

T.C.
YEDITEPE UNIVERSITY
INSTITUTE OF HEALTH SCIENCES
DEPARTMENT OF PROSTHODONTICS

**THE EFFECTS OF DIFFERENT SURFACE TREATMENTS ON
SHEAR BOND STRENGTH OF POLYETHERETHERKETONE
(PEEK) AND POLYETHERKETONEKETONE (PEKKTON)
MATERIALS TO VENEERING COMPOSITE**

PhD Thesis

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DECLARATION

I declare that this work is my own work, that I followed all academic and ethical guidelines in gathering the data for it, that I cited all sources for data and comments not used in the creation of this work, and that I did not violate any copyright or patent laws. I further declare that I did not engage in any unethical behavior while planning or writing this thesis.

Berk Aksoy



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LIST OF SYMBOLS AND ABBREVIATIONS

Al ₂ O ₃	Aluminum Oxide
ANAB	Accelerated Neutral Atom Beam
BHT	2,6-di-tert-butyl-methylphenol
BioHPP	Ceramic reinforced high performance polymer
Bis-GMA	Bisphenol-A glycidyl dimethacrylate
CAD/CAM	Computer Aided Design/Computer Aided Manufacture
CFR	Carbon fibre reinforced
CQ	Camphorquinone
GFR	Glass fibre reinforced
GPa	Giga pascal
HA	Hydroxyapatite
HEMA	2-hydroxyethyl methacrylate
H ₂ SO ₄	Sulfuric acid
ICI	Imperial Chemistry Industries
LED	Light Emitting Diodes
MMA	Methyl methacrylate
MDPB	12-methocryloyloxydodecylpyridinium bromide
MEHQ	Hydroquinone monomethylether
MPa	Mega pascal
n-TiO ₂	Nano-titanium dioxide
n-FA	Nano-flourineapatite
PAC	Plasma Arc
PAEK	Poly-aryl-ether-ketone
PEEK	Poly-ether-ether-ketone
PEKKTON/PEKK	Poly-ether-ketone-ketone
PEKEKK	Polyaryl-ether-ketone-ether-ketone-ketone
PETIA	Pentaerythritol Thiacylate
QTH	Quartz Tungsten Halogen
SEM	Scanning Electron Microscopy
SBS	Shear Bond Strength
SiCl ₄	Silicon chloride
Sr-HA	Strontium-containing hydroxyapatite

TBS	Tensile Bond Strength
TEGDMA	Triethylene glycol dimethacrylate
UDMA	Urethane dimethacrylate
UV	Ultraviolet
W/MK	Watts per kelvin-meter
W/cm ²	Watt/square centimetre
J/Kg.K	Joule/kilogram. Kelvin
K	Kelvin
μm	Micrometer
mm	Milimeter
nm	Nanometer
°C	Degrees Celsius

ABSTRACT

Aksoy, B. (2022). The Effects of Different Surface Treatments on Shear Bond Strength of Polyetheretherketone (PEEK) and Polyetherketoneketone (PEKKTON) Materials to Veneering Composite. Yeditepe University, Institute of Health Sciences, PhD thesis, Istanbul.

Purpose: The purpose of this in vitro study was to evaluate the effects of four different surface treatments and thermocycling process on shear bond strength between PEEK/PEKKTON and indirect composite.

Materials and Methods: 115 PEEK and 115 PEKKTON discs were divided into five groups according to surface treatment methods; no treatment (control), air abrasion with 50 μm Al_2O_3 , air abrasion with 110 μm Al_2O_3 , silica coating with 3M Cojet, etching with 98% sulfuric acid.. The surface roughness was examined with profilometer and scanning electron microscopy (SEM). After surface treatments, Visio.link adhesive with GC Gradia veneering composite was applied on PEEK and PEKKTON surfaces and light-cured. Then, all groups were divided into two subgroups according to whether thermocycling process was applied or not (n=11). Shear bond strength was measured and failure analysis was performed. The data were analyzed using a Two-Way ANOVA, Three-Way ANOVA.

Results: The highest surface roughness values in PEEK and PEKKTON samples were seen in the air abrasion with 110 μm Al_2O_3 groups ($p<0.05$). In the PEEK samples, the group with the highest shear bond strength values was in the air abrasion with 50 μm Al_2O_3 group, while the highest values in the PEKKTON samples were observed in the air abrasion with 110 μm Al_2O_3 group ($p<0.05$). Shear bond strength values decreased in all groups after thermocycling. Adhesive failure is the most common in PEEK samples, while mixed failure in PEKKTON samples.

Conclusions: In the samples of PEEK and PEKKTON, the most effective surface treatment in terms of surface roughness and shear bond strength is air abrasion with Al_2O_3 particles. The bond strength decreased in the thermocycled samples.

Keywords: PEEK, PEKKTON, air abrasion, SEM, shear bond strength.

ÖZET

Aksoy, B (2022), Polyetheretherketone (PEEK) ve Polyetherketoneketone (PEKKTON) Materyalleri Üzerine Farklı Yüzey İşlemleri Uygulanarak Veneerlenmiş Kompozit ile Arasındaki Makaslama Kuvvetinin Değerlendirilmesi. Yeditepe Üniversitesi, Sağlık Bilimleri Enstitüsü, Doktora tezi, İstanbul.

Amaç: Bu in vitro çalışmanın amacı, PEEK ve PEKKTON materyalleri ile veneerlenmiş kompozit arasındaki makaslama kuvveti üzerinde dört farklı yüzey işlemi ve termosiklus işleminin etkilerini değerlendirmektir.

Gereç ve Yöntem: 115 PEEK ve 115 PEKKTON diski yüzey işlemlerine göre 5 gruba ayrıldı; yüzey işlemi uygulanmayan grup (kontrol), 50 µm'lik Al₂O₃ ile kumlama uygulanan grup, 110 µm'lik Al₂O₃ ile kumlama uygulanan grup, 3M Cojet ile silika kaplama uygulanan grup, %98'lik sülfürik asit uygulanan grup. Yüzey pürüzlülüğü profilometre ve taramalı elektron mikroskobu (SEM) ile incelenmiştir. PEEK ve PEKKTON yüzeylerine visio.link adeziv ve ardından GC Gradia veneerlenmiş kompozit uygulanmış ve ışıqla sertleştirilmiştir. Ardından tüm gruplar termosiklus işlemi uygulanıp uygulanmamasına göre iki alt gruba daha ayrılmıştır (n=11). Makaslama bağlanma kuvveti ölçülmüştür ve başarısızlık analizi yapılmıştır. Veriler, İki Yönlü ANOVA, Üç Yönlü ANOVA kullanılarak değerlendirildi.

Bulgular: PEEK (1.325 µm) ve PEKKTON örneklerinde en yüksek yüzey pürüzlülük değerleri 110 µm'lik Al₂O₃ ile kumlama gruplarında görülmüştür (p<0.05). PEEK örneklerinde en yüksek makaslama bağlanma kuvveti değerlerine sahip grup 50 µm'lik Al₂O₃ ile kumlama grubu iken, PEKKTON örneklerinde en yüksek değerler 110 µm'lik Al₂O₃ ile kumlama grubunda gözlenmiştir (p<0.05). Termosiklus sonrası tüm gruplarda makaslama bağlanma kuvveti değerleri azalmıştır. PEEK örneklerinde en çok adeziv kopma görülürken PEKKTON örneklerinde karma kopma görülmüştür.

Sonuç: PEEK ve PEKKTON örneklerinde yüzey pürüzlülüğü ve makaslama bağlanma kuvveti açısından en etkili yüzey işlemi Al₂O₃ partikülleri ile kumlama olmuştur. Termosiklus uygulanmış örneklerde bağlantı kuvveti azalmıştır.

Anahtar Kelimeler: PEEK, PEKKTON, kumlama, SEM, makaslama bağlanma kuvveti.

1.INTRODUCTION and PURPOSE

As one of the most important materials in dentistry, polymers are characterized by their superior physical and mechanical qualities and biocompatibility. Polymers are used to create various removable appliances, restorations, and denture base materials (1,2). The most common used members of thermoplastic polymers of the polyaryl-ether-ketone (PAEK) family are polyether-ketone-ketone (PEKKTON) and polyether-ether-ketone (PEEK) (3).

PEEK and PEKKTON contain aromatic rings that vary in the ratio of ether- and keto-groups. PEKKTON has a second ketone group, which improves polarity and backbone stiffness, resulting in a higher glass transition and melting temperature. Furthermore, the additional ketone group in PEKKTON has strong polymer chains and improved physical and mechanical qualities including flexure, tensile, and compressive strength (4).

Polyether-ether-ketone (PEEK) is a popular material for use in dentistry due to its excellent thermomechanical properties, chemical stability, biological inertness, stability with nearly all organic and inorganic chemicals, good strength, stiffness, toughness, and fatigue properties (5). PEEK material is utilized in dentistry as a framework material for metal-free fixed dental prostheses, removable dental prostheses, implant-supported fixed prostheses, implant-retained overdentures, endocrowns, and resin bonded fixed dental prostheses due to its exceptional qualities. It has also been used to make dental implants, implant abutments, healing abutments, and occlusal splints (6). Like PEEK, PEKKTON is also used in dentistry; as an implant biomaterial, abutments, and prosthesis, removable partial frameworks and attachments, crowns and bridges, endodontic posts-core and endocrowns (7).

Even though they have exceptional properties, the poor bond strength of these materials due to their low surface energy and inert hydrophobic surface has made them a significant focus of study (8,9). Numerous experiments are conducted to improve the bond strength of these materials. In the studies, various roughening processes were applied to the surfaces of these polymers in order to increase their surface energies and strengthen their adhesion capabilities. These surface treatments includes; application of various particle sizes of air abrasion (10–20), different concentrations of sulfuric acid

(8,14,15,17–21), piranha solution (9,17,22), various particle sizes of silica coating (12–14,18–20), plasma (9–11,15) and laser (12,13,18).

Based on the findings, no obvious strategy to improve adhesion has been identified. Because the use of surface treatments to improve adhesion is a common topic in most research, the current study investigated the change in adhesive properties of PEEK and PEKKTON materials by applying various surface treatments. Therefore, the aims of this thesis are to measure the surface roughness values of the surfaces of PEEK and PEKKTON materials created by surface treatments such as air abrasion, acid etching, silica coating with a profilometer and to examine the surface topography with scanning electron microscope (SEM), the effect of the formed rough surfaces on adhesion and the effect of thermocycling process on bond strength.

The first null hypothesis was that there is no statistically significant difference between the roughness values created by the roughening processes applied to the PEEK and PEKKTON surfaces.

The second null hypothesis was that there is no statistically significant difference between the roughening processes applied to PEEK and PEKKTON surfaces when shear bond strength values are measured.

The third null hypothesis was that the applied thermocycle process does not have a statistically significant effect on shear bond strength.

2.GENERAL INFORMATION

2.1.Polyether-ether-ketone (PEEK)

PEEK (polyether-ether-ketone) is a semi-crystalline thermoplastic polymer with a high melting point that belongs to the polyaryl-ether-ketone family (PAEK). This methacrylate-free polymer has a linear aromatic backbone molecular chain that is linked by ketone and ether functional groups. PEEK is resistant to thermal, oxidative, mechanical, and high-temperature attacks due to its aromatic rings. Its exceptional mechanical properties, biocompatibility, and stability with organic and inorganic substances make it an excellent material for use in medicine and dentistry (23).

2.1.1.Synthesis of PEEK

There are two primary pathways for the manufacturing of PAEKs. Linking aromatic ketones with an ether bond is the first approach successfully commercialized for both industrial and medicinal purposes. This procedure utilizes a nucleophilic displacement process. The second technique involves connecting aromatic ether species through ketone groups. This procedure incorporates an electrophilic reaction and Friedel-Crafts acylation chemistry (24).

2.1.2.Chemical structure of PEEK

Polyether-ether-ketone (PEEK) is a linear polycyclic aromatic thermoplastic polymer with a semi-crystalline structure. PEEK, a member of the polyaryletherketone family, possesses an aromatic molecular backbone with ketone and ether functional groups arranged between the aryl rings. This unique chemical structure confers stability to the chemical and physical characteristics of PEEK. It is wear-resistant and stable at high temperatures; it is resistant to attack by all chemicals except sulfuric acid in concentrated form; and it is stable through sterilizing operations (25).

2.1.3.History of PEEK

Polyaryletherketones (PAEKs) are increasingly used as biomaterials for orthopedics, trauma treatment, and spinal implants, after confirmation of their biocompatibility twenty years ago (23). Polyaryl-ether-ether-ketone (PEEK) and polyaryl-ether-ketone-ether-ketone-ketone (PEKEKK) are two PAEK polymers formerly utilized for orthopedic and spinal implants (3).

In 1978, the Imperial Chemical Industries (ICI) Company created and patented the substance (26). PEEK became the dominant high-performance thermoplastic contender for replacing metal implant components, particularly in orthopedics and trauma, by the late 1990s. In 1992, PEEK began to be utilized in dental applications, initially as cosmetic abutments and later as implants. Since then, several compositional alterations have been made to change and enhance the operating features of the implant (27). In April 1998, PEEK was introduced commercially as an implant biomaterial (Invibio, Ltd., Thornton-Cleveleys, United Kingdom). PEEK biomaterials research blossomed because to a steady supply and is predicted to continue to progress in the future.

2.1.4.Fabrication of PEEK

As a thermoplastic that can withstand high temperatures, PEEK may be processed using a number of conventional commercial procedures, such as injection molding, extrusion, and compression molding.

Injection molding is an appealing production method that is well-suited for the mass production of PEEK implant components.

The production of long stock shapes, such as rods, sheets, and monofilament fibers, can be accomplished through a manufacturing process known as extrusion. Extrusion typically begins with the raw material consisting of PEEK pellets or granules as the starting material.

The production line for stock forms, such as plates or thick sheets, is referred to as compression molding. In most cases, compression molding is utilized for low-volume production, prototyping and evaluation work, as well as for the manufacturing of industrial components with extremely thick sections (24).

2.1.5.Classification of PEEK

The PEEK polymers were divided into two groups according to the size of the incorporating bioactive materials (28):

1. Conventional PEEK polymers include; carbon fibre-reinforced PEEK (CFR-PEEK), glass fiber-reinforced PEEK (GFR-PEEK), hydroxyapatite/PEEK (HA/PEEK), strontium-containing hydroxyapatite/PEEK (Sr-HA/PEEK).

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

2.1.5.1. Carbon fibre-reinforced PEEK (CFR-PEEK)

Carbon fibers have superior qualities, including a greater Young's modulus, greater strength, greater thermal conductivity, and superior electrical properties. The addition of carbon fibers significantly enhances the mechanical properties of PEEK composites. PEEK composites reinforced with short carbon fibers have a somewhat high tensile modulus, strength, and fracture toughness. Short carbon fibers additionally boost the PEEK composites' creep resistance, hardness, and compressive strength (29).

2.1.5.2. Glass fibre-reinforced PEEK (GFR-PEEK)

GFR-PEEK is composed of glass fiber and PEEK with dimensions between a few microns and tens of microns and has an elastic modulus comparable to that of human bone. With the use of GFR-PEEK, the optimal environment for osteocalcin formation may be produced. Thus, the bone growth process can build a strong link between GFR-PEEK and the surrounding bone, thereby increasing the success rate of oral implants (30).

2.1.5.3. Hydroxyapatite/PEEK (HA/PEEK)

The chemical and crystallographic structure of hydroxyapatite (HA) resembles that of bone substance. HA is osteoconductive and biocompatible with human skeletal tissue (31). On the basis of the bone-like rigidity of PEEK polymer, it is envisaged that by integrating bioactive HA and adjusting the quantity, a composite with an elastic modulus equivalent to that of genuine bone might be created, while simultaneously rendering the PEEK polymer bioactive (32).

