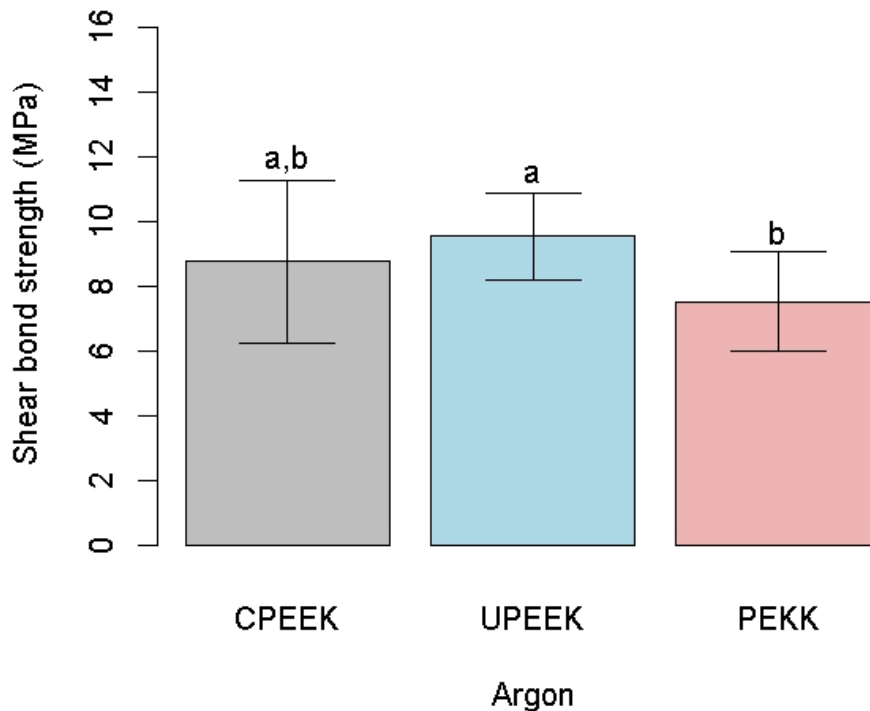


Figure 34: Comparison between means and standard deviations of shear bond strength of different PAEK materials within argon groups

(4) Oxygen group

*Table 13: Multiple pairwise comparisons using post-hoc Tukey’s test to assess pairwise differences in shear bond strength across different materials regarding oxygen surface treatment - results showing p-value**

Oxygen	CPEEK	UPEEK	PEKK
CPEEK	-		
UPEEK	0.0032	-	
PEKK	0.022	<0.0001	-

*Significance level at p-value ≤ 0.05 .

- The differences between the shear bond strength of all groups were statistically significant.

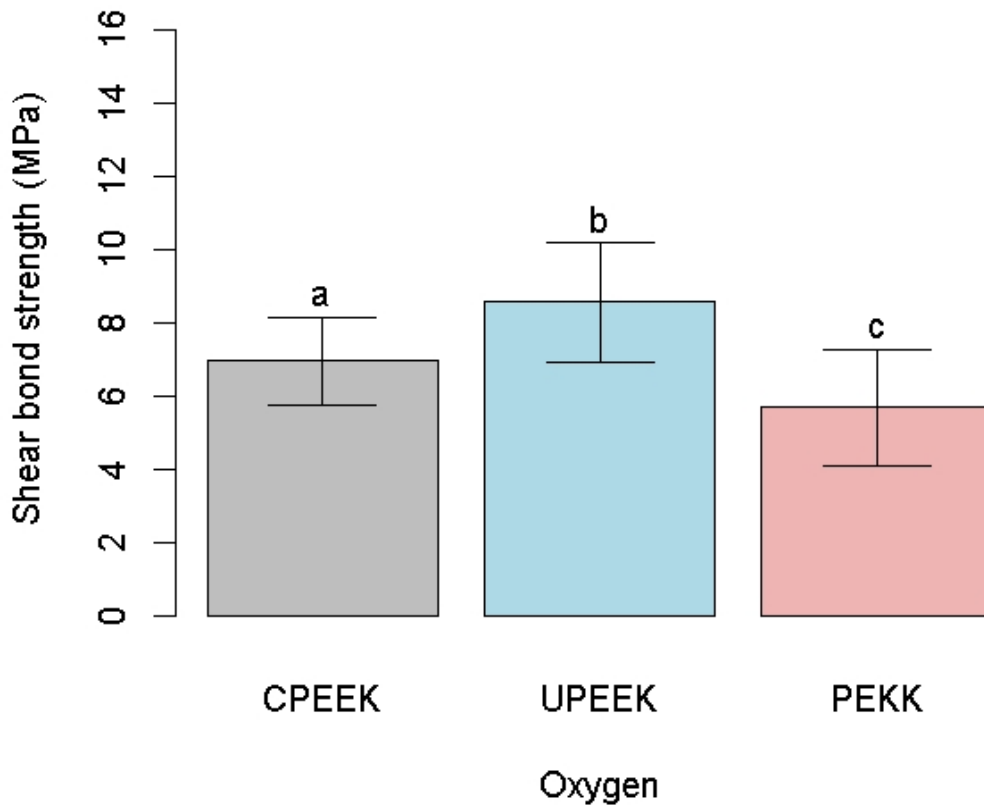


Figure 35: Comparison between means and standard deviations of shear bond strength of different PAEK materials within oxygen groups

(5) Nitrogen group

*Table 14: Multiple pairwise comparisons using post-hoc tests according to Conover to assess pairwise differences in shear bond strength across different materials regarding nitrogen surface treatment - results showing p-value**

Nitrogen	CPEEK	UPEEK	PEKK
CPEEK	-		
UPEEK	0.00056	-	
PEKK	0.12941	<0.0001	-

*Significance level at $p\text{-value} \leq 0.05$.

- The differences between shear bond strength of the UPEEK and both CPEEK and PEKK groups were statistically significant. While the difference between CPEEK and PEKK was insignificant.

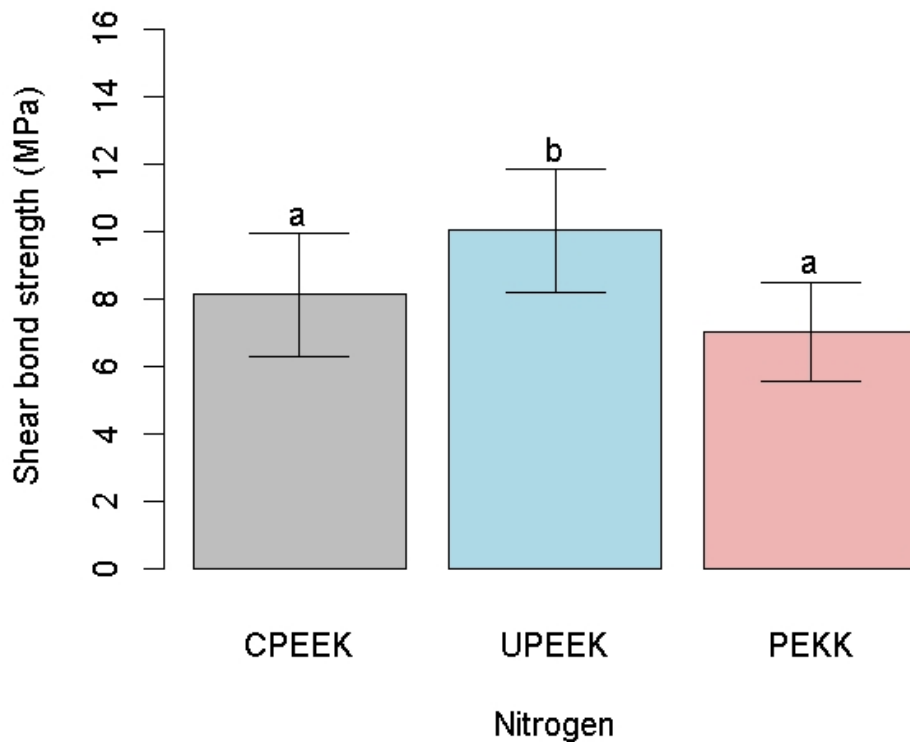


Figure 36: Comparison between means and standard deviations of shear bond strength of different PAEK materials within nitrogen groups