2.1.5.4. Strontium-containing hydroxyapatite/PEEK (Sr-HA/PEEK)

Strontium is a bioactive element that promotes bone repair, fracture prevention, and osteoblast adhesion and mineralization. The incorporation of Sr-HA into PEEK can enhance its bioactivity and modify its mechanical characteristics. Sr-HA has a high elastic modulus of around 80 GPa compared to 4 GPa for PEEK (33).

2.1.5.5. Nano-titanium dioxide/PEEK (n-TiO₂/PEEK)

TiO₂ is bioactive, biocompatible, hydrophilic, and resistant to corrosion. On a PEEK substrate, a micron-thick TiO₂ coating was formed, which increased osteoblast cell adhesion, proliferation, and differentiation (34). Nanoparticles of TiO₂ are more

bioactive than micron-sized particles. A TiO₂ nanotube surface substantially enhances osteoblast adhesion and demonstrates robust bone bonding (35).

2.1.5.6.Nano-flourineapatite/PEEK (n-FA/PEEK)

Bacterial adhesion is a significant problem of polymer and titanium implants after insertion, and bone loss can possibly result in implant loss. Therefore, when selecting implant material, antibacterial qualities of the material should be addressed. It has been discovered that fluoride ions hinder bacterial adhesion and enzyme function. By covering PEEK implant surfaces with fluoride ions from n-FA, antibacterial characteristics are conferred to PEEK implants (36).

2.1.5.7.Nano-hydroxyapatite/PEEK (n-HA/PEEK)

Due to the low physical binding energy between PEEK and HA, the HA/PEEK composites have worse mechanical performance compared to pure PEEK. In contrast, the n-HA/PEEK composite exhibited superior mechanical properties and bioactivity when n-HA was incorporated into PEEK. In addition, no debonding occurred between the PEEK matrix and the equally dispersed HA nanoparticles (25).

2.1.6.Properties of PEEK

The mechanical, thermal, chemical, structural properties and biocompatibility and bioactivity of peek polymers will be examined under six main headings.

2.1.6.1.Structural properties

Polyetheretherketone is a synthetic, tooth-colored, somewhat bioinert, semi-crystalline polymer with a low attraction for dental plaque and no allergic responses (37–39). It is radiolucent, allowing for radiographic examination. It is stable at high temperatures (above 300°C) and chemically resistant. It has a strong electron and gamma-beam radiation resistance (40). Unmodified PEEK is intrinsically hydrophobic, having a water-contact angle between 80 and 90°. It is easily modifiable by the addition of other substances (37).

PEEK may be processed by injection molding, extrusion, and compression molding at temperatures ranging from 390 to 420°C. PEEK is in its "glassy" state at room temperature and body temperature because its glass transition temperature is

around 143°C, whereas its crystalline melt transition temperature is approximately 345°C (3).

2.1.6.2. Chemical stability

PEEK structure gives exceptional chemical resistance. The ketone and ether groups at opposing ends of the aryl ring in PEEK link the aryl rings. PEEK is intrinsically nonreactive and resistant to chemical, thermal, and postirradiation deterioration due to its resonance-stabilized chemical structure. PEEK is impervious to all solvents except for strong sulfuric acid. The biocompatibility of PEEK is due to its chemical structure, which is intrinsically inert (41,42).

2.1.6.3. Thermal stability

Thermal deterioration of PEEK occurs between the glass transition and the melt transition temperature, however volatile degradation products need temperatures above the processing temperature of PEEK. Thermal deterioration is not an issue during clinical usage of PEEK biomaterials at 37°C (43,44).

2.1.6.4. Mechanical properties

PEEK combines high strength with a Young's modulus (3–4 GPa) that is closer to that of human bone, hence reducing stress shielding through surrounding tissues (45). Mechanical and thermal properties summarize in table 2.1. (46).

Table 2.1. Mechanical and thermal properties of PEEK (46)

Mechanical Properties		Thermal Properties	
Elastic modulus (GPa)	3.6	Thermal conductivity (W/m K)	0.29
Poisson's ratio	0.38	Specific heat (J/kg K)	2180
Density (kg/m ³)	1300	Glass transition temperature (K)	416
Yield stress (MPa)	107	Melt transition temperature (K)	616

PEEK polymer offers high temperature performance, great wear qualities, superior chemical resistance, hydrolytic stability, and exceptional toughness and strength due to its linear, aromatic, ordered structure. Under static, fatigue, and impact situations, the reinforcing effects of crystallinity or filler will alter the mechanical characteristics of PEEK polymer. Higher crystallinity will result in greater modulus and

yield stress, whereas crystal size and the mobility of the amorphous phase govern roughness and elongation (47).

To increase the mechanical characteristics of the PEEK polymer, many fibers are included into its composition. Carbon is the most common additional fiber for implantable devices. Carbon fiber reinforcement of PEEK increases its mechanical and tribological characteristics and boosts its modulus to 18 GPa, which is closer to that of cortical bone and essential for the material's medical use (48). When the proportion of carbon fibers added to PEEK polymer is raised, the material's tensile strength and elastic modulus rise. Consequently, the material becomes more durable and less elastic (49).

2.1.6.5.Biocompatibility of PEEK

Biocompatibility considers interrelations between the biomaterial and its host ecosystem. Biocompatibility applies to the connection between materials and biological systems in a specific application that is deemed suitable for the premises. Material by itself is not biocompatible; biocompatibility is an incident or interaction, not an inherent property of a biomaterial. To be biocompatible, a material must be non-toxic, non-mutagenic, non-immunogenic, and non-carcinogenic (50).

2.1.6.5.A.Cytotoxicity and genotoxicity

WHO and ISO 10993 suggests that there are two different valid test mechanisms for the detection of cytotoxic and mutagenic effects of the implant material PEEK. First of which is the signs of mutagenesis and toxicity in bacteria *Salmonella typhimurium* (Ames Test) and the second mechanism is mutagenesis in the Chinese hamster fibroblasts (V79). During the course of the research conducted on PEEK, no mutagenic or cytotoxic effects were discovered (51).

2.1.6.5.B.Immunogenicity

In most cases, there has been no link established between PEEK and immunogenicity. There are only two reports of allergic reactions in the available literature (52,53). There is no evidence linking PEEK to an immunological response, with the exception of these individual case studies.

2.1.6.6.Bioactivity of PEEK

A favorable interaction with tissue differentiation or the promotion of tissue wound healing is what we refer to as bioactivity. It is common knowledge that PEEK polymers do not support biological growth. An inert biomaterial does not undergo any undesirable reactions and does not release any components or ions. The chemical inertness, low surface energy, and hydrophobic nature of PEEK contribute to the material's low level of adhesion. PEEK polymers are not known to be bioactive materials unless they have additional coatings or modifications applied to them (54).

PEEK is considered to be a bioinert material; therefore, when it is used as an implant material, the level of cell adhesion is low, and there is insufficient integration of the implant with bone. Recent studies have been focused on finding ways to improve the way PEEK implants integrate with surrounding bone (55).

2.1.7.Improvement of PEEK bioactivity

There are various studies currently being conducted on a wide variety of approaches to alter the surface energy of PEEK in order to enhance bone integration. These can be broken down into two major classifications. First, there is the procedure known as deposition, which involves particles and/or a coating substance being deposited onto the surface of the PEEK. The second strategy is known as direct surface modification concepts, and it involves changing the surface chemistry as well as the topography of PEEK (55). When compared to surfaces that aren't modified and have a lower energy, those that are modified and have a higher energy boost cell spreading and adherence (23).

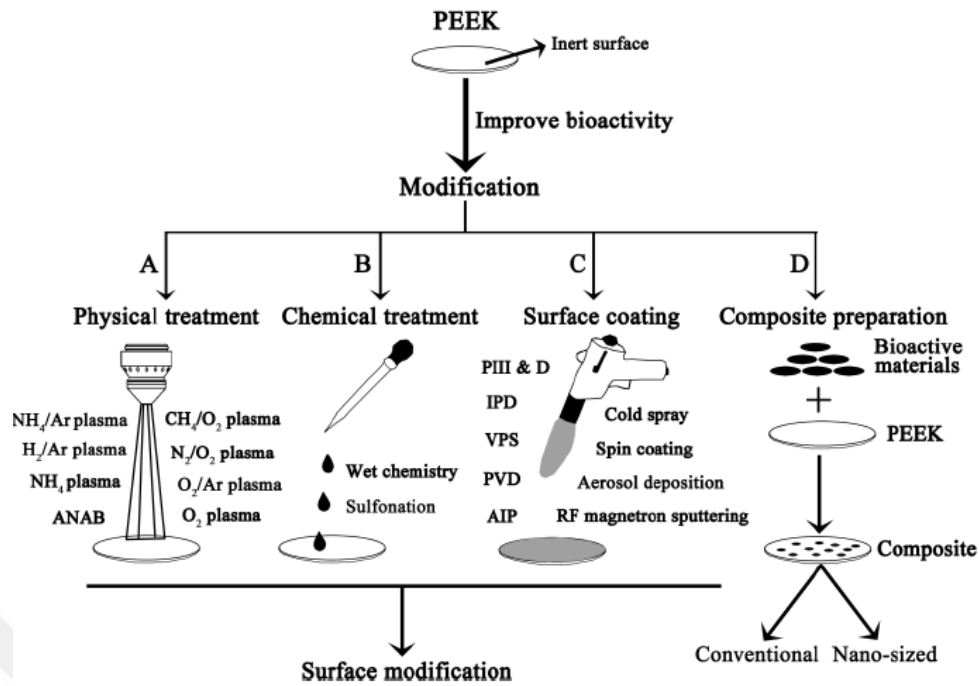


Figure 2.1.Current strategies to improve the bioactivity of PEEK (25).

2.1.7.1. Deposition techniques

The practices consist of vacuum plasma spraying with calcium phosphate and titanium, plasma coating, and functionalization. There is also the possibility of utilizing laser sintering or compounding in order to incorporate particles into the PEEK.

The bioactivity of PEEK can be significantly increased with the application of surface coatings such as hydroxyapatite, titanium, gold, titanium dioxide, diamond-like carbon, and terbutoxides. The bioactive material known as hydroxyapatite is used for PEEK coating at a much higher rate than any other material (25).

2.1.7.1.A. Plasma treatment

Plasmas are ionized gases that can be produced by excitation of a low-pressure gas mixture in a closed reactor framework with electromagnetic radiation. This process results in the generation of plasmas. The reactive particles that are produced in this manner are able to interact with the surface of the biomaterial that has been placed in the reactor, thereby affecting its physical and chemical surface characteristics. However, they are able to do so without affecting the material's mechanical, electrical, or optical qualities, which are essential to the material's application (56,57).

Plasma treatment has been shown to increase the surface energy of the material and improve cell adhesion in tests to boost the adhesion of PEEK, which was shown to improve adhesion (25).

2.1.7.2.Direct surface modification techniques

These include wet chemical and physical forms of treatment such as exposure to corona, UV/ozone, and high energy species. In addition, these treatments can be combined.

2.1.7.2.A.Wet chemical treatment

PEEK was chemically modified through the use of wet surface chemistry, which resulted in the production of a number of surface-functionalized PEEKs. According to the findings of the studies, sulfonation and subsequent water absorption into the surface of the PEEK material induced pre-osteoblast functions such as preliminary cell adhesion, proliferation, and osteogenic differentiation. These functions also included improved osseointegration and bon-implant bonding strength (58).

2.1.7.2.B.Physical surface treatment

Laser surface treatment

Since lasers are a source for photons, they have the potential to produce both high energy and high intensity. It is common practice to employ them in the polymer industry to bring about chain scission and cross-linking. It has been demonstrated through research that the application of laser treatment can remove oxygen from the surface of oxygen-containing polymers, resulting in a modification (59). The surface chemical improvements and the rise in surface wettability that are brought about by this treatment are responsible for the improvement in adhesion properties that are brought about by this treatment (60).

Accelerated neutral atom beam (ANAB) surface treatment

Intensive collinear beams of coincidentally accelerated neutral gas atoms can be produced by using accelerated gas cluster ions as the source material. While permeating target surfaces, these accelerated neutral atom beams have been found to be able to produce excellent smoothing, amorphization, doping, reactive transformation, and sputter removal behaviors. The research that has been done to this point has shown that

beams of energetic neutral atoms can modify the surface properties of candidate biomaterials in a way that is beneficial without compromising the mass characteristics of those materials.

It has been demonstrated that treating PEEK with an ANAB significantly improves osteoblast adhesion. PEEK surfaces became hydrophilic after being exposed to neutral atom beams, and it is feasible that this may have been one of the contributing factors that led to the observation of the cell response (61).

Ultraviolet/ozone surface treatment

Exposure to sunlight, which contains photons with short wavelengths, can break down polymers because it causes chemical reactions to take place. Photooxidation is the name given to the process that takes place when surfaces are subjected to ultraviolet radiation in the presence of oxygen (62). The treatment with ultraviolet light and ozone makes use of this process, which results in the photon-activated cross-linking or fragmentation of the surfaces of polymer molecules. Changes are brought about in the surface oxygen chemistry as well as free energy, both of which contribute to improvements in surface polarity and wetting (63). The modification that it produces is consistent, in addition to being relatively easy and inexpensive to implement.

Corona treatment

Corona treatment is known to have an effect on polymers down to a depth of approximately 10 nm, it increases the surface roughness due to pitting, and can also lead to the formation of low-molecular-weight species, both of which can have an effect on the adhesive properties. It accomplishes this by adding polar groups to the surface, which leads to an increase in surface energy. As a result, the bonding and wetting properties of the substance are enhanced (64).

2.1.8.Applications of PEEK

The application areas of peek polymers are divided into three as; medical, industrial and dental.

2.1.8.1.Industrial application of PEEK

PEEK's chemical structure makes it resistant to chemical and radiation damage, stable at elevated temperature, compatible with a wide variety of reinforcing agents, and

stronger than a great number of metals. These characteristics, along with its increased strength than many metals, make it an extremely desirable material for use in industrial applications such as airplane and turbine blades (3).

2.1.8.2. Medical application of PEEK

Because of its superior chemical, mechanical, and thermal properties, PEEK is now utilized in a variety of applications within the medical industry. These properties are expressed by the material's high strength in conjunction with its adequate milling and grinding properties.

With some of its chemical adjustments and commercial compositions, PEEK material has been managed to bring to the desired state for use in medical and surgical applications. This is due to the fact that PEEK material has demonstrated advancements in the dental industry. The use of PEEK in spinal surgery has been improved thanks to the material's advantageous biomechanical properties, long lifespan, and biocompatibility. In spite of its widespread application, there have been no documented cases of allergy or hypersensitivity to PEEK (65).

Craniofacial deformities are another area of medicine in which PEEK is preferred over other materials. PEEK has been shown to be effective in treating craniofacial deformities, despite the fact that no material has yet been identified as being entirely suitable for this purpose. It is regarded to be a viable alternative to other graft materials due to the fact that it is chemically inert, it can be decontaminated by steam or gamma rays, it has an elasticity that is similar to that of cortical bone tissue, it is biocompatible, it is strong, and it is radiolucent. All of these qualities make it an ideal graft material. According to a number of studies, carbon fiber reinforced PEEK is an excellent choice as a material for the fixation of femurs and tibias (66).

2.1.8.3. Dental application of PEEK

Due to the fact that PEEK possesses superior attributes, it has recently begun to be utilized in the field of dentistry, following its application in the industrial and medical topics. Because the tensile properties of PEEK are similar to those of bone, enamel, and dentin, this material is well-suited for use in dental restorative applications. PEEK is reliably used for implants, abutments, framework material for removable and

fixed prosthesis, endocrowns, and post-core systems due to its high degree of biocompatibility and the properties listed above (37).