(6) Air group

*Table 15: Multiple pairwise comparisons using post-hoc Tukey’s test to assess pairwise differences in shear bond strength across different materials regarding air surface treatment - results showing p-value**

Air	CPEEK	UPEEK	PEKK
CPEEK	-		
UPEEK	0.8038	-	
PEKK	0.0154	0.0025	-

*Significance level at p-value ≤ 0.05 .

- The differences between shear bond strength of the PEKK and both CPEEK and UPEEK groups were statistically significant. While the difference between CPEEK and UPEEK was insignificant.

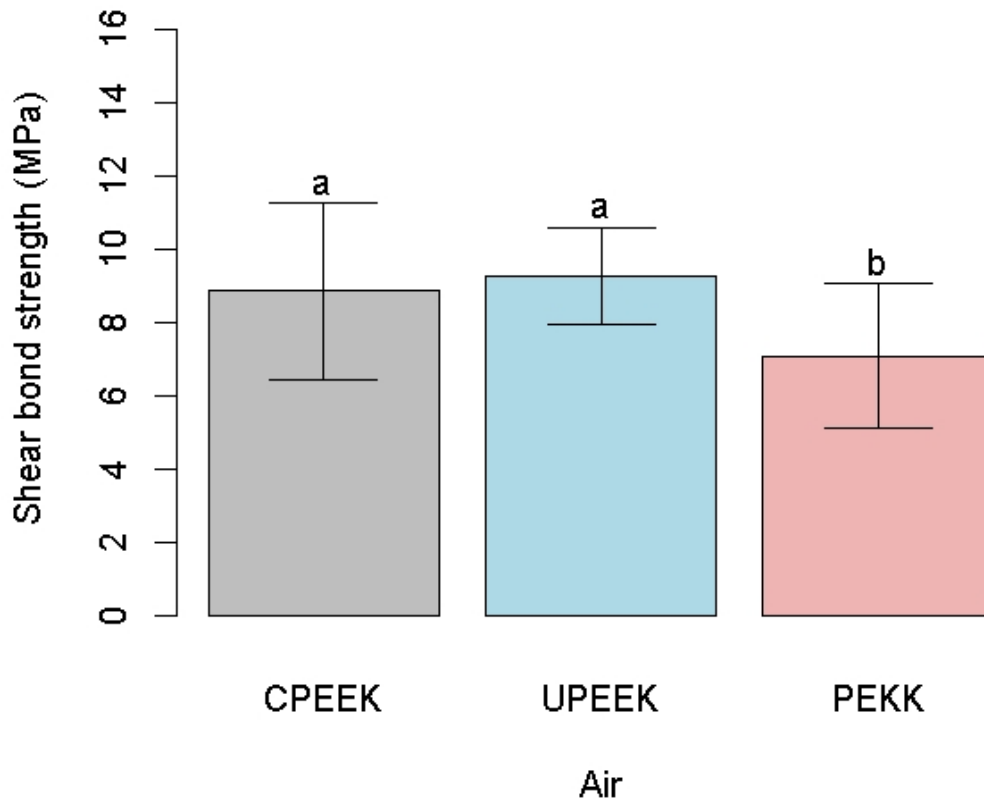


Figure 37: Comparison between means and standard deviations of shear bond strength of different PAEK materials within air groups

(7) Acetylene group

*Table 16: Multiple pairwise comparisons using post-hoc tests according to Conover to assess pairwise differences in shear bond strength across different materials regarding acetylene surface treatment - results showing p-value**

Acetylene	CPEEK	UPEEK	PEKK
CPEEK	-		
UPEEK	1	-	
PEKK	1	0.46	-

*Significance level at $p\text{-value} \leq 0.05$.

- The differences between the shear bond strength of all groups were statistically insignificant.

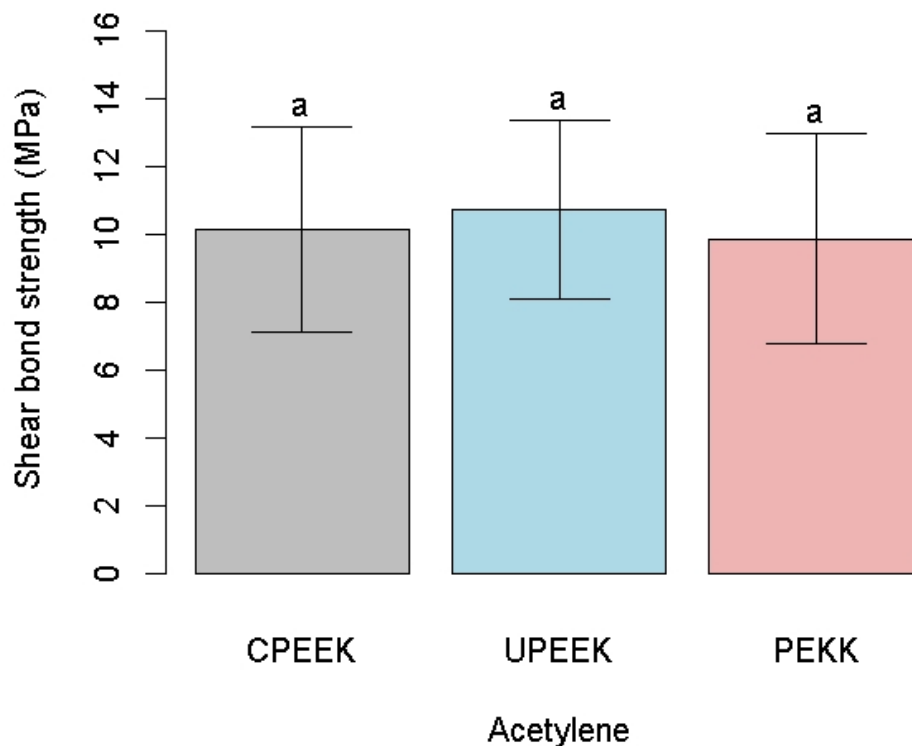


Figure 38: Comparison between means and standard deviations of shear bond strength of PAEK materials within acetylene groups

(8) Ammonia group

Table 17: Multiple pairwise comparisons using post-hoc tests according to Conover to assess pairwise differences in shear bond strength across different materials regarding ammonia surface treatment - results showing p-value*:

Ammonia	CPEEK	UPEEK	PEKK
CPEEK	-		
UPEEK	0.0027	-	
PEKK	0.0542	0.8616	-

*Significance level at $p\text{-value} \leq 0.05$.

- The difference between the shear bond strength of the CPEEK and UPEEK group was statistically significant. While the differences of the PEKK with CPEEK and UPEEK groups were insignificant.

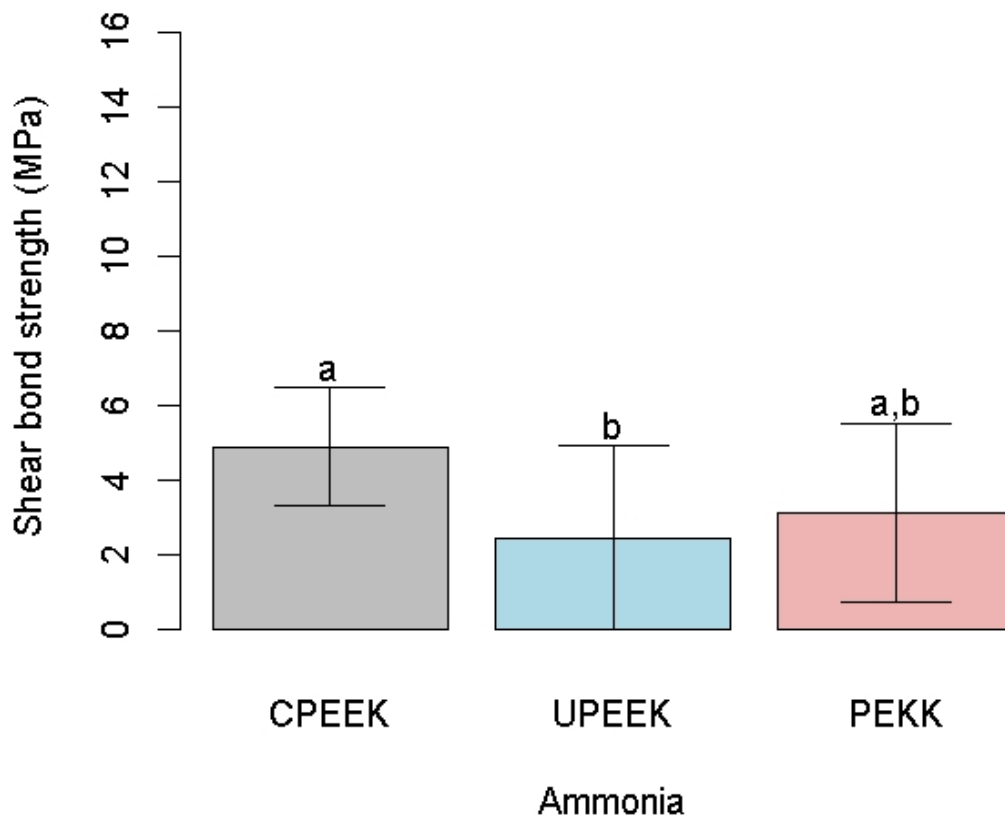


Figure 39: Comparison between means and standard deviations of shear bond strength of different PAEK materials within ammonia groups

(9) Tetrafluoromethane and oxygen group

Table 18: Multiple pairwise comparisons using post-hoc tests according to Conover to assess pairwise differences in shear bond strength across different materials regarding CF₄/O₂ surface treatment - results showing p-value:*

CF ₄ /O ₂	CPEEK	UPEEK	PEKK
CPEEK	-		
UPEEK	0.029	-	
PEKK	0.061	1	-

*Significance level at p-value ≤ 0.05.

- The difference between the shear bond strength of the CPEEK and UPEEK group was statistically significant. While the differences of the PEKK with CPEEK and UPEEK groups were insignificant.

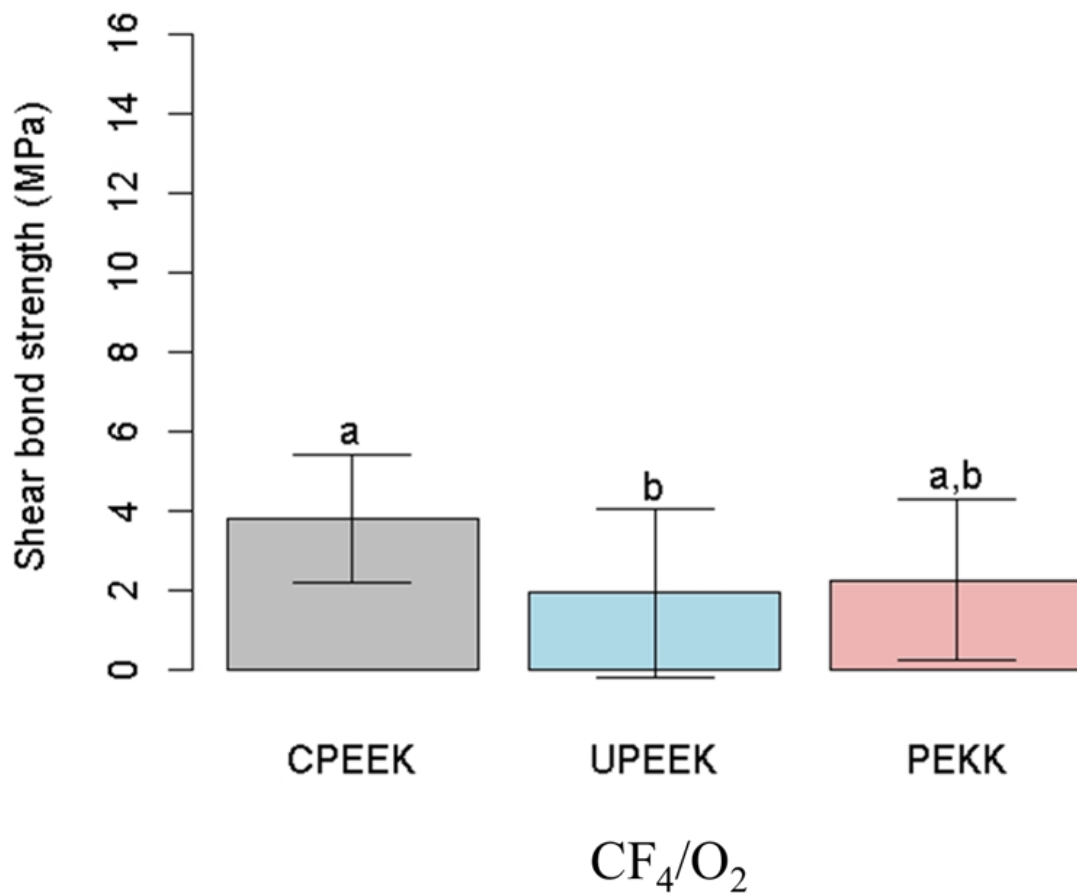


Figure 40: Comparison between means and standard deviations of shear bond strength of different PAEK materials within CF₄/O₂ groups

3.3 Fracture mode analysis

the specimens of the three materials showed 100% adhesive mode of failure.