2.1.8.3.A.PEEK implant material

With its low elastic modulus (Young's modulus), which is close to human bone, PEEK is a prominent material that can be used as an implant. Because of this, it can stimulate favorable stress and deformations, thereby minimizing the stress shielding effect and bone resorption (67).

PEEK in its unfilled state has an elastic modulus of between 3 and 4 Gpa. It can be easily altered and enhanced with reinforcing agents such as carbon (CFR-PEEK) and glass (GFR-PEEK), and the elastic modulus of PEEK can increase up to 18Gpa, which is comparable to the elastic modulus of bone (14Gpa) (68).

Unmodified PEEK is thought of as a bioinert material; however, there is no definitive proof that it has osseointegrative effects; as a result, the survival of unmodified PEEK implants is a matter of debate. PEEK must first undergo a number of treatments in order to achieve the desired level of bioactivity before it can be used as an implant material (69).

When implants are going to be placed in the front of the mouth and the gingiva has a thin phenotype, using PEEK implants rather than titanium implants will produce more aesthetically pleasing results (70).

2.1.8.3.B.PEEK implant abutments

Because PEEK abutments exhibit bone resorption and soft tissue inflammation that are similar to those of titanium abutments, they can be used as implant abutments. In addition, the elastic modulus of bone and PEEK should be closely matched, as this will reduce the stress shielding effect and promote bone remodeling (37).

PEEK demonstrates a fracture resistance that is lower than that of titanium alloys when used in an abutment material (71). Due to the semi-crystalline framework of PEEK, the material's fragility is significantly reduced; as a result, deformation is observed rather than breakage. As a consequence of this, PEEK abutments can be easily replaced in the event that problems arise in upper structures. This allows for the avoidance of problems that might otherwise occur as a result of the difficulty of removing a broken screw (70).

2.1.8.3.C.PEEK removable prosthesis material

PEEK is used in removable partial dentures instead of metal braces and hooks as an alternative material option. It has been demonstrated that PEEK hooks have a lower retentive strength when compared to chrome-cobalt-based partial prostheses (72). They relieve the metallic taste that can cause allergic reactions, are able to be polished to a high degree, and have reduced plaque accumulation. It is possible to make metal braces and hooks out of PEEK because the material is white in color and has a high resistance to wear and tear. It is possible to use it in the implantation of supporting bars. PEEK can be utilized with acrylic teeth as a substitute material for removable partial prostheses if it is combined with a high-performance polymer and then fabricated into the appropriate shape.

Because of the elasticity of the material, the amount of torque force and stress on the tooth may be reduced. As a direct result of this, lighter prostheses are able to be manufactured, which results in increased patient contentment and comfort. It has been observed that PEEK is more resistant to color shifts than other prosthesis resin materials. This has been observed to be the case (70).

When compared to the metal formwork, it is simpler to produce, and those manufactured with CAD-CAM systems are simpler to apply with abrasion in a short amount of time without damaging the burs. Due to the low water absorption and solubility properties, PEEK material may be recommended for long-term restorations. It is possible to rehabilitate large oronasal defects using PEEK because of the material's low weight (73).

2.1.8.3.D.PEEK fixed prosthesis

Because it contains inorganic chemicals, PEEK can be utilized in fixed prostheses as it possesses suitable mechanical properties for such applications. The fact that PEEK material can be repaired more easily than ceramics, that it does not wear down within the mouth, and that there is no deterioration seen in the material characteristics during processing increases the possibility that it can be used as crown material. In addition to this, despite having a low elasticity modulus and hardness, because of its high resistance to wear, this material is capable of competing favorably with metallic alloys (74).

Because of its high level of tensile strength, PEEK is an excellent choice for the framework of a fixed dental prosthesis. The biocompatibility of materials made of PEEK is significantly higher than that of ceramics made from metal. Because of its lower weight, PEEK could serve as an acceptable substitute for chromecobalt ceramics. It is resistant to corrosion even when brought into close proximity with other metals in the mouth. PEEK is insoluble in water and has a low level of chemical reactivity with other materials; as a result, it might be an option worth considering for patients who are allergic to metals or who have a heightened sensitivity to the taste of metals (75).

Because PEEK is a white-gray color, it needs to be veneered with composites in order to achieve the desired aesthetic. Due to the fact that PEEK is chemically inert, a variety of approaches have been investigated and tried in order to achieve a strong bond with veneering materials (68).

2.1.8.3.E.PEEK endocrowns

The endocrown is a restorative option for teeth that have suffered from significant loss of coronal enamel. It has been suggested that teeth with short clinical crowns and root canals that are calcified, short, or curved should get endocrowns rather than post and core restorations because endocrowns offer more benefits. Patients who have narrow interocclusal space, which hinders sufficient thickness for both the ceramic veneer and the metal or ceramic structure, are another patient population that can benefit from these restorations.

The biocompatibility and mechanical properties of a material called BioHPP, which is a modified form of PEEK and contains twenty percent ceramic fillers, are excellent. This material is manufactured by Bredent GmbH. This modified PEEK material has a modulus of elasticity of 4 GPa, which makes it as elastic as bone and enables it to act as a stress breaker and reduce the forces that are transmitted to the restoration and the tooth root accordingly. This is the primary benefit of using this material instead of traditional dental materials. PEEK could be a feasible alternative for the restoration of endodontically treated teeth by means of endocrowns as a result of this, in addition to having good adhesion features to tooth structures when cemented with resin cements.

PEEK restorations have been shown to have excellent mechanical properties, as well as a good fit and esthetic appearance. It appears that microleakage is a significant

drawback, but the fact that PEEK is radiolucent may make it easier to detect recurrent caries (76).

2.1.8.3.F.PEEK post-core systems

The inclusion of a dental post and core is frequently necessary in order to restore teeth that have been treated endodontically and have experienced more than fifty percent loss of coronal tooth structure. The stability of the restoration is impacted by the dental post design as well as the post material, both of which play an important part in determining the chances of survival of endodontically treated teeth.

Because of its high fracture resistance and biocompatibility, the high-performance polymer PEEK has been proposed as a potential replacement for dentine as a material for dental posts. PEEK's elastic modulus is comparable to that of dentine. It has been indicated that uniform distribution of stress occurs in dental materials that have an elastic modulus that is comparable to dentin. Since the elastic modulus of PEEK matches that of dentin, this is a major benefit that helps reduce the forces that are transferred to the restorations and makes it possible for this material to perform as a stress breaker. In addition to this, its radiolucency makes it possible to conduct an evaluation of the treatment protocols in a step-by-step fashion.

According to studies, the PEEK post appears to have advantages over other available dental post options in terms of bond strength and stress dispersion profile. When considering the cost-effectiveness of the treatment, the use of PEEK material as a dental post may be a good option to consider because it has been demonstrated that the use of PEEK framework designs can reduce costs. The creation of PEEK posts using a CAD/CAM platform requires specialized training, the purchase of scanning equipment, and results in material waste due to the subtractive method. As a result, this technique is more expensive than traditional milling methods (77).

2.2.Polyether-ketone-ketone (PEKK/PEKKTON)

There are no methacrylates present in the thermoplastic high-performance polyether-ketone-ketone material. It was first presented to the public by Bonner in 1962, and ever since that time it has been utilized for a variety of purposes in both the commercial and the military spheres. PEKKTON, which has properties that make it suitable for use in dental and medical applications, has become an increasingly popular

biomaterial in recent years. The PEKKTON is useful for a variety of dental procedures, including implant dentistry, prosthetics, and restorative dentistry. When it comes to the development of cranial and orthopedic implants, PEKKTON shows a lot of promise as a material. Their extensive biomedical applications can be attributed to their superior mechanical strength as well as the presence of a second ketone group, which makes it possible to make more surface modifications to the substance's surface (7).

2.2.1. Structure and synthesis of PEKKTON

The PAEK is a form of a linear aromatic polyether ketone, and it is represented by polyethylene with an extremely high molecular weight. Both PEEK and PEKKTON have aromatic rings in their structures, but the proportions of ether- to keto-groups in these rings are different (4). The presence of a second ketone group in PEKKTON contributes to an increase in both polarity and backbone rigidity. This, in turn, causes an elevation in both the glass transition temperature and the melting temperature. PEKKTON can behave in either an amorphous or crystalline manner, and this allows for a variety of products to be made from it. Additionally, PEKKTON possesses robust polymer chains thanks to the presence of an additional ketone group. This contributes to the material's improved physicommechanical properties, such as its compressive strength.

PEKKTON is a liner thermoplastic polymer that is made up of a benzene ring that has ether or ketone-groups attached to it in a consecutive order. Producing PEKKTON involves combining diphenyl ether, iso- and terephthaloyl chlorides, aluminum chloride, and nitrobenzene in the appropriate proportions (78).

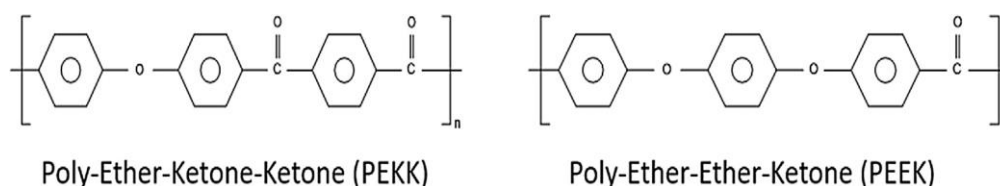


Figure 2.2. Comparison of PEEK and PEKKTON structures (78).

2.2.2. Properties of PEKKTON

The properties of pekk material can be examined in two parts as physical and mechanical properties and biological properties.

2.2.2.1. Physical and mechanical properties

The physical and mechanical properties of PEKKTON, such as melting point and compressive strength, are among the best in the industry. The mechanical properties of PEKKTON are superior to those of PEEK in terms of flexure, tensile, and compressive strength (79).

When compared to unreinforced PEEK, the compressive strength of a product manufactured by PEKKTON (Pekkton@ ivory Cendres + Métaux, SA, Switzerland) is approximately eighty percent higher (80). The incorporation of titanium dioxide into PEKKTON results in an increase in both the material's hardness and its resistance to wear (81).

PEKKTON's ability to absorb shock due to its suitable strength (65 MPa) and fracture resistance characteristics raises the possibility that it could be used as a restorative material (82). When compared to dentin, the PEKKTON possesses a compression strength that is comparable despite having a lower modulus of elasticity (83). In a manner comparable to that of PEEK, the elastic modulus of PEKKTON is similar to that of bone. Therefore, PEKKTON has the potential to be utilized as a biomaterial for dental implants due to its superior mechanical properties and improved stress distribution (7).

Table 2.2. Comparison of mechanical properties of PEEK and PEKKTON (7).

	PEKKTON	PEEK
Tensile strength (MPa)	115	100.69
Elastic modulus (GPa)	5.1	3.5
Flexural strength (MPa)	200	163.88
Compressive strength (MPa)	246	118-169
Melting temperature (° C)	363-386	334-350
Hardness	252 MPa	26-29 VHN
Water absorption (µg/mm³)	8.7	0.1-0.5
Density (g/cm³)	FEFF1.3	1.3

2.2.2.2.Biological properties

PEKKTON has been introduced as a potentially more beneficial alternative material to titanium for use in long-term orthopedic applications because of its high level of biocompatibility. In addition to this, PEEK is being put to extensive use in the dental industry as a biomaterial for prosthetics and implants. It provides restorations that don't use any metal, which is beneficial for those who have metal allergies (82).

According to the findings of the studies, the ability of PEKKTON's surface to undergo chemical modification is enhanced by the presence of another ketone group. This results in a complex surface topography, a greater surface area, and a microrough surface, all of which will have an effect on the behavior of the cells and the osteointegration on the surface of PEKKTON (84).

In terms of its antibacterial properties, the research indicates that PEKKTON displays less bacterial adhesion on its surface when compared to the PEEK used in the orthopedic industry (85).

2.2.3.Dental applications of PEKKTON

PEKKTON has recently found use in a variety of different areas of dentistry due to its superior mechanical properties, including its fracture resistance, shock-absorbing capabilities, and better stress distribution. The PEKKTON is considered an alternative to both ceramics and metals because it does not contain any metals in its restorations, which contributes to its excellent biocompatibility. PEKKTON is utilized in the manufacturing of dental implants, abutments, crowns, post-core systems, and endocrowns. Additionally, it is a framework element for removable prostheses.

2.2.3.1.PEKKTON prosthetic material (crowns)

The PEKKTON material has a high strength to weight ratio, low elastic modulus, acceptable wear resistance, and a low density. It has the potential to be used as a restorative material in fixed prosthodontics, which is one of its potential applications (86).

Recent years have seen the introduction of CAD/CAM technology in the process of fabricating PEKKTON prosthetic restorations (87,88). Pekkton[®] ivory PEKKTON is used for monolithic and bi-layered material with an indirect composite veneer (80).

In restorative and prosthetic dentistry, it is absolutely necessary for PEKKTON to bond to the various restorative materials. In order to bond PEKKTON using a variety of different adhesives systems, different surface treatment techniques of PEKKTON have been developed. According to the findings of the studies that compared the bond strength of PEKKTON to dental resin composite using a variety of surface treatment methods, mechanical surface treatment performed significantly better than chemical surface treatment (14).

Another crucial aspect of prosthetic dentistry is ensuring that the dental restoration is a good fit for the patient. Plaque buildup, recurrent caries, and periodontal damage can all result from inadequate marginal fit, which can ultimately lead to the restoration failing. In a study on marginal fit, compared with zirconia, they found that the marginal fit fell within the acceptable range. This was discovered through observation. On the other hand, the PEKKTON showed a lower stress distribution around its loading areas, and the PEKKTON coping was found to have a higher level of fitness when compared to the zirconia coping (87).

In an ideal situation, the tooth and enamel wear that is caused by dental restorations should not be any worse than the natural wear and tear that occurs on teeth over time. The selection of appropriate restorative materials, the goal of which is to have a degree of hardness that is almost similar to that of enamel, is essential for minimizing or impeding the detrimental and irreversible ramifications of tooth or enamel wear. According to the findings of the studies, PEKKTON led to the greatest amount of material wear while causing the least amount of adverse tooth wear (89).

2.2.3.2. PEKKTON implant biomaterial, abutments and prosthesis

PEKKTON has the benefit of having sufficient strength, being lightweight, being resistant to wear, and having an elastic modulus that is comparable to that of dentin. Implant abutments (90) framework material for implant prosthesis (91–93), prosthetic crown materials (80,94), and implant biomaterial are all possible applications for PEKKTON (95).

PEKKTON is a material that does not contain any metals and offers an alternative to titanium implants (95). The advantage of using PEKKTON abutments as the framework for an implant-supported prosthesis is that they are adjustable, compatible with a wide variety of veneering materials, and can be used as a framework

(96). A potential material for providing long-term retention in implant prostheses is a combination of the PEKKTON attachment system and titanium (97).

When subjected to compressive stress, the PEKKTON framework exhibits lower levels of stress to the implant and tissue than it does when subjected to tensile stress. Because of this, the PEKKTON framework ought to have some restrictions placed upon it in certain areas so that it can maintain its resilience. There is a wide range of applications for PEKKTON in oral implantology; however, these applications should be made for appropriate reasons, and additional research is required to investigate the chemical modulation of PEKKTON in order to improve implant contact (98).

2.2.3.3. PEKKTON removable partial frameworks and attachments

Clasps made of metal in removable dental prostheses have the drawback of being unaesthetic. Additionally, some patients may experience oral galvanism and allergic reactions if they are used (99). Thermoplastic materials have provided a partial solution to these types of problems (100). In recent years, PEKKTON has become popular for use in removable partial dentures as dental clasps and frameworks through the application of digital technology (86).