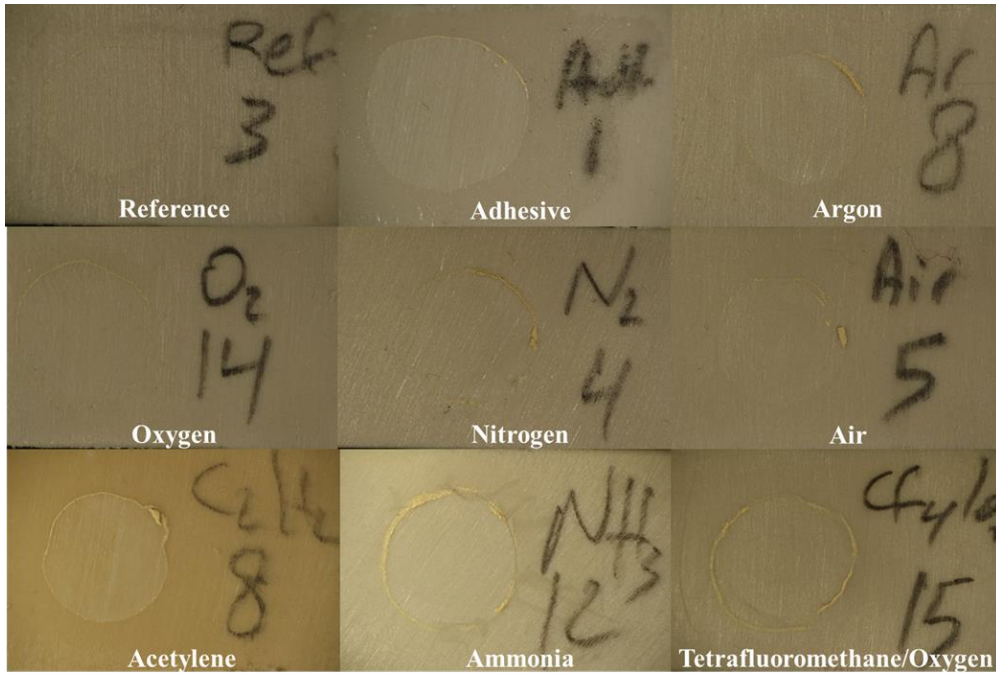


Figure 41: Unfilled PEEK specimens showing exemplary adhesive failures after shear bonding strength testing



Figure 42: Ceramic filled PEEK specimens showing exemplary adhesive failures after shear bonding strength testing

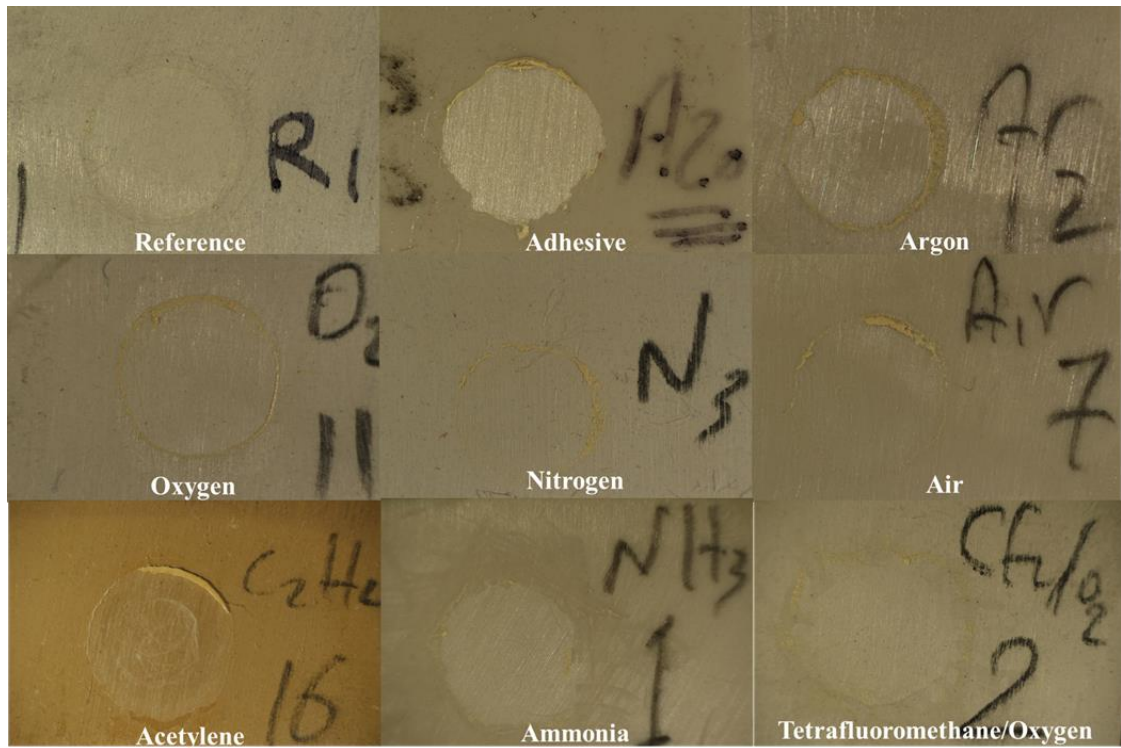


Figure 43: PEKK specimens showing exemplary adhesive failures after shear bonding strength testing

4. Discussion

4.1. Discussion of materials and methods

Indeed, all laboratory tests cannot replicate by far all intraoral conditions. Nevertheless, they are still crucial to screen and compare the effects of different surface treatments, adhesives, and substrate materials on the quality of adhesion between substrates and their veneering. Laboratory tests might only be used for prediction of material's behavior clinically, only if these tests are standardized and supplemented with dynamic and artificial aging tests. Therefore, thermal cycling was performed in this study to anticipate clinical situations and long term durability of the applied bonding protocol.¹³²

Regarding standardization, Roeder et al., Sirisha et al. and Virgílio Vilas Boas et al., assessed different bond strength tests used in dental research fields through literature review. They emphasized the need and importance to standardize bonding test procedures for better inference of the results and comparison with other similar studies in the literature.^{126,128,142,143} In addition, good knowledge of the limitations of each test and how to inference bond results are paramount. After laboratory studies, clinical trials should follow to assess and confirm the clinical performance.^{126,128,136}

The type of used test was shear bond test following Leibrock et al. who stated that the type of stresses acting on the veneered framework used in the anterior region were shear stresses. These stresses pull off the veneering material from the framework surface resulting in its chipping or even fracture.¹⁴⁴ Unfortunately, until now there are no guidelines for shear bond strength testing between composite and polymer substructures. Therefore, shear bond strength test was done according to international organization of standardization (ISO) technical specification number 10477 which was designed primarily for testing polymer-based dental crown and bridges materials that are attached to metal substructure. Implementation of ISO 10477 helped to standardize the steps of bond testing following the instructions of specimen size, jig formation, steps of testing, storage, artificial aging and bond strength measurements in addition to other test methods. The type of bond test was a macro shear bond test as the surface area of bonding interface was 5 mm² according to ISO 10477.¹⁴⁵ Using CAD/CAM systems to mill PEEK and PEKK blanks in addition to 3D printing of jigs helped to standardize the specimen's dimensions and the bonding procedures.¹⁴⁵

Another objective was to standardize the surface roughness in all specimens in addition to have surface roughness values which are able to provide the highest bond strength after plasma treatment. Selection of suitable abrasive papers to produce a standardized surface roughness was done following Rosentritt et al. study because of the similarities to his study settings.¹³⁵ Prior to surface treatment, 40 specimens were polished using different abrasive papers, then the comparison of surface roughness measurements with that of Rosentritt et al. study was made. Rosentritt et al. studied the effect of different chemical etching and sandblasting techniques on shear bond strength between PEEK and veneering composites. He found that the highest bonding strength values could be obtained after sandblasting with 50 µm alumina which had a roughness value (Ra) of $0.96 \mu\text{m} \pm 0.07$.¹³⁵ Moreover, polishing specimens with abrasive discs (P320) produced average roughness value (Ra) of $0.92 \mu\text{m} \pm 0.4$, which was comparable to that of sandblasting with 50 µm alumina of Rosentritt et al. study. Therefore, the polishing protocol started with P180, followed by P320. After polishing, ultrasonic cleaning with ethanol was done to get rid of any debris that could remain after milling of specimens and their subsequent polishing and retaining ultimately clean surfaces ready for bonding.¹⁴⁶

Different studies examined the effect of different surface treatments in combination with different adhesives on the bond strength between PEEK and veneering composites. Visiolink adhesive from Bredent company performed very well in these studies and showed high bond strength measurements after its application on different pretreated PEEK surfaces.^{80,102,133,136} Keul and Schmidlin et al. rationalized the positive effect to its composition of methyl methacrylate monomers, PENTIA (Pentaerythritol-triacrylate) and dimethacrylate. They alleged that PETIA dissolved first the surface of PEEK, then MMA monomers swelled the dissolved surface, and finally dimethacrylate monomers supplied PEEK with two carboxyl groups as potential binding sites for bonding to the veneering composites.^{20,136}

Although ceramic filled PEEK was white, unfilled PEEK and PEKK had opaque greyish color shades, which were extremely unaesthetic and necessitated opaquer placement in clinical applications.⁹⁸ Moreover, in the literature, many studies reported that higher bond strength results could be achieved after application of opaquer.^{18,135,139,147} Özcan et al. studied the effect of composition and thickness of different types of opaquers on shear bond strength to metal frameworks. He tested different types of opaquers supplied in

powder-liquid form or paste form. The results showed that the thickness of opaquer had no significant effect on bond strength, while the composition of opaquer did have one. Sinfony powder-liquid opaquer from 3M showed the highest bond strength values, and therefore, it was chosen in this study.¹⁴⁸ Accordingly, to simulate a true clinical situation, it was decided to add opaquer from the same company of veneering composite in all study groups.

Plasma surface treatment is more advantageous than other conventional treatments like sandblasting and chemical etching. The main drawbacks of air abrasion are the inconsistency of the treatment and being operator dependent. While in respect to chemical etching, because of the chemical structures of PEEK and PEKK, their etching requires utilization of powerful acids like sulfuric acids or piranha acids in high concentrations. This is considered inconvenient and unsafe for dental clinic or laboratory settings. Also, it requires meticulous handling from the operator; otherwise the risk of serious injuries will be high.¹⁴⁹⁻¹⁵¹

Unlike sandblasting and chemical etching, plasma is clean energy, environmentally friendly with no contamination expected. The treatment is consistent and not operator dependent; in addition, surfaces of complexly shaped structures can be effortlessly treated. Finally, plasma modifications are confined to a very superficial layer, about 10 nanometers, so it will not alter the bulk properties of the treated material.^{149,150} Hence, plasma provides good balance in comparison to other surface treatments as it can increase surface roughness for improved micromechanical bonding, plus increasing the surface's energy and its wettability, and delivering chemical functional groups that can interact with the veneering resins.¹⁴⁹⁻¹⁵¹

Plasma treatment can be adjusted through different parameters, such as frequency, power, pressure, mass flow controller, gas flux, and temperature. This gives manifold possibilities of surface treatments, which is advantageous as it allows a wide range of surface modifications by applying different settings. Unfortunately, it is still extremely challenging when using plasma to fine-tune these parameters and create the best cocktail capable of optimizing the surface of PEEK/PEKK for strong and durable bonding with veneering resins.¹³⁴ In this study, settings of plasma parameter were chosen based on the recommendations of plasma manufacturer.

4.2. Discussion of the results

According to ISO 10477, values of shear bond strength higher than 5 MPa were considered acceptable for clinical use.¹⁴⁵ All groups showed mean values of bond strength higher than 5 MPa except NH₃ and CF₄/O₂ plasmas, which showed very low bond strength values with all tested materials. The null hypothesis in this study was partially rejected, as the results revealed that 4 plasma gases out of 7, regardless type of PAEK, could establish an improvement in shear bond strength in comparison with the reference groups. These feeding gases were acetylene, nitrogen, argon, air.

Before going into details of possible reactions that occurred during plasma treatments, it is important to emphasize that plasma surface interactions result from numerous simultaneously occurring elementary reactions. This is why, most of the time, it is difficult to describe in detail the physical and chemical behaviors of plasma. Another difficulty is the variety of functional groups that can be formed during plasma treatment, which is not easy to restrict them into a well-defined set of species.¹⁵² Regarding bonding, the ultimate goals of any plasma surface treatment are to improve surface hydrophilicity and introduce active functional groups (e.g., carboxyl and hydroxyl groups), which can bond chemically with functional groups of composite resins. As emphasized earlier, each gas (with other plasma parameters) contributes to these goals in a different way.

I. Acetylene plasma

Acetylene is a colorless odorless gas, which is unstable and very reactive in its pure form and can be explosive. Chemically, it is a linear molecule with a triple bonding between the two carbon atoms and 1:1 carbon-hydrogen content ratio (HC≡CH).¹⁵³ In the field of plasma, C₂H₂ can be found as a by-product in applications of thermal plasmas for disposal of various wastes. This process is called thermal plasma pyrolysis where oxygen atoms react at high temperatures with carbonaceous compounds producing different by-products such as hydrogen, methane, and acetylene.¹ The second application of acetylene is acting as feeding gas in low-pressure plasmas for dry etching processes. This is normally accompanied by deposition of hydrogenated diamond-like carbon-hydrogen (C:H) layers along sidewalls of etchant surface through polymerization of carbon atoms available in C₂H₂ feeding gas. Eventually, this will produce more vertical etching (anisotropic etching), which increases surface roughness.¹

The formation of coatings through plasma polymerization occurs by the reaction between free radicals formed on the surface of the substrate (C_2 and CH radicals) and a monomer which is present in the gas phase.¹⁵⁴ Therefore, plasma polymerization is thoroughly different from the well-known conventional polymerization simply because it does not consist of repeated monomers. Furthermore, it consists of complex structures of cross-linked, fragmented, and rearranged units of gas monomers.¹⁵⁵ It is worth noting that in this study, the formation of carbon coatings occurred not only at the substrate surfaces but also at all surfaces in the plasma treatment chamber. Increasing the duration of treatment will increase the formation of these coatings on the substrate surface, which can restrain further chemical etching. Polymerization of carbon atoms on a polymer substrate will form highly cross-linked, pinhole-free coatings which are strongly bonded to that substrate.¹⁵⁶ These plasma polymerized films are biocompatible, sterile, and can protect the substrate in a hostile body environment.²¹ For that reason, they are considered for biomedical applications and tissue engineering.¹⁵⁴