PEKKTON clasps have the capability of providing retention for an extended period of time. In addition, PEKKTON can be utilized as an insert material for removable partial dentures (72). When compared to the nylon inserts, the PEKKTON insert demonstrated significantly lower levels of retention change and abrasion (101).

Research concluded that the amount of stress evenly distributed in the framework material of three and four unit small bridges had a significant impact on the structure's integrity. Because of the choice of material, the surrounding tissues were not affected in any way by the strain that was applied to the surrounding area. This demonstrated that PEKKTON, a polymer, has the potential to serve as an alternative to metal framework (102).

2.2.3.4. PEKKTON endodontic post-core and endocrowns

Given its adequate mechanical strength, appropriate processing, and shock-absorbing ability, the PEKKTON biomaterial has attracted interest in post-core systems. In comparison to metal and fiberglass post-core systems, the biomechanical performance of PEKKTON is significantly higher. Because of its lower elastic modulus

and higher flexural strength, the PEKKTON demonstrated superior fracture resistance in comparison to metal and fiberglass post-core systems (103,104).

When compared to traditional post-core materials, the PEKKTON post-core exhibited a more beneficial stress dispersion at the intraradicular surface. This suggests that there is a lower risk of root fracture with this post-core material. PEKKTON was able to transfer greater stresses to the materials that were in contact with it. As a result, the likelihood of crown and cement debonding failure would be higher at the interface level than it would be with rigid post-core systems, which would be more likely to result in root fracture (104).

The PEKKTON post-core provides an advantageous stress distribution, which lessens the likelihood of a root fracture occurring. Despite this, there is a possibility that debonding and crown failure will occur more frequently in PEKKTON post-core because of its flexibility. The use of PEKKTON material acts as a stress breaker and inhibits the forces that are transferred to the restoration and the tooth root. PEKKTON can be utilized in place of endocrowns for teeth that have had endodontic treatment. In addition to this, PEKKTON posts are appropriate for the fabrication of posts (7).

2.3.Composite Resin

A composite is a blending of two or more materials that has the properties of a single material when viewed from the perspective of materials science and engineering more generally. By combining different kinds of materials, composites can be made to have the benefits of their primary components while minimizing the drawbacks of each of those components individually.

Structures composed of dental resin-based composites can be broken down into three primary components: a highly cross-linked polymeric matrix that has been reinforced with a dispersion of glass, mineral, or resin filler particles and/or short fibers that have been coupled to the matrix (105).

2.3.1.History of composite resin

Silica was the tooth-colored substance of choice for cavity restoration during the first half of the twentieth century. However, because silicates become gravely eroded within just a few years, they are currently almost exclusively used for the treatment of deciduous teeth. Despite the fact that silicates are excellent at preventing cavities and

releasing fluoride, they are almost exclusively used for the treatment of deciduous teeth (106).

Acrylic resins quickly replaced silicates as the material of choice due to their toothlike presence, inertness in oral fluids, simplicity of manipulation, and low cost. Acrylic resins are comparable to the materials that are used to make dentures and custom impression trays. Unfortunately, these acrylic resins had a relatively low resistance to wear and had a propensity to shrink significantly during the curing process. This prompted them to pull away from the cavity walls, which resulted in the production of crevices or gaps that made it easier for leakage to occur within these gaps (107).

In 1962, Bowen came up with an innovative type of composite material that was able to circumvent the majority of these issues. The two most significant contributions made by Bowen were the development of a monomer known as bisphenol-A glycidyl dimethacrylate (bisGMA), which is capable of forming a cross-linked matrix that is exceptionally long-lasting, and a surface treatment that made use of an organic silane compound known as a coupling agent in order to bond filler particles to the resin matrix (108,109).

In the 1970s, a category that is now known as traditional composites was created; this contained quite sizeable particles of ground amorphous silica and quartz, which conveyed substantial advancements in mechanical attributes, water sorption, polymerization shrinkage, and thermal expansion compared with unfilled acrylic. Traditional composites are also known as conventional or macrofilled composites (110).

Lastly, developments in curing technology have produced lightcured systems, which not only make it possible to toughen resins on demand but also shorten the amount of time it takes to work with them and make it easier to manipulate them. In the beginning, an ultraviolet (UV) curing system was used; however, because it had several drawbacks, it was quickly replaced by visible blue-light curing systems. These systems require less than one minute of exposure, and they have many other benefits as well (106).

2.3.2.Composition of composite resin

Dental composites are composed of three primary components; a heavily cross-linked polymeric resin matrix, which is bolstered by a dispersion of glass, silica, crystalline, metal oxide or resin reinforcing filler particles or their variations and/or short fibers, which are bonded to the matrix by silane coupling agents; a short fibers, which are bonded to the matrix by silane coupling agents.

Additionally, dental composites include a number of other components, one of which is an activator-initiator system. This system is necessary for the resin paste to be transformed from a soft, moldable filling material into a hard, long-lasting restoration. Pigments are used to achieve a color match with the tooth structure. The color stability of chemically activated resins can be improved with the addition of ultraviolet (UV) absorbers and other additives. Additionally, chemically activated resins can have their storage lives extended and their working times extended with the addition of polymerization inhibitors (106).

2.3.2.1.Organic resin matrix

The resin matrix is composed of a mixture of aromatic and/or aliphatic dimethacrylate monomers, such as bis-GMA and urethane dimethacrylate (UDMA), in order to produce polymer structures that are highly cross-linked, robust, and long-lasting. This matrix creates a continuous phase that allows for the dispersion of the reinforcing filler (106).

Because of their high viscosity, UDMA and bis-GMA are difficult to merge together and manipulate. To achieve resin pastes that are sufficiently fluid for clinical manipulation and for incorporating sufficient filler to reinforce the cured resin, it is essential to use various ratios of lower-molecular-weight highly fluid monomers such as triethylene glycol dimethacrylate (TEGDMA) and other lower molecular weight dimethacrylates to blend with and dilute the viscous components. This is because it is necessary to use lower-molecular-weight highly fluid monomers (106).

Both bis-GMA and TEGDMA monomers comprise of two reactive double bonds, and when polymerized, these reactive double bonds form cross-links, which are covalent bonds connecting different polymer chains. The properties of the matrix phase

were improved through the process of cross-linking, and as a result, the composite that was produced had enhanced mechanical and physical properties (106).

Unfortunately, these diluent monomers that are smaller experience significantly larger polymerization shrinkage, which partially cancels out the benefit of using large monomers like bis-GMA. In general, the greater the proportion of these "diluting" monomers, the greater the polymerization shrinkage, and the increased the likelihood of eventual leakage in marginal gaps, as well as the potential problems that may result (106).

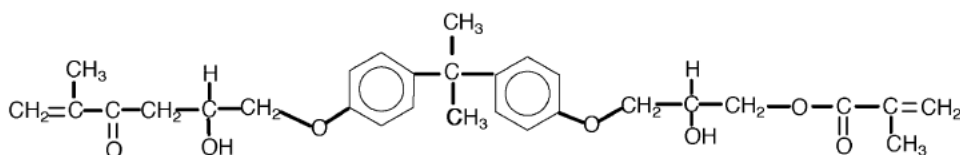


Figure 2.3.Chemical structure of Bis-GMA (106).

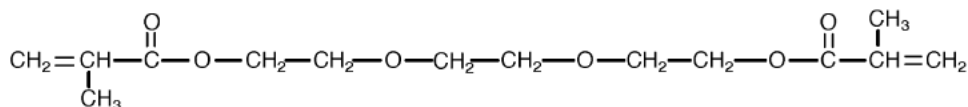


Figure 2.4.Chemical structure of triethylene glycol dimethacrylate (TEGDMA) (106).

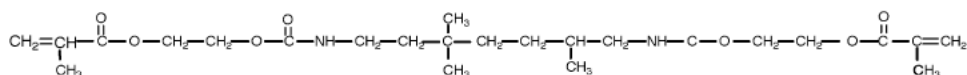


Figure 2.5.Chemical structure of urethane dimethacrylate (UDMA) (106).

2.3.2.2.Coupling agents

It is essential that filler particles be bonded to the resin matrix. This allows the more flexible polymer matrix to transfer stresses to the higher-modulus filler particles. The chemical bond between the two phases of the composite is formed by a coupling agent.

If the coupling agent is applied correctly, it can improve the material's physical and mechanical properties as well as prevent leaching by preventing water from permeating the interface between the filler and the resin. Although titanates and

zirconates are both viable options for the role of coupling agent, organosilanes like -methacryloxypropyl trimethoxysilane are by far the more common choice (106).

2.3.2.3.Activation/initiation system

The addition polymerization mechanism, which is initiated by free radicals, is responsible for the polymerization of composite resin materials. Chemical activation or activation by an external energy source can both result in the production of free radicals (heat, light, or microwave). Chemical activation, light activation, or a combination of both can be used in the processing of dental composites intended for direct placement.

2.3.2.3.A.Chemically activated (self-cure) resins

Chemically activated resins come in the form of two different pastes, one of which consists an initiator made of benzoyl peroxide, and the other of which contains an activator made of aromatic tertiary amine. The formation of free radicals and the beginning of addition polymerization both occur when the two pastes are combined and mixed together. The amine reacts with the benzoyl peroxide to produce the radicals (106).

2.3.2.3.B.Photo activated (light-cure) resins

The photo-activated resins come packaged as a single paste that is housed inside of a syringe that is opaque to light. This paste holds the components necessary to start a chain reaction involving free radicals. These components are a photosensitizer and an amine initiator. These two components will not interact with one another so long as they are shielded from the light. However, when the photosensitizer is subjected to light in the blue region (with a wavelength of approximately 468 nm), an excited state is produced. This excited state then interacts with the amine to form free radicals, which then begin the process of addition polymerization. Camphorquinone, also known as CQ, is a photosensitizer that is frequently utilized and absorbs blue light with wavelengths ranging from 400 to 500 nm. A number of amine initiators, such as dimethylaminoethyl methacrylate, are suitable for interaction with CQ (DMAEMA) (106).

2.3.2.3.C.Dual-cure resins

Dual-cure resins are made up of two light-curable pastes, one of which contains benzoyl peroxide and the other of which contains an aromatic tertiary amine accelerator. Both pastes are cured by exposure to light. They are designed to self-cure in a manner

that results in a very slow setting time after being mixed. The curing process is then sped up on "command" by means of light curing, which is facilitated by the combination of amine and camphorquinone (106).

2.3.2.4. Inhibitors

Inhibitors like phenols, 2,6-di-tert-butyl-methylphenol (BHT), and hydroquinone monomethylether (MEHQ) are added to the resin formulation in order to prevent premature polymerization while the composite is being stored and to avoid uncontrolled photopolymerization by normal room light while the cavity is being prepared and filled in. This is done in order to prevent the composite from disintegrating prematurely. Inhibitors serve two purposes: first, they lengthen the amount of time the resin can be stored, and second, they make sure there is enough working time (106).

2.3.2.5. Optical modifiers (pigments)

Dental composites need to have visual shading and translucency that are comparable to the relating properties of tooth structure in order to give the impression that they are natural. The addition of a variety of pigments, which typically comprise extremely minute volumes of metal oxide particles, results in the creation of shading. Adjustments are made to the translucent and opaque properties as required to simulate enamel and dentin. Dental restorative materials now come in a wide variety of colors and translucencies, which has led to an improvement in the aesthetic result of restorations (111).

2.3.2.6. Inorganic filler

The curing shrinkage and thermal expansion of composites can be reduced by using a variety of transparent mineral fillers. These fillers also help to strengthen and reinforce composites. These include borosilicate, also known as "hard glass," fused quartz, aluminum silicate, lithium aluminum silicate, ytterbium fluoride, and barium, strontium, zirconium, and zinc glasses. "Soft glass" refers to borosilicate, while "hard glass" refers to borosilicate.

2.3.2.6.A. Functions of fillers

- An increased filler loading will, in most cases, result in an increase in the material's compressive strength, tensile strength, modulus of elasticity, and

toughness. These physical and mechanical properties are what determine a material's clinical performance and durability.

- An increase in filler loading results in a reduction in curing shrinkage that is proportional to the filler volume fraction.
- An increase in the filler loading of the composite material results in a decrease in the overall coefficient of thermal expansion of the material. This is because glass and ceramic fillers thermally expand and contract less than polymers do.
- The workability and viscosity of the material can be adjusted by varying the amount and size of the filler.
- An increase in filler loading will result in a reduction in water sorption. The resin becomes softer when it absorbs water, which also makes it more susceptible to abrasive wear and staining.
- The most common method for achieving radiopacity is by incorporating specific glass filler particles that contain heavy metal atoms, such as Ba, Sr, or Zn, as well as other heavy-metal/heavy-atom compounds (106).

Microfillers and macrofillers are the two categories that are used to describe the filler phase when discussing particle size. The macrofillers, which have an average particle size that ranges from 0.2 to 20 micrometers, are produced by milling and mechanical crushing of larger quartz or glass particles. The microfillers are typically pyrogenic silica particles, which are created through a heat treatment procedure using silicon chloride (SiCl_4) to a size of approximately 0.04 micrometers (106).

2.3.3. Classification of resin composites based on filler particle size

Traditionally, composites were classified according to the sizes of the filler particles, either hybrid, conventional or macrofilled composites, and this method of classification is still valid.

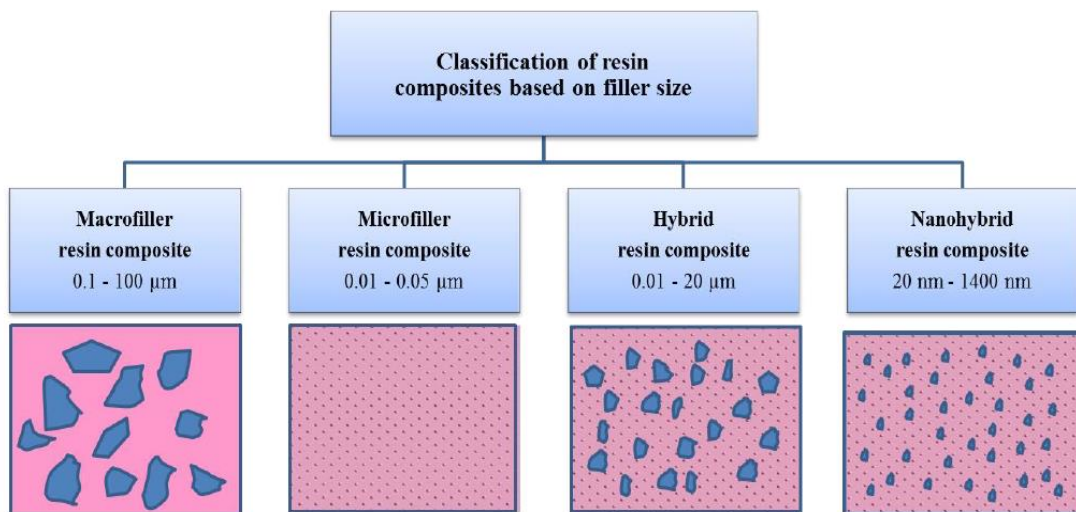


Figure 2.6. Classification of resin composites based on filler size (106).

2.3.3.1. Macrofilled (conventional) composites

In the late 1950s, macrofilled composites were first made available to the public. They were the product of a mechanical process that consisted of grinding larger particles consisting of radiopaque glass, quartz, or ceramics into smaller particles. These particles were the result. Fillers of this essence incorporated glass or quartz filler particles with sizes ranging from 0.1 microns to 100 microns, and they were added to the resin matrix in amounts of up to 70–80 percent by weight. As a consequence, the properties of the filled resin polymers were improved in comparison to those of the unfilled resin polymers (106).

The fact that the color of the quartz particles and the resin were able to be perfectly matched enabled these composites to have excellent optical properties. Because of the high filler loadings, the filler particles interact with one another and therefore significantly contribute to the reinforcing mechanism. This occurs since the particles are coming into contact with each other that a result of the high filler loadings. It is true that macrofilled composites continue to maintain their superior strength over microfilled composites. The most common application for them is in load-bearing repairs and restorations (112).