In the literature, the description of the polymerization process of these films is still complicated because of the multiplicity of plasma parameters. Moreira et al. analyzed the characteristics of the deposited films from acetylene plasma through FTIR spectroscopy in addition to contact angle measurements. He observed the formation of carboxyl (-COOH) and hydroxyl groups (-OH) on the surface of acetylene coatings. As chemically, acetylene does not contain oxygen, the introduction of oxygen and formation of these functional groups could be attributed to the presence of oxygen inside of the plasma chamber and/or exposure of the specimens to atmospheric oxygen after plasma treatment and subsequent reaction with unsaturated hydrocarbon species in the deposit. These groups were crucial because of their high reactivity and their contribution to covalent bonding with monomers of veneering composites.^{104,157} On top of that, Friedrich et al. stated that these functional groups were highly retentive in acetylene plasma films, which was a critical feature for maximizing adhesion between polymers and laminates.¹⁵⁸ The mentioned advantages might explain the significant increase in bond strength after acetylene plasma treatment in all tested PAEK materials.

Very interestingly, acetylene coatings could cover the greyish shade of both PEEK and PEKK specimens with a color shade close to conventional opaquers which could enhance optical properties. Thus, a question arose whether it would be possible to use acetylene

plasma not only as an adhesion-promoting layer but also as a replacement of the traditional opaquers used during conventional veneering to cover the greyish color of PEEK and PEKK. The facing challenge was to optimize treatment duration and mix with other gases to produce films which had a color shade similar to that of conventional opaquers. It was noted during the performance of acetylene plasma treatment in this study that the longer the treatment duration, the darker the shade of produced films would be. Concerning this point, further studies are now running.

II. Argon plasma

Argon is an inert gas that does not directly generate functional groups on the polymer surfaces, but it has higher crosslinking capabilities than other gases. Through ion bombardment and UV radiation, argon is beneficial in providing free radicals, which become very reactive to oxygen (oxidation) upon exposure to the atmosphere as a post-treatment reaction. This was validated by studies that did XPS analysis to argon treated specimens and compared it to untreated ones where XPS showed an increase in the oxygen relative atomic percentage on the surface of PEEK and different oxygen functional groups on surfaces which ultimately improved hydrophilicity and increased surface energy.^{114,159,160} Therefore, recent studies used a mixture of argon/oxygen to improve adhesion qualities of different PEEK materials.^{18,141} It is worth mentioning that another study showed that the surfaces of PEEK become rougher after argon treatments revealing that argon had a higher etching capacity.¹⁰³ The mentioned effects might explain high bonding strength after argon treatment in all three materials.

III. Nitrogen plasma

Nitrogen plasma was reported to improve the adhesion qualities through the formation of special nitrogen functional groups, namely amine (C–N) and imine functional (C=N) groups. In addition to their reactivity and being able to bond with functional groups in opaquer, they are potentially more resistant to aging effects than oxygen-containing functional groups.^{114,161} In nitrogen plasma, a significant improvement in shear bond strength was evident only with unfilled PEEK and PEKK. Interestingly, ceramic PEEK was not influenced by nitrogen plasma, and there was no improvement in bond strength in comparison with the reference group.

IV. Air plasma

Air contributed to better wettability and adhesion directly through the formation of oxygen-containing functional groups as carboxyl, ether, carbonyl, hydroxyl as well as nitrogen functional groups as nitro (NO₂), nitrates (NO₃), imine and amide functional group.^{162,163} This was because of the simultaneous presence of reactive oxygen and nitrogen species in air plasma. These groups rendered the surface more polar with higher surface energy and hydrophilicity.^{162,163} Regarding etching properties, air plasma had an insignificant effect on surface roughness.^{162,163}

V. Oxygen plasma

In comparison to control groups, oxygen plasma improved bond strength significantly with unfilled PEEK and insignificantly with PEKK while with ceramic PEEK, it couldn't improve the bond strength. In the literature, oxygen plasma treatment could introduce wide variations and also high concentration of oxygen-containing functional groups as carboxyl or ester (O–C=O), carbonyl as an aldehyde or ketone (C=O), ether, hydroxyl, or epoxy, (O–H, C–O) groups and low C–C/H functional groups without the presence of any nitrogen functional groups. The bond strength increased as the total oxygen content and number of these functional groups increased.^{114,159} However, Zhang et al. stated in his study that the formation of carbonyl groups (C=O) adversely affected the bond strength.¹⁵⁹ Comparing to previous gases, this could explain the weak improvement of bond strength when applied to unfilled PEEK or PEKK.

VI. Ammonia plasma

Surprisingly, Ammonia plasma presented an adverse effect on the bond strength within the three tested materials. The bond strength values were lower than in the control groups, and these results were significant in ceramic filled PEEK while in unfilled and PEEK not significant. In ammonia treatment, NH₂ functional groups were formed at the surface with subsequent production of amide groups, which were unreactive and therefore not beneficial for adhesion improvement as stated by Grace et al.^{114,164} Furthermore, the unavailability of the oxygen-containing functional groups because of the reduction reaction in the presence of hydrogen atoms of ammonia compounds might play a role in the decreased bond strength.¹⁶⁵ Creatore et al. pointed out that using NH₃ as a feeding gas

was an intense plasma treatment for the grafting of nitrogen functional groups at polymer surfaces.¹⁶⁴ Therefore, the treatment should be softened either by decreasing the time of treatment or its power. Otherwise, the degradation of polymers during plasma treatment, following to deterioration of their aromatic rings, would occur. Subsequently, this might be the reason for lower bond strength values to veneering composite resins.

VII. CF₄/O₂

CF₄ is known as tetrafluoromethane or carbon tetrafluoride. It is a colorless non-flammable gas, which is used mainly as a low-temperature refrigerant. In plasma, it can be used alone or in combination with oxygen to etch silicon and polymers in microelectronics industries.¹⁶⁶

Liu et al. studied the effect of three atmospheric plasma treatments using oxygen, argon, and tetrafluoromethane feeding gases on the shear bond strength between yttria-stabilized zirconia and veneering porcelain.⁹ CF₄ didn't improve the surface roughness but significantly improved the hydrophilicity of zirconia and showed highest values of bond strength even after thermocycling. Through XPS analysis, he justified this improvement by the increased fluorine content on the surface and the formation of zirconium oxyfluoride phases. These phases were very reactive and could produce hydroxyl groups on the surface upon exposure to atmosphere.⁹ A similar studies, were done by Piascik et al., although using different fluorinated gas (SF₆), showed an improvement of surface energy and hydrophilicity of zirconia in addition to improving the bond strength between zirconia and composite resins after plasma treatment.^{167,168}

For polymers, Choi et al. stated that oxyfluoride ions were good etchants of polymeric substances and capable of cutting the C–C bonds in a polymer backbone.¹⁶⁹ On the other hand, Liston et al., stated that using CF₄ alone in plasma treatment of polymers would replace the H atom with F atoms in the molecular structures on the surface which would prevent the grafting of oxygen atoms and subsequent formation of oxygen-containing functional groups and would ultimately lead to the production a hydrophobic inert surface with low surface energy.¹¹⁵ Based on previous investigations, a gas mixture of tetrafluoromethane and oxygen was chosen in a trial to generate oxyfluoride ions (OF-) and to study their subsequent effects on PAEK materials.¹⁶⁹ The results showed adverse effects on the bond strength between all tested materials and veneering composites in

addition to pre-testing failures of three unfilled PEEK specimens that could not survive thermocycling step. This might be attributed to the formation of CF_3 , $-\text{CF}_2$, and $-\text{CF}$ functional groups on the specimen's surface as they were known to decrease surface energy and increase contact angle, rendering the treated surface hydrophobic.^{115,170,171}

VIII. Discussion of the results within each PAEK material

Acetylene showed mean values of bond strength higher than argon, nitrogen air, and oxygen. This difference was statistically insignificant in case of unfilled PEEK and ceramic PEEK and statistically significant in PEKK (only between acetylene, nitrogen, and air, while with argon insignificant). The reason might be due to acetylene films formed on the surface and their advantages as previously explained.¹⁵²

In addition, post plasma treatment reactions that occur after any plasma treatment as the grafted functional groups on the surface from argon, oxygen, nitrogen and air migrate to the subsurface where treated polymer layers with high surface energy try to reorient themselves into a state close to the unmodified polymer surface which has stable lower surface energy. These surface modifications are known as Aging effects.¹⁵² Aging or hydrophobic recovery is one of the critical aspects that affect the stability of a plasma-treated polymer. It is a time-dependent surface transformation from a hydrophilic state to a hydrophobic state.¹⁵¹ This alteration occurs directly upon exposure to air and continues relatively rapidly over the first five days, then it stabilizes with time. Following the first 24 days, the decrease of wettability stops and becomes stable, and the O/C ratio is approximately the same.^{151,152} This phenomenon occurred firstly due to migration of polar groups away from the surface into the bulk of the material and secondly because of increasing the surface contamination and the precipitation of organic particles and dust on specimens when they are exposed to air. It is worth noting that surface contamination is a self-limiting process because, after the formation of a monolayer of organic particles, the surface energy decreases and becomes stable, thus inhibiting the growth of this layer regardless of the environment.^{151,152}

It is worth to mention that acetylene had comparable bond strength results with adhesive. In unfilled PEEK and PEKK, acetylene showed significantly higher values than Visioliink adhesive. This revealed the dominant physical and chemical effects of plasma polymerization over methylmethacrylate (MMA) based adhesives. While in ceramic

filled PEEK, Visiolink showed a significant increase to bond strength in comparison to all plasma treatment groups. This might be because of the fact that both ceramic PEEK and Visiolink were designed by the same manufacturer to optimize each other.³³

IX. Discussion of the results between PAEK materials

In the control groups, ceramic filled PEEK showed higher, significant bond strength values than unfilled PEEK and PEKK. The reason might be due to the added ceramic fillers, which allowed for better bonding to the opaquer. Up to date, there is no study in the literature that compared the effects of various fillers added to PEEK on the bonding to veneering composite and clearly identify whether they have a positive or negative influence on bonding strength and durability to veneering composites.¹⁸

Regarding adhesive groups, ceramic filled PEEK showed a significant effect compared to unfilled PEEK and PEKK. Although Visiolink showed beneficial effects with different PEEK materials and under surface treatment in comparison to other adhesives.^{80,102,133,136} It seems that methylmethacrylate (MMA) and Pentaerythritol thiocrylate (PTIA) components of Visiolink produce more markable effects on ceramic filled PEEK than other types of PAEK. The same results were also found in the control groups of the study done by Schwitalla and Bötzel et al.^{18,141}

In respect of acetylene, the improvement was not significant between the three materials. As the treatment with acetylene produced the plasma polymer (coating), the bonding interface was transferred from the surface of the PEEK/PEKK specimen and opaquer to the acetylene coating layer and the opaquer. In this case, the three materials were sharing the same interface, which led to indifference improvement among each other.

Regarding plasma treatment using argon, nitrogen, air, oxygen gases, unfilled PEEK showed the highest mean bond strength values compared to the other materials. While with ammonia or the gas mixture of tetrafluoromethane and oxygen, unfilled PEEK showed lowest mean bond strength values compared to the other materials. This meant that the positive effects of argon, nitrogen, air, oxygen plasmas, and negative effects of NH₃, CF₄/O₂ plasmas were more pronounced in unfilled PEEK materials than in ceramic PEEK then PEKK. So, the surface reactions like chains scission, formation of free radicals and grafting of functional groups are easier and more effective on unfilled PEEK

than other materials. Thus, unfilled PEEK being a raw material with no fillers was more susceptible to the effects of plasma than the PEEK material modified with ceramic fillers and PEKK, which had extra ketone group. These observations were also confirmed by the study done by Schwitalla et al. but at the same time contradicted the results of the study done by Bötzel et al.^{18,141} This might be attributed to the fact that Bötzel et al. did sandblast all specimens before plasma treatment which resulted in variations of surface roughness values across the used PEEK materials.¹⁴¹ PEKK, because it contained an extra ketone group, was more inert and less active than ceramic filled PEEK and unfilled PEEK. Therefore, it showed the lowest bond strength value in comparison to unfilled PEEK and ceramic filled PEEK in all groups except with NH₃ and CF₄/O₂ (it was higher than both PEEKs because of the higher resistance to the adverse effects of these plasmas). This observation was consistent with a previous publication testing different PAEK materials.²⁴

Lastly, in the present study common gases of different types were tested including oxidizing gases such as air and oxygen, noble gases such as argon, active gases as nitrogen and ammonia, polymerizing gases such as acetylene and fluorinated gases such as a mixture of tetrafluoromethane with oxygen. From the results, it could be inferred that plasma treatment with all mentioned gases except acetylene did not create a unique functionality on the surface of PAEK materials. Only functional groups were created, which differ in the concentration and distribution and reactivity according to the type of gas and other plasma parameters such as temperature, pressure, power.

Moreover, not all functional groups are important for optimal adhesion between PAEK and veneering composites. As the results showed that functional groups of NH₃ and CF₄/O₂ had severe adverse effects on the bond strength (lower than control groups). In addition, bonding between polymer and veneering composite resins can involve more than one species of functional groups. Accordingly, determining which type of functional groups essential for optimum adhesion is required in the near future. For this purpose, a technique called imaging of radicals interacting with surfaces (IRIS) can be used, as it enables studying the bonding interface and probing interactions at the surface that is exposed to the plasma. In this technique, active species are monitored as they hit the sample surface then interact with the surface and are finally scattering back. This will provide information on reactivity of species with polymer surfaces and enable to tailor

the composition and distribution of functional groups to have a better adhesion by adjusting plasma parameters.¹¹⁴

Until finding the best plasma parameters that help to provide strong, durable adhesion with veneering composites, bonding of PAEKs and veneering composite through micromechanical interlocking and tag formation will continue to be the major factor in promoting their adhesion.

5. Summary

In this study, the influence of different gaseous plasma surface treatments on shear bond strength of three different types of PAEKs (unfilled PEEK, ceramic filled, PEKK) to veneering composites was studied. 180 samples of each type of PAEK were milled and allocated in 9 different surface treatment groups; untreated (control), adhesive, acetylene, argon, nitrogen, oxygen air, ammonia, and a gas mixture of tetrafluoromethane and oxygen. Surface roughness measurements were made to ceramic PEEK to determine the suitable polishing protocol for standardization of surface roughness of all specimens before starting any surface treatment.