In addition, there were a lot of drawbacks, such as poor wear resistance because of crack propagation at the matrix/filler interface and loss of the filler particles (113),

which in turn tends to lead a poor polishability (114); early discoloration and staining because of the surface roughness; and so on.

2.3.3.2. Microfilled composites

In the late 1970s, microfilled resin composites were developed as a new type of material. A filler content of 35 percent by weight is achieved by using amorphous silica particles in an organic matrix with a filler size ranging from 0.01 to 0.05 micrometers and averaging approximately 0.02 micrometers. It is possible to increase the filler loading by first pre-polymerizing the resin that already contains the colloidal silica, then grinding the colloidal silica into particles and introducing it as filler. Because of this, an increase in weight of between 50 and 60 percent would be possible (115,116).

The final finish achieved with microfilled resin composites has a significant degree of smoothness, and the surface continues to become even smoother over time, which is an extremely beneficial effect. When a restoration needs to combine a moderate amount of strength with an attractive appearance and a smooth finish, these are the materials that are most often recommended (117).

2.3.3.3. Hybrid composites

The characteristics, and more specifically the positive aspects, of microfilled and macrofilled composites are brought together in hybrid composites. There is a broad array of particle sizes that can be found in hybrid composites. This extensive range of particle sizes has the potential to cause high filler loading, which would then lead to increased strength. Fillers in hybrid composites typically have an average particle size between 15 and 20 micrometers and between 0.01 and 0.05 micrometers (112).

2.3.3.4. Nanofilled composites

The application of nanotechnology has resulted in the creation of a brand-new resin composite. This is distinguished by the presence of nanoparticles with a size of 20 or 75 nm, and nanoaggregates with a size of approximately 0.6-1.4 μm , which are composed of zirconium/silica or nanosilica particles. Both of these elements are present. The aggregates are given a silane treatment in order to increase the likelihood of their adhesion to the resin. A high load, up to 75 percent of the total weight, is produced as a result of the distribution of the filler, aggregates, and nanoparticles (118).

As nanohybrid type material, nanocomposites are currently on the market. It is possible to increase the filler load by decreasing the dimensions of the particles, which results in the particles' having a wide size distribution. As a consequence of this, the polymerization shrinkage is decreased, and the material's mechanical properties, including its tensile strength, compressive strength, and fracture resistance, are increased. These characteristics are significantly more desirable than those of microfilled composites, which themselves are significantly better than those of universal composites (119).

2.3.4.Properties of composite resin

The surface characteristics, polymerization shrinkage, hygroscopic expansion, water sorption and solubility, wear, and fracture toughness of composite resins will be researched under a total of six primary titles.

2.3.4.1.Polymerization shrinkage

Polymerization shrinkage has been considered the "greatest limitation" of using resin composite because the negative sequelae that stem from this shrinkage include poor marginal seal, marginal staining that can lead to possible esthetic concerns, and recurrent caries. These sequelae stem from the fact that shrinkage is caused by polymerization (120). Tensile forces pull the material away from the tooth surfaces as the material shrinks. This can result in marginal degradation, enamel crazing or cracking, restoration debonding, and/or material fracture. During the polymerization process, it has been suggested that resin composites experience a volumetric contraction of between 2.9 and 7.1 percent (121).

Polymerization shrinkage can be affected by a wide variety of factors, some of which are as follows: curing period, temperature, resin thickness, form of filler, curing radius, and volume of organic material.

In an ideal world, reducing the associated polymerization shrinkage can be accomplished by modifying the material constituents in form, percentage (volume), and/or size in order to achieve a higher degree of conversion in the material (122).

2.3.4.2.Hygroscopic expansion

It is possible for the hygroscopic expansion of the resin composite to compensate for the shrinkage caused by the polymerization process, which would then

result in improved marginal sealing. Following this, during the process of polymerization, the movement of water molecules inside the matrix causes saturation of ions, while the movement of unset monomers and ions derived from activators and fillers occurs on the outside of the matrix. The removal of components contributes to a greater reduction in volume and loss of weight, whereas hygroscopic expansion results in an increase in volume and a gain in weight (123).

2.3.4.3. Water sorption and solubility

The absorption of water can have a significant influence on the characteristics of composite resin fillings. Water has the properties of both a plasticizer and a stress corrosion agent, which causes the particle matrix interface to become more fragile. Because of the presence of water in the oral cavity, dental resin composites have the potential to absorb water, which can lead to a decline in their physical and mechanical properties. This is primarily as a consequence of the hydrolytic dissolution of the bond between silane and filler particles, the matrix/filler interface, or the fillers themselves (124).

Debonding may result in hydrolytic breakdown if there is localized swelling at the matrix/filler interface. This swelling may be caused by the occurrence of debonding. Temperature fluctuations and the effects of solvents both play a role in the acceleration of the breakdown that occurs on the surface of resin composites. Temperature and the rate at which water is absorbed by a substance are directly related to one another; specifically, the higher the temperature, the more quickly water is absorbed. A material's tensile strength, modulus of elasticity, flexural strength, and wear resistance are some of the other properties that suffer when it absorbs water (125–127).

2.3.4.4. Wear

Wear is defined as the progressive loss of substance that results from mechanical interaction of two contacting surfaces that are in relative motion. This interaction occurs when two surfaces rub against one another (128). The wear tolerance of a restorative material has a direct bearing on how long that material is expected to last before showing signs of wear and tear. The ability to resist the damaging effects of functional, parafunctional, and abrasive activity on the resin composite is desirable. These three types of activity all act upon the resin composite. Because the size of the filler particles is an intrinsic quality that is strongly attributable to wear resistance, a significant

amount of clinical research has focused on modifying filler particle size. It has been discovered that the less interparticle spacing that occurs as a result of a finer particle size, which helps to protect the softer resin matrix and results in improved wear resistance of the material, the finer the particle size.

Because reinforcing fillers have been refined over the past ten years, wear is less of a concern in today's materials than it was in those of ten years ago. However, extreme caution is required before incorporating resin composites into large preparations or when using them to fabricate substitutes for functional cusps (122).

2.3.4.5.Fracture toughness

It is generally agreed that the most common reason for clinical failure is the bulk fracture of resin composite restorations. The brittleness of materials, such as dental composites, can be determined by examining a material's fracture toughness, which is a mechanical property. Fracture toughness can be affected by a wide variety of factors, such as chemical composition, fillers (loading and size), bond of matrix/filler interface, or degree of resin matrix conversion. A material that has a higher value of fracture toughness is one that is less probable to chip or fracture easily (129). Compared to those of micro-filled resin composites, the fracture toughness attributes of hybrid and nano-filled resin composites are substantially higher (130).

2.3.4.6.Surface properties

Surface properties of composite resins will be examined under three headings; color stability, gloss, and hardness.

2.3.4.6.A.Colour stability

Because a change in the color of a resin composite restoration is considered to be a major aesthetic failure, the color shade discrepancy of resin composites is one of the primary reasons for replacing restorations.

The color shift that occurs in resin composites is caused by a combination of factors that are both inherent and external to the material. Changes in the material's composition caused by chemical reactions are examples of intrinsic factors. The oxidation of the amine accelerator, exposure to various forms of energy, and storage in water over a period of time are the three factors that are thought to be responsible for the change in chemical color. Extrinsic factors entail bond staining or the diffusion of

stains caused by food and drink, such as beverages and stained drinks. Extrinsic factors also include stains that result from food and drink (131,132).

Changes in color can be associated with the aging of certain materials, which can lead to variations in how light is scattered and absorbed by those materials (133). Because of insufficient polymerization of the resin, the resin composites are prone to easily absorbing stains, which can cause the color to shift (134).

Hydrophilic resin composites have a greater propensity to absorb water than hydrophobic resin composites. Hydrophilic stains are easily and quickly soluble in aqueous solutions, and as a result, they are able to easily penetrate various materials (135). Therefore, hydrophobic resin composites have superior color consistency and resistance to color fading (131,132).

2.3.4.6.B.Gloss

The capacity of a material to reflect direct light is one of the characteristics that define gloss. The morphology and size of the fillers, in addition to the resin matrix, both have an impact on the gloss. Gloss may be affected and discoloration may become more severe as a result of the surface roughness that wear and chemical deterioration may cause. According to clinical research, the aesthetic appearance of certain materials is improved when they have a glossy surface (136).

2.3.4.6.C.Hardness

The ability of a material to resist being dented is referred to as its hardness. Because it is related to compressive strength, wear resistance, and the degree of conversion, hardness is one of the most essential properties. The load that is applied and the amount of time that passes while being tested both affect the hardness. Both the sorption of water and the hydrolytic degradation of resin composites can have an effect on the surface hardness of the material. If a resin composite has a low hardness value, this indicates that the chemical and physical bonding between the matrix and filler interface is weak (137).

2.4.Bonding Agents

Bonding and adhesion are two different terms that refer to the same multifaceted set of physical, chemical, and mechanical mechanisms that enable one substance to attach to and bind to another. Providing resistance to the detachment of an adherend

substrate (enamel, dentin, metal, composite, ceramic, etc.) from a restorative or cementing material is the first of three essential functions that a dental bonding system performs. The second function distributes stress along bonded interfaces, and the third function seals the interface via adhesive bonding between dentin and/or enamel and the bonded material, increasing resistance to microleakage and decreasing the risk for postoperative sensitivity.

Dental bonding agents are formulated to provide an interface between restorative composites and tooth structure that is sufficiently strong to withstand the effects of mechanical forces as well as the stress caused by shrinkage (106).

2.4.1.Composition of bonding agents

Regardless of the number of bottles or materials, a typical dentin bonding system contains etchants, resin monomers, solvents, initiators and inhibitors, fillers, and occasionally numerous different functional products such as antimicrobial agents.

2.4.1.1.Etchants

Etchants are fairly powerful acids (pH=1–2) that are used to dissolve the mineral phase and remove smear layers from enamel and dentin in order to facilitate the formation of micromechanical interlocking. Etchants have a pH range of 1–2. Phosphoric acid, typically at a concentration of 37 percent but ranging from 30 to 50 percent, is the etching agent of choice because it produces etching patterns that are consistent while protecting the pulp from being harmed (138).

2.4.1.2.Primers

Priming is required in order to keep an expanded collagen network whilst also simultaneously removing any residual water in order to make room for the infiltration of a hydrophobic adhesive monomer. Primers are solutions that contain hydrophilic monomers that have been dissolved in a solvent such as acetone, ethanol, or water. Because of its strong hydrophilicity and solvent-like nature, HEMA, also known as 2-hydroxyethyl methacrylate, is a monomer that is frequently used as a primer (138).

2.4.1.3.Solvents

Priming systems also make significant use of solvents, which plays vital roles in the process. Water, ethanol, and acetone are the kinds of solvents that are utilized the

most frequently. In addition to improving the wetting of hydrophilic dentin, the specific contribution that each solvent makes to the improvement of bond adhesion should not be overlooked. In addition to re-expanding the collapsed collagen network, water has the ability to ionize acidic monomers. Both ethanol and acetone have better solubility with monomers that are relatively hydrophobic, and their ability to "chase" water makes it easier to remove water from the system (138).

2.4.1.4.Adhesives

When bonding dentin, the primary function of adhesives is to fill the interfibrillar space of the collagen network, thereby producing a hybrid layer and resin tags which provide micromechanical retention upon polymerization. This is done so that the adhesive can successfully perform dentin bonding.

It is necessary for adhesives to have a hydrophobic nature in order to prevent liquid from passing through the intermediate layer. At the same time, adhesives need to have a certain level of hydrophilicity in order for them to diffuse into the hydrophilic dentin that has been primed with water.

In most cases, adhesive resins are made up almost entirely of hydrophobic dimethacrylates like bis-GMA, TEGDMA, and urethane dimethacrylates (UDMA), along with a trace amount of a hydrophilic monomer like HEMA (106).

2.4.1.5.Initiators

Initiation of polymerization can occur through the use of a photoinitiator system, which consists of a photosensitizer (such as camphorquinone) and an initiator (such as tertiary amine), a self-cure system, which includes a chemical initiator (such as benzoyl peroxide), or a dualcure initiator system. All three of these systems are capable of producing the same results (138).

2.4.1.6.Filler particles

Certain adhesives have had nanometer-sized particles of silica added to them in order to strengthen the adhesive and, as a result, generate higher bond strengths. The addition of fillers serves another purpose, which is to effectively modify the viscosity of the adhesive so that it has a consistency that is thicker and more paste-like. When such an adhesive is implemented to an etched dental surface, it results in the formation of a more substantial bonding layer, which, by preventing oxygen inhibition and thereby

enhancing the bond's potential for strength, can promote increased bonding. In addition, because it is more flexible than restorative composites, a thick adhesive layer has the potential to reduce the amount of stress caused by shrinkage (138).

2.4.1.7. Other ingredients

In order to accomplish a wide range of distinct goals, dentin bonding agents are typically combined with a variety of supplemental ingredients. As a desensitizer, glutaraldehyde is included in the mix. Antimicrobial agents such as the monomer 12-methacryloyloxydodecylpyridinium bromide (MDPB) and the compound parabene have been developed. Fluoride is added to the water supply to ward off secondary cavities. In order to stop the breakdown of collagen, benzalkonium chloride and chlorhexidine are sometimes used (106).

2.4.2. Properties of bonding agents

The properties of bonding agents will be investigated under three headings; bond strength, microleakage, and aging effects.

2.4.2.1. Bond strength

The measurement of bond strength, which can be determined by loading bonded test specimens in shear or tension until fracture occurs, is the standard method for determining how effective dentin adhesives are. A value of 20 MPa or higher has been suggested as a reasonable goal, despite the fact that there has not been an agreement reached among all parties regarding the minimum bond strength necessary to provide successful bonding.

It is evident that current dentin bonding agents are capable of producing higher bond strength values, which can move the location of clinical failure from the interface to within dentin adjacent to the restoration or, for some cases, within the restoration itself adjacent to the interface. This is the case regardless of the numerical differences that are generated by different laboratory test methods.

It is clearly evident that the inherent bond strength is no longer the limiting factor in the efficacy of bonded restorations, and this is the case irrespective of the bond test that is chosen. At least for large restorations, the limiting factor now appears to be induced stresses produced throughout curing shrinkage within the resin-based

composite itself. This is the case even though the shrinkage occurs during the curing process (139).

2.4.2.2.Microleakage

Tracers and staining agents can be allowed to penetrate the restoration in order to monitor the amount of microleakage that occurs at the interface between the restoration and the tooth. In the same way that the results of tests to determine bond strength can vary greatly from one laboratory to the next, the leakage data can also be quite different depending on the method that was applied and the duplicitous parameters that were applied when the bonding agents were being placed. There is not always a strong correlation between bond strength and the amount of microleakage that occurs. In spite of this, it seems that the more recent systems are superior in terms of preventing interfacial leakage between the conditioned tooth structure and the adhesive resin (139).

2.4.2.3.Aging effects and degradation of the hybrid layer

The rate of change in bond strength over time is an exceptionally valuable sign of relative clinical lifetime. Accelerated aging tests in vitro provide a means by which this indicator can be evaluated. As a result of the aging effect, the bond strength in three-step systems was found to significantly decrease over time, whereas in two-step systems, very little or no decrease in bond strength was observed at all during the course of the research conducted. It has also been demonstrated through research that peripheral bonding to etched enamel, which prevents the resin bond from coming into contact with water, can substantially increase bond durability.

Research done with transmission electron microscopy has revealed that collagen fibrils in the hybrid layer deteriorate at the same time that bond strength decreases. These findings suggest that degradation of the hybrid layer contributes to the aging of dentin bond integrity (139).

2.4.3.Classification of bonding agents

This classification is further subdivided into the number of steps in the process, and it is based on the mainly two methods to etching, priming, and applying the bonding resin to the surfaces of dentin and enamel. As a result, the two primary classifications of bonding systems are referred to as "etch-and-rinse" and "self-etch" systems, with two distinct categories for each, according to the amount of clinical steps required (140).

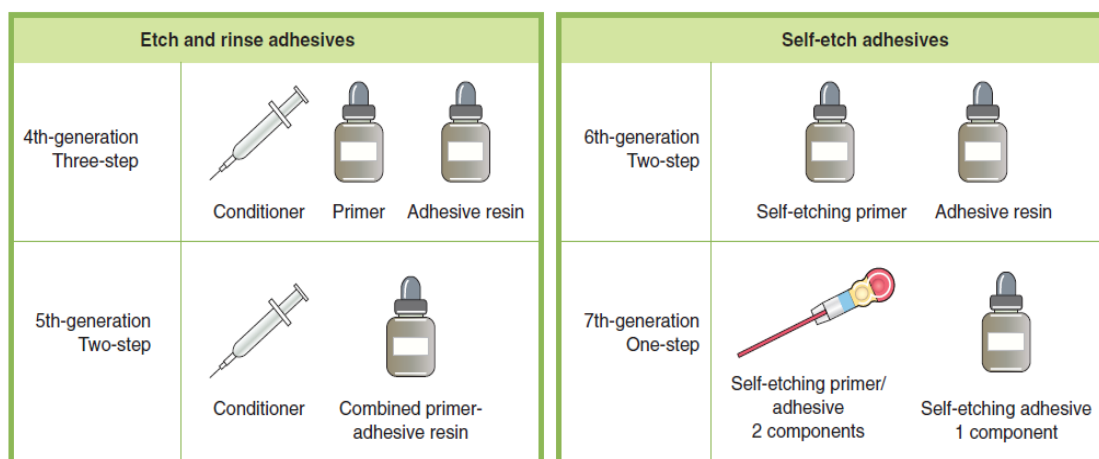


Figure 2.7.Classification of current adhesive systems (141).

2.4.3.1.Etch-and-rinse adhesives

2.4.3.1.A.Three-step (fourth generation)

This method includes three stages: the first stage involves applying an acid etchant, the second stage involves applying the primer, and the third stage involves applying the actual bonding agent or bonding resin. A hydrophilic functional monomer can be found in the primer, and it has been dissolved in an organic solvent such as acetone, ethanol, or water. As was mentioned earlier in the chapter, the usage of a hydrophobic resin constitutes the third step in the process (141).

2.4.3.1.B.Two-step (fifth generation)

Using this approach will only require one application of both the primer and the adhesive resin. This etch-and-rinse approach is the most effective method for achieving efficient and stable bonding to enamel because it removes surface contaminants. Etching, which typically involves the use of a gel containing between 30 and 40 percent phosphoric acid and is then removed by rinsing, encourages the dissolution of enamel rods. This results in the formation of pores, which are then filled with bonding agents via capillary action and then followed by the polymerization of resin (141).

2.4.3.2.Self-etch adhesives

2.4.3.2.A.Two-step (sixth generation)

With this method, there is no need for a different etching step to be taken. In this particular instance, the tooth is conditioned and primed simultaneously with the help of

an acidic monomer that is not rinsed off. Because self-etching adhesives only dissolve the dentin surface in a partial manner, there is still a sizeable quantity of hydroxyapatite present within the hybrid layer. After that, particular carboxyl or phosphate groups found in functional monomers are able to engage in chemical interaction with the residual hydroxyapatite. The bond to dentin is stronger than that of etch-and-rinse adhesives thanks to the mineral content of this layer (141).

2.4.3.2.B. One-step (seventh generation)

With this approach, the functions of conditioner, primer, and bonding resin are all performed in a single step. In comparison to multistep etch-and-rinse adhesives, one-step, self-etching adhesives offer clinicians the benefit of requiring a smaller number of clinical steps that are also simpler to perform. This makes these adhesives an appealing option for use in clinical practice. Due to the fact that there is not an etch step, the tooth structure does not require any additional steps such as rinsing or drying.

When compared with the two-step self-etch and etch-and-rinse products, the products that fall into the category of "one-step self-etch" have less clinical experience, and as a result, less is known about their performance and bond longevity under long-term clinical conditions (141).

2.5.Light Curing Devices

There are four main types of light sources that have been developed for use in the polymerization of light-curable dental materials:

1. Quartz Tungsten Halogen Curing Lights (QTH)
2. Plasma Arc Curing Lights (PAC)
3. Light Emitting Diodes Curing Light (LED)
4. Laser Curing Lights

2.5.1.Quartz tungsten halogen curing lights (QTH)

In QTH lamps, the quartz bulb contains a tungsten filament that emits both ultraviolet and white light. This light needs to be filtered in order to remove heat as well as all wavelengths other than those in the violet-blue range (about 400 to 500 nm) (106).

The lifespan of QTH lamps is limited to 100 hours, with subsequent degradation of the bulb, reflector, and filter caused by high operating temperatures and a

considerable quantity of heat being produced during operating cycles. This is because high operating temperatures cause QTH lamps to produce a lot of heat during their cycles of operation. This indicates that there will be a gradual decrease in the curing efficiency as a result of the components aging over time. Because the intensity of the bulb decreases as it is used, a calibration meter is necessary in order to obtain an accurate reading of the intensity (142).

2.5.2. Plasma arc curing lights (PAC)

In order to generate a plasma, PAC lamps make use of a xenon gas that has been ionized. The high-intensity white light is filtered to eliminate heat and make room for the emission of blue light with a wavelength of approximately 400 to 500 nm. PAC lamps produce more intense visible light and were created with the primary intention of reducing the amount of irradiation time needed, which is an important economic consideration (143).

2.5.3. Light emitting diodes curing light (LED)

Light sources that make use of a solid-state electronic process emit radiation exclusively in the blue region of the visible spectrum, between 440 and 480 nanometers in wavelength. Due to the fact that the spectral emittance of gallium nitride blue LEDs completely covers the absorption spectrum of camphorquinone, LED light curing units do not need to be equipped with filters (144). LEDs have a low wattage requirement, can be powered by a battery, do not produce any heat, and do not require a cooling fan, so they are very quiet. Despite the fact that they naturally emit radiation of the weakest possible intensity. LEDs have a lifespan of more than 10,000 hours and experience very little loss of output over the course of their lifetime. LEDs are not easily damaged by vibration and shock, and their operation requires very little power (145).

LEDs are able to convert electrical power into visible blue light in a more efficient manner than halogen lamps, and they do not produce the large quantities of heat that are associated with those lamps (146).

2.5.4. Laser curing lights (argon laser)

Argon laser lamps produce light of a single wavelength and are capable of producing the greatest intensity. The wavelength of the argon laser, which ranges between 450 and 500 nanometers, has proven to be an effective method for

polymerizing composite resins. This is due to the fact that, in comparison to the more traditional method of curing with visible light, it improves the material's inherent physical properties. Due to the low amount of infrared energy that they emit, lasers produce very little heat (147).

The fact that arc and laser lamps have such a small light guide (or spot size) is one of their most significant drawbacks. If the restoration is going to be larger than the curing tip, the clinician is going to have to overlap some of the curing cycles (148).

2.6. Bonding of Composite to PAEK Polymers

PEEK and PEKK are examples of high-performance polymers that are members of the PAEK family of polymers. These materials are not appropriate for monolithic esthetic dental restorations due to the low translucency and grayish or pearl-white opaque color of PAEK polymers. In order to achieve satisfactory aesthetics, it is necessary to use a resin composite surface veneer.

In addition, the chemical inertness of PAEK polymers, combined with their low surface energy and resistance to surface modification, has made it difficult to bond different materials to PAEK polymers. Increasing the surface free energy of PAEK polymers and, as a result, their bonding performance has become a major focus of recent research. This has led to the modification of the surface properties of PAEK polymers.

The composite resin veneer's mechanical retention is dependent on its viscosity and, as a result of that, the loading of the filler content. The higher the percentage of particles that make up the substance, the higher the viscosity will be. The spreading of the adhesive material across the surface of the adherent, also known as the substrate, is the primary requirement for long-lasting bonding. Only in the event that the surface free energy of the adherent is greater than that of the adhesive will there be adequate spreading. Surface energies of adhesives are typically higher than those of untreated PEEK, which has poor bonding properties. This is because adhesives are typically manufactured using chemical processes. Because it is difficult to alter the surface energy of the adhesive, multiple attempts are made to enhance the surface energy of PEEK by employing a variety of surface modification techniques (25).

2.7.Bond Strength Tests

Bond strength tests are used extensively in the screening process during the innovation of resin adhesives. These tests are also utilized in the evaluation of adhesives that are currently on the market for dental practitioners (149). Bond strength tests divided into two as macro tests and micro tests.

2.7.1.Macro tests

The analysis of the bond strength macro tests demand samples with 3 to 4 mm² of adhesive.

2.7.1.1.Tensile test (butt joint)

A macro-tensile bond-strength approach, which is less common, can be used to measure the bond strength of cements to hard materials like ceramics and metal alloys. However, this method is not as widely used as the micro-tensile approach. However, it has never been implemented as a universal bond-strength testing method. This is most likely due to the more tedious specimen preparation that is involved, in addition to the more time-consuming methodology. However, it seemed like this method would be very useful for testing whether or not posts were retained in root canals (150).

When a butt joint is subjected to tension, the stresses that are caused in the adhesive layer can sometimes be quite complicated. When both the adhesive and the adherend have the same moduli, the tensile stress that is being applied to the adhesive layer will be distributed evenly throughout the layer. However, if the moduli are not the same, the tensile stress will be nonuniform, and there will be a shear stress superimposed on top of it. In the butt joint, the stress is not distributed evenly. It differs gradually near the center of the adhesive layer, but it increases rapidly as you get closer to the boundary between the adhesive layer and the air (151).

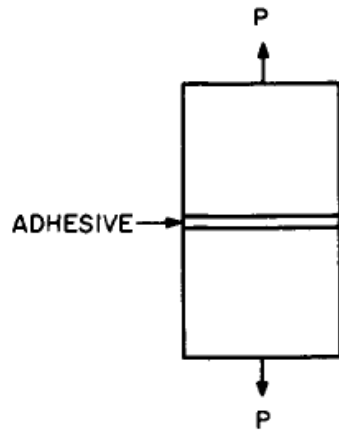


Figure 2.8.Tensile test on a butt joint (151).

2.7.1.2.Shear test (lap joint)

The shear bond-strength technique is without a doubt the one that is utilized the majority of the time. Because there is no need for any additional specimen processing after the bonding procedure, it is the method that is the easiest and quickest to perform (152).

The stresses that are induced in a single lap joint when it is loaded in tension are quite complicated and nonuniform. Shear stresses are caused by differing straining of the adherends in the overlap region, whereas tearing (peel) stresses are caused by eccentric bending of the adherends. Both types of stresses are produced by the overlap region. The magnitude of these two stresses is greatest at or very close to the overlap ends. Therefore, the majority of the load that has been applied is supported by the terminal locations of the overlap region (151).

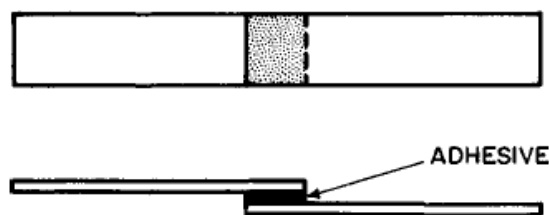


Figure 2.9.Single shear test specimen (151).

2.7.1.3.Peel test

The peel test is a common method for adhesion measurements because the concept behind it and the geometry involved are both relatively straightforward. The geometry consists of a film that has been adhered to a substantial substrate, and the next

step of the test involves determining the amount of force that is necessary to peel the film away from the substrate. Following that, the characteristics of the interface are correlated with this peel force. The peel force can be thought of as an indirect measurement of the interfacial toughness under certain limiting conditions. The geometry, the fundamental characteristics of the film and substrate, and the cohesive characteristics of the interface all have an effect on the peel force (153).

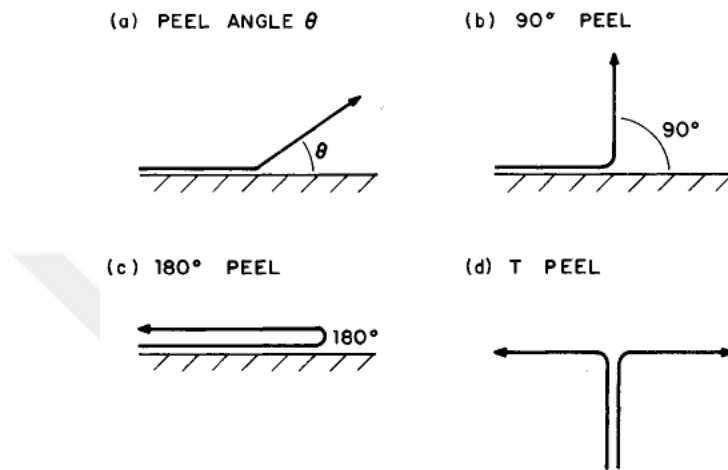


Figure 2.10. Peel test configurations (151).

2.7.2. Micro tests

The analysis of the bond strength micro tests demand samples with up to 1 mm² of adhesive.

2.7.2.1. Microtensile test

Following the bonding procedure, some additional specimen processing or the proper planning of the micro-specimens is required. Because of this, the test becomes more tedious and technique-sensitive.

A better economic use of teeth (with multiple micro specimens originating from one tooth) is one of the advantages of micro bond strength tests in comparison to macro bond strength tests. Other benefits include a better control of regional differences (such as peripheral versus central dentin) and a higher stress distribution at the true interface (avoiding cohesive failure in tooth substrate or composite) (154).

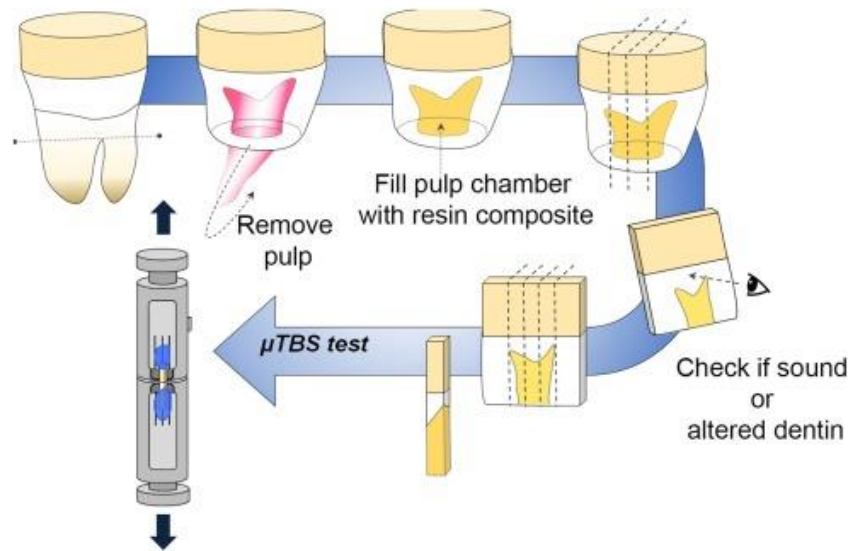


Figure 2.11. Illustration of micro tensile bond strength test (155).

2.7.2.2. Microshear test

This test integrates the convenience of easy manipulation with the capacity to examine multiple specimens for each tooth. However, the combination of a very fine composite build-up (cylinder) with a typical diameter of 0.7 mm and a relatively thick adhesive layer may result in considerable bending as well as variable and non-uniform loading conditions. In addition, it is impossible to contain the adhesive to the area that is being tested, which is a requirement of ISO-standard No. 11405 (150).