In the control group, the bonding protocol started directly without any surface treatment. Opaquer was added and cured followed by addition of veneering composite resins then curing. In the adhesive group, the surface of PAEK specimens was conditioned with Visiolink primer followed by opaquer application then veneering composite in the same way as the control group.

In plasma-treated group, the surfaces of PAEK specimens were treated with cold low-pressure plasma using various gases at constant parameters. This followed by the bonding of opaquer and veneering composite in the same way as the control group.

After bonding, surface area measurements of composite resins were made. Thermocycling test was then done through 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 thermal cycling, macro shear bond strength testing was done to all specimens using a universal testing machine.

The results showed that plasma generally improved the shear bond strength of PAEK to veneering composite regardless of the type of PEEK used. Acetylene was the most effective gas and showed a statistically significant increase in shear bond strength within each type of PEEK. Ammonia and gas mixture of tetrafluoromethane and oxygen showed severe adverse effects on the bond strength within each material. Unfilled PEEK was the most sensitive material to plasma surface reactions while PEKK was the most resistive one.

6. Conclusions and Recommendations

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

- I. Plasma can be a competitive method to sandblasting for providing good bonding of dental PAEK to veneering composites resins.
- II. Acetylene, argon, nitrogen, and air are preferable feeding gases for plasma surface treatment
- III. Unfilled PEEK should be the material of choice if surface treatment using plasma is considered because of its more sensitivity to the treatment

Recommendations

- I. More studies on plasma polymers (coatings) deposition in dentistry for a better understanding of their influence are required. This can help improving bonding to PEKK which has very inert surface.
- II. Regarding plasma parameters, establishing the optimum protocol of treatment time, feeding gas, temperature, power, and pressure will consistently realize an improved bonding between the dental PAEK substrates and resin materials
- III. Studying the combined effect of sandblasting, followed by plasma then adhesive and opaquer application to maximize the advantages of each step would be interesting.
- IV. Studying the effect of different surface treatment and different filled PEEK (ceramic, glass, and carbon filled PEEK) on the surface roughness and bond strength to veneering composite will be beneficial to understand the role of fillers under different surface treatments.

7. Zusammenfassung

In dieser Studie wurde der Einfluss verschiedener Oberflächenbehandlungen mit gasförmigem Plasma auf die Scherhaftfestigkeit zwischen 3 verschiedenen PAEK-Typen (ungefülltes PEEK, keramisch gefülltes PEEK, PEKK) und Verblendkompositen untersucht. Von jedem PAEK-Typ wurden 180 Proben gefräst und in 9 verschiedene Oberflächenbehandlungsgruppen eingeteilt: unbehandelt (Kontrolle), Klebstoff, Acetylen, Argon, Stickstoff, Sauerstoff, Luft, Ammoniak, Gasgemisch aus Tetrafluormethan und Sauerstoff. Die Oberflächenrauheit wurde an keramischem PEEK gemessen, um das geeignete Polierprotokoll zur Standardisierung der Oberflächenrauheit aller Proben vor Beginn einer Oberflächenbehandlung zu bestimmen.

In der Kontrollgruppe begann das Verbindungsprotokoll direkt ohne Oberflächenbehandlung. Opaquer wurde zugegeben und gehärtet, gefolgt von der Zugabe von verblendenden Kompositharzen, dann dessen Härtung. In der Klebergruppe wurde die Oberfläche der PAEK-Proben mit Visiolink-Primer konditioniert, gefolgt von Opaquer-Auftrag und anschließendem Verblendungskomposit auf dieselbe Weise wie die Kontrollgruppe. In der plasmabehandelten Gruppe wurden die Oberflächen der PAEK-Proben mit kaltem Niederdruckplasma unter Verwendung verschiedener Gase bei konstanten Parametern behandelt. Anschließend wurden Opaquer- und Verblendkomposit wie die Kontrollgruppe verklebt. Von fertigen Prüfkörper wurden mikroskopische Bilder gemacht und die Fläche mit einer Bildanalyse vermessen. Anschließend wurde eine thermische Alterung durchgeführt mit 5000 Zyklen Thermocycling (5 und 55° C, Tauchzeit pro Bad 30 Sekunden, Transferzeit zwischen den Bädern 5 Sekunden). Danach wurden alle Proben mit einer Universalprüfmaschine auf Scherfestigkeit in Anlehnung nach ISO 10477 geprüft.

Die Ergebnisse zeigten, dass Plasma die Scherhaftfestigkeit von PAEK an Verblendkomposit unabhängig von der Art des verwendeten PEEK im Allgemeinen verbessert. Acetylen war das effektivste Gas und zeigte einen statistisch signifikanten Anstieg der Scherhaftfestigkeit in jedem PEEK-Typ. Ammoniak und Gasgemisch aus Tetrafluormethan und Sauerstoff zeigten starke nachteilige Auswirkungen auf die Haftfestigkeit in jedem Material. Ungefülltes PEEK war das empfindlichste Material für Plasmaoberflächenreaktionen, während PEKK das resistensteste war.

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Erklärung zum Eigenanteil der Dissertationsschrift

Die Arbeit wurde in der Sektion Medizinische Werkstoffkunde und Technologie unter Betreuung von Prof. Dr. Jürgen Geis-Gerstorfer durchgeführt.

Die Konzeption der Studie erfolgte in Zusammenarbeit mit Herrn Sebastian Spintzyk (M.Sc).

Sämtliche Versuche wurden nach Einarbeitung durch Labormitglieder von mir eigenständig durchgeführt.

Die statistische Auswertung erfolgte unter Anleitung von Attera Ahmed und wurde dann selbstständig von mir durchgeführt.

Ich versichere, das Manuskript selbständig verfasst zu haben und keine weiteren als die von mir angegebenen Quellen verwendet zu haben.

Firma Juvora Ltd (Lancastershire, UK) hat mich mit ungefüllten PEEK Proben unterstützt. Firma Diener electronic GmbH (Ebhausen, Germany) hat mich bei der Durchführung der Oberflächenbehandlung mit Plasma unterstützt.

Tübingen, den 18. Dezember 2018

Mohamed Younis

Veröffentlichungen

Teile der vorliegenden Dissertationsschrift wurden bereits in den folgenden Publikationen veröffentlicht

1- Younis M, Unkovskiy A, ElAyouti A, Geis-Gerstorfer J, Spintzyk S. The Effect of Various Plasma Gases on the Shear Bond Strength between Unfilled Polyetheretherketone (PEEK) and Veneering Composite Following Artificial Aging. *Materials (Basel)*. 2019;12(9):1447. veröffentlicht am 04.05.2019. DOI:10.3390/ma12091447

2- Als Poster (Posternummer 118) auf dem Zahnärztetag 10.11.2018 in Frankfurt vorgestellt. Younis M, Spintzyk S, ElAyouti A, Schille C, Geis-Gerstorfer J Einfluss unterschiedlicher Plasmabehandlungen auf den Haftverbund von Polyetheretherketon und einem Verblendkomposit.

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