3.MATERIALS and METHODS

3.1.Materials

Specifications, chemical composition, batch number and manufacturers of the materials used in this study are listed below (Table 3.1.).

Table 3.1.Product name, manufacturer, composition, manufacturer's instructions and batch number.

Product Name	Manufacturer	Composition	Lot. No
KETRON 1000 PEEK	Mitsubishi Chemical Advanced Materials, Belgium	Polyether-ether-ketone	
PEKKTON IVORY	Cendres Metaux SA, Switzerland	Polyether-ketone-ketone	0000380260
Visio.link	Bredent Senden, Germany	MMA, PETIA, Photoinitiators	204809
Gradia	GC Corporation, Japan	UDMA, EDMA, microfine pre-polymer resin fillers	210608A
Silica	3M ESPE, Germany	30 μm Cojet sand	7864945
Sulfuric acid	Tekkim Chemical Industry, Turkey	98% H_2SO_4	151221171001
Aluminum Oxide	Renfert GmbH, Germany	50 μm Al_2O_3	15941112
Aluminum Oxide	Renfert GmbH, Germany	110 μm Al_2O_3	15831012

3.2.Methods

115 specimens were manually sectioned out of a PEEK rod (KETRON 1000 PEEK, Mitsubishi Chemical Advanced Materials, Belgium) using a diamond cutting disc (BUEHLER, ISOMET 1000, Germany), with dimensions of 8 mm diameter and 2 mm thickness (Fig.3.1.).



Figure 3.1. Illustration of device for PEEK specimen dissection. (BUEHLER, ISOMET 1000, Germany)

115 specimens were milled from a CAD-CAM PEKKTON block (PEKKTON IVORY) using a cutting bur (IMES-ICORE, Germany), with dimensions of 8 mm diameter and 2 mm thickness (Fig.3.2.).

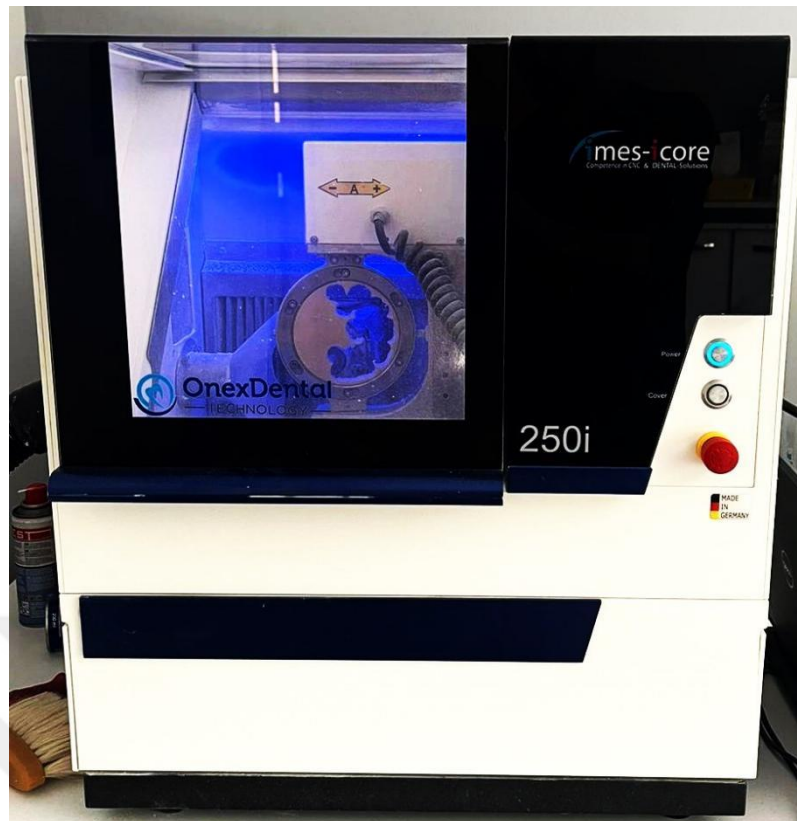


Figure 3.2. Illustration of PEKK specimen dissection. (IMES-ICORE, Germany)

The bonding surface of each disc was polished using the polishing device (Phoenix Beta Twin Whell, Buehler, Germany), which involved a series of rotating silicon carbide abrasive paper working in conjunction with water cooling. (600 grit, 800 grit, 1200 grit) (Fig.3.3.).



Figure 3.3. Illustration of polishing device. (Phoenix Beta Twin Whell, Buehler, Germany)

Before beginning surface treatment and veneering procedure, the value of surface roughness (R_a) of the samples was determined by a surface profilometer (Perthometer M1, MAHR, Germany) (Fig.3.4.).



Figure 3.4. Illustration of profilometer. (Perthometer M1, MAHR, Germany)

3.2.1. Grouping of the samples

Before veneering the composite onto the disks, the 115 PEEK specimens were randomly divided into five completely distinct groups according to the various surface treatments that will be utilized. Every group contained 23 discs ($n=23/\text{group}$).

Before veneering the composite onto the disks, the 115 PEKKTON specimens were randomly divided into five completely distinct groups according to the various surface treatments that will be utilized. Each group contained 23 discs ($n=23/\text{group}$).

3.2.2. Application of surface treatments

115 PEEK and 115 PEKKTON specimens were at random divided into 5 groups separately in line with the surface treatment protocol as follows:

- Group 1: The disks didn't receive any surface treatment (control).
- Group 2: Disk surfaces were subjected to air-abrasion with (Basic Master, Renfert, Germany) 50 μm alumina particles (Renfert GmbH, Germany) perpendicular to the surface of the disc from 10 mm distance for 10 seconds with a pressure of 2 bar.

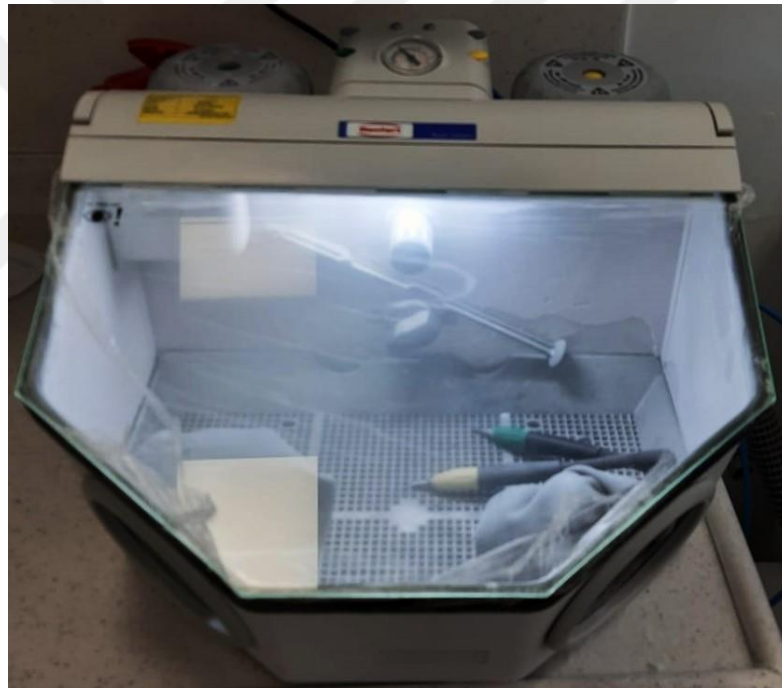


Figure 3.5. Illustration of device for air abrasion process. (Basic Master, Renfert, Germany)

- Group 3: Disk surfaces were subjected to air-abrasion with (Basic Master, Renfert, Germany) 110 μm alumina particles (Renfert GmbH, Germany) perpendicular to the surface of the disc from 10 mm distance for 10 seconds with a pressure of 2 bar.

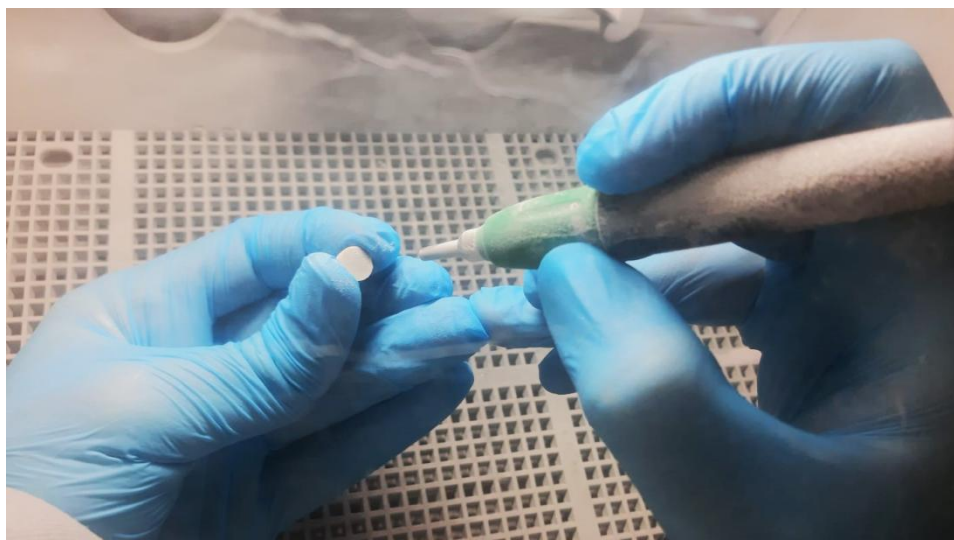


Figure 3.6. Illustration of air abrasion and silica coating of specimens.

- Group 4: Disk surfaces were silica-coated with 3M Cojet (Fig.3.7.) by air abrasion with (Basic Master, Renfert, Germany) 30 μm silica-coated alumina particles perpendicular to the surface of the disc from 10 mm distance for 10 seconds with a pressure of 2 bar.



Figure 3.7. Illustration of silica coating agent. (3M Cojet)

- Group 5: Disk surfaces were etched with 98% sulfuric acid (H_2SO_4) (Tekkim Chemical Industry, Turkey) for one minute (Fig.3.8.). After etching, the surface were rinsed with distilled water and air-dried at room temperature.

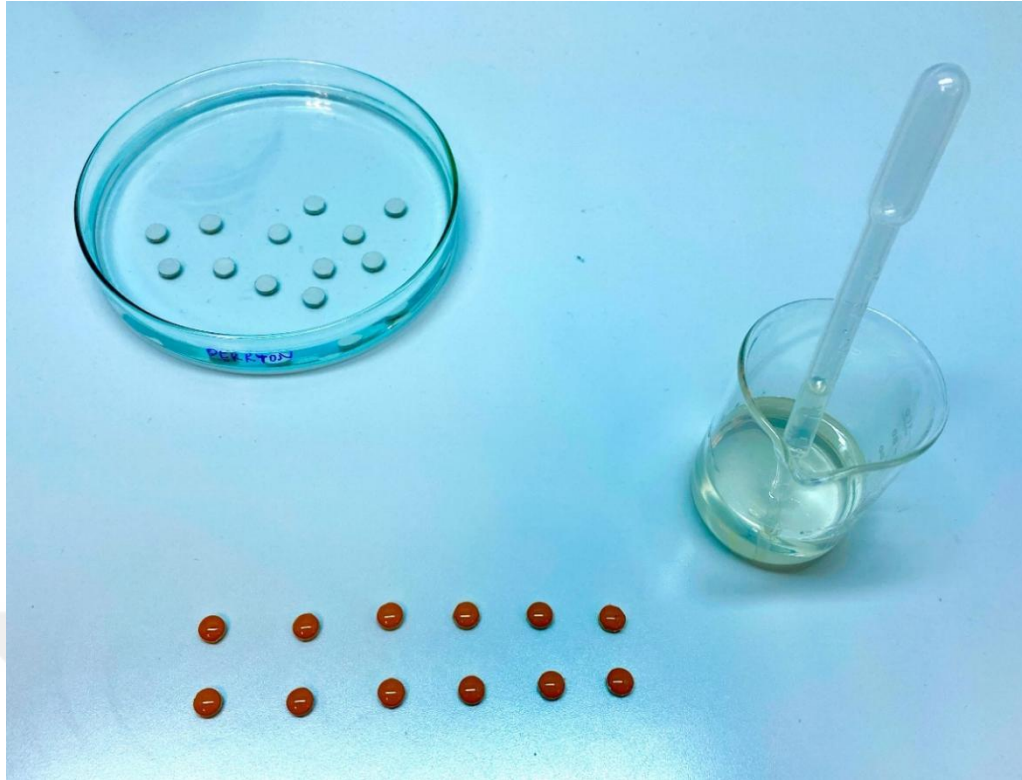


Figure 3.8. Illustration of etching specimens with 98% H_2SO_4 .

Before applying of the adhesive agent, all specimens were cleaned with ultrasonic bath with distilled water (Tchibo GmbH, Germany) (Fig.3.9.) for 5 min and dried on a clean bench at room temperature.



Figure 3.9. Ultrasonic bath for cleaning the samples. (Tchibo GmbH, Germany)

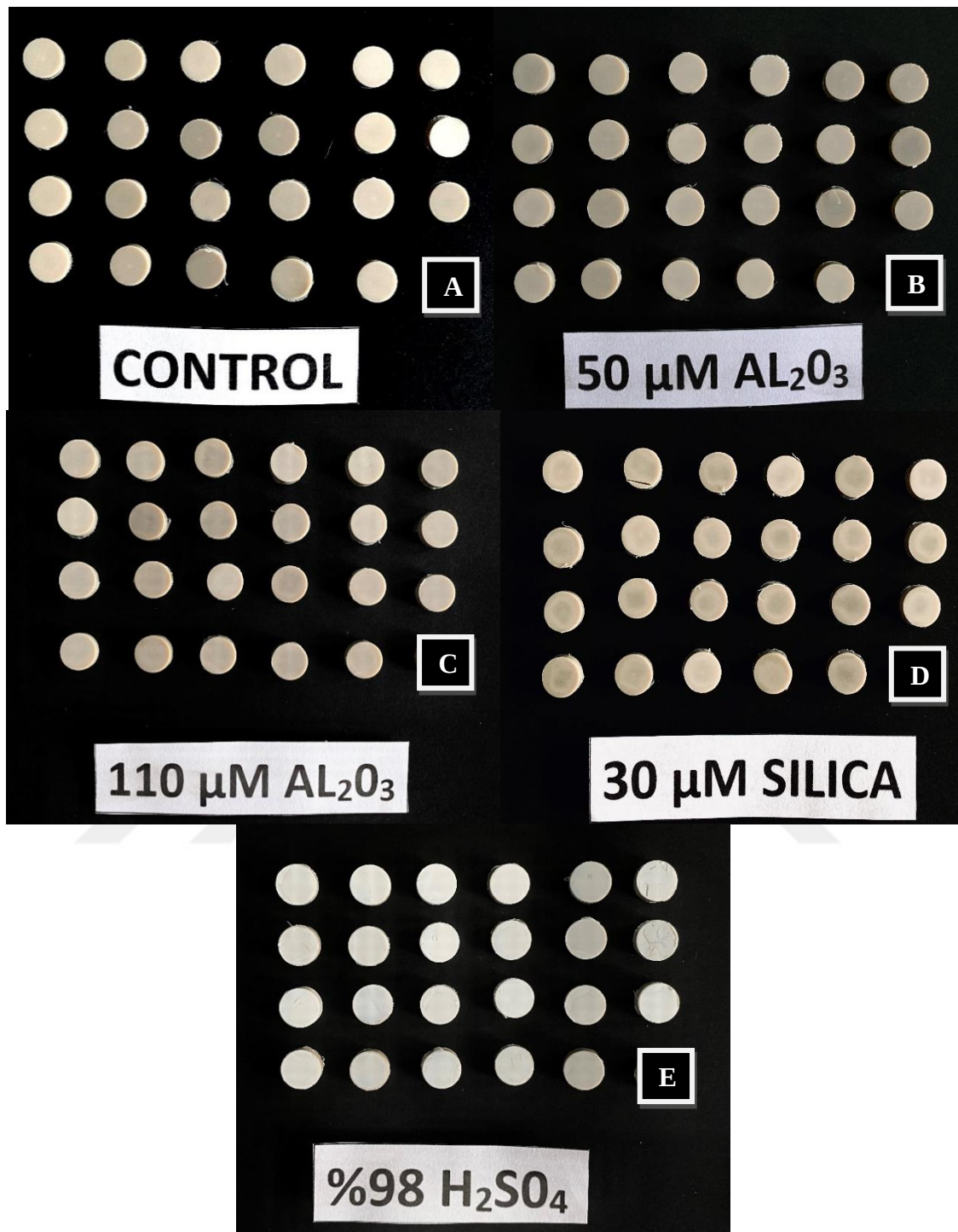


Figure 3.10. The PEEK samples were divided into groups according to their surface treatments. **A.** No treatment (control) group, **B.** Air abrasion with 50 μm Al_2O_3 group, **C.** Air abrasion with 110 μm Al_2O_3 , **D.** Silica coating with 3M Cojet system group, **E.** Etching with 98% sulfuric acid (H_2SO_4) group.

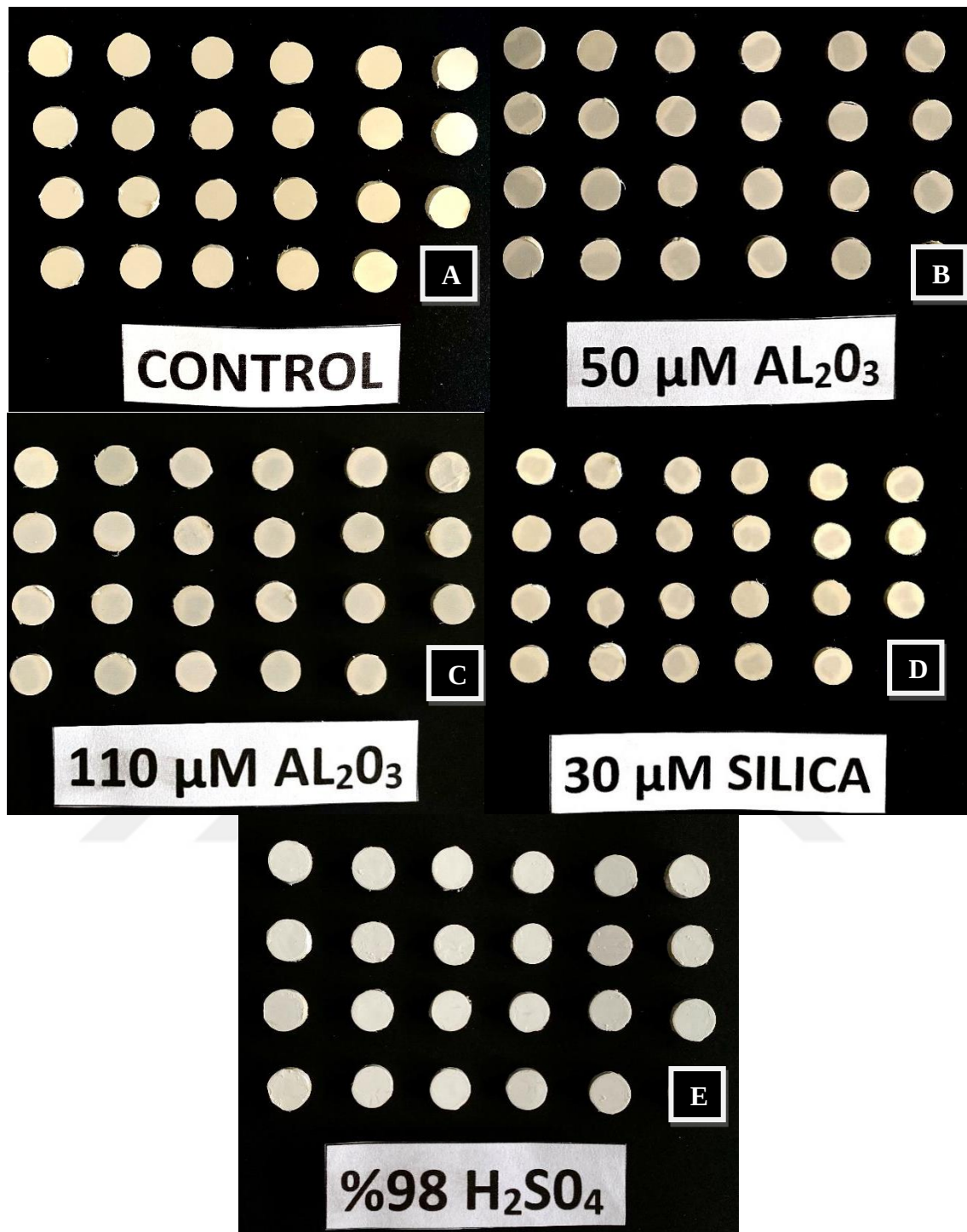


Figure 3.11. The PEKK samples were divided into groups according to their surface treatments. **A.** No treatment (control) group, **B.** Air abrasion with 50 μm Al_2O_3 group, **C.** Air abrasion with 110 μm Al_2O_3 , **D.** Silica coating with 3M Cojet system group, **E.** Etching with 98% sulfuric acid (H_2SO_4) group.

The surface roughness values (Ra) of the disks was determined by a surface profile-meter (Perthometer M1, MAHR, Germany) after surface treatments.

The surface topography of each treated group (n=1) was examined with a scanning electron microscopy (SEM) (JSM-6510LV, JEOL Ltd, Japan) once sputter-coating with gold (Fig.3.12.).

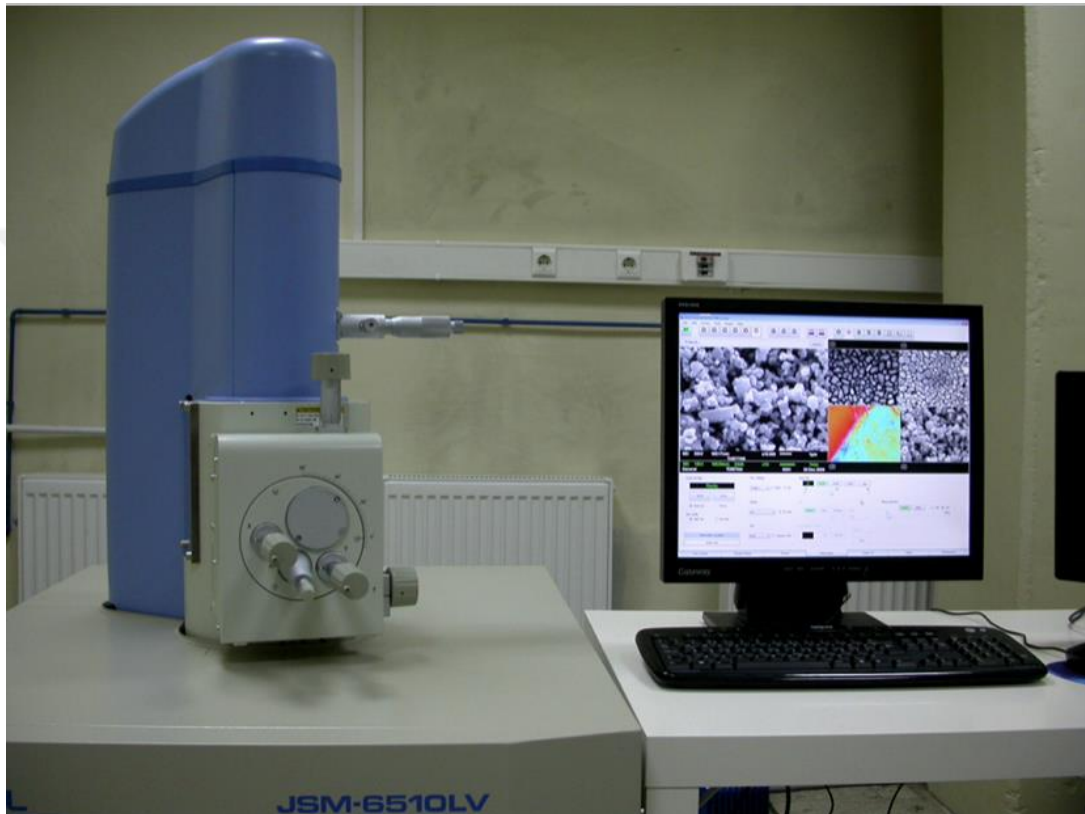


Figure 3.12. Illustration of scanning electron microscopy (SEM). (JSM-6510LV, JEOL Ltd, Japan)

3.2.3. Application of adhesive

After surface roughness measurements, an adhesive consisting of MMA, PETIA and photoinitiators (Visio.link, Bredent, Senden, Germany, LOT 204809.) (Fig.3.14.) was applied on the bonding surfaces of samples using a brush and light polymerized by curing machine (OPTILUX 501) for 90 seconds.



Figure 3.13.Illustration of adhesive procedure.



Figure 3.14.Illustration of bonding agent (Bredent Visio.link).



Figure 3.15. Illustration of light curing machine (OPTILUX 501).

3.2.4. Application of composite resin

For reproduction and similarity, a cylindrically formed acrylic mold with an inner diameter 4 mm and height 4 mm was used to define the veneering area (Fig.3.16.).

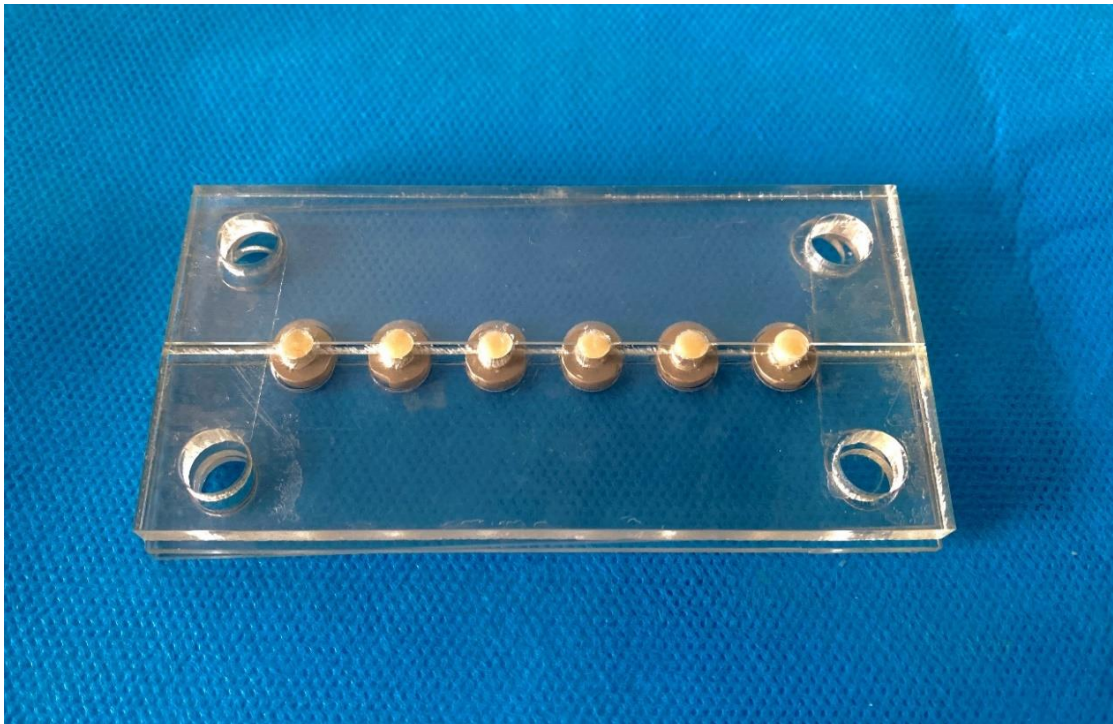


Figure 3.16. Acrylic mold for application of composite resin.

The specimens were inserted in casted acrylic mold. Two layers of 2 mm thick veneering composite Gradia (GC corporate, GC Dental Product Group, Japan, LOT 210608A) (Fig.3.17.) was applied to the surface of the discs. Each layer was cured for 20 seconds by curing lamp (OPTILUX 501) with the light perpendicular to the surface. All materials were applied consistent with the manufacturer's instructions.



Figure 3.17. Illustration of composite resin (GC Gradia).

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

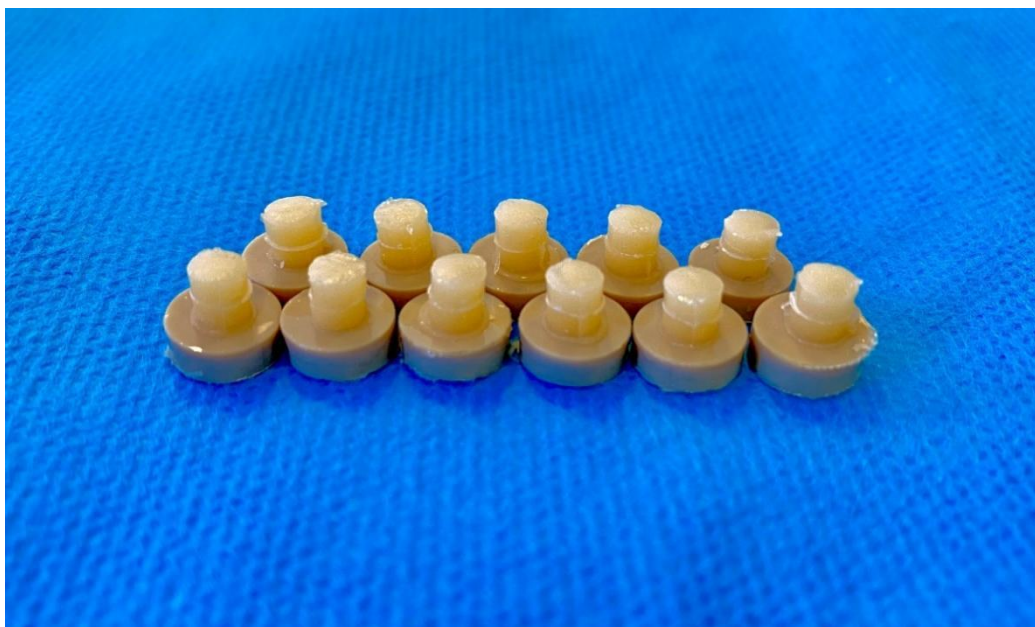


Figure 3.18. Illustration of composite veneered samples.

Half of each group (n=11) was then subjected to the shear bond strength (SBS) test. The other half of the group was thermocycled for 5000 cycles (water temperature between 5°C and 55°C; dwell time: 20 s per bath).



Figure 3.19.Thermocycling device. (Salubris Technica, Dentester, Turkey)



Figure 3.20.Samples prepared for thermocycle.

3.2.5. Measurement of shear bond strength

PEEK and PEKK specimens prepared in this study were embedded in metal rings with acrylic resin (Fig.3.21.).



Figure 3.21. Illustration of the samples in metal rings.

Shear bond strength was measured with the universal testing machine (INSTRON, 3345, USA). Samples embedded in metal rings were placed in the instron device with the bonding surface parallel to the incoming force and shear force was applied at a cross-head speed of 1 mm/min until failure was observed (Fig.3.22.). The shear bond strength was then calculated and expressed in Mega-Pascals (MPa) using the following formula: Shear bond strength (MPa) = Load (N)/area (mm²).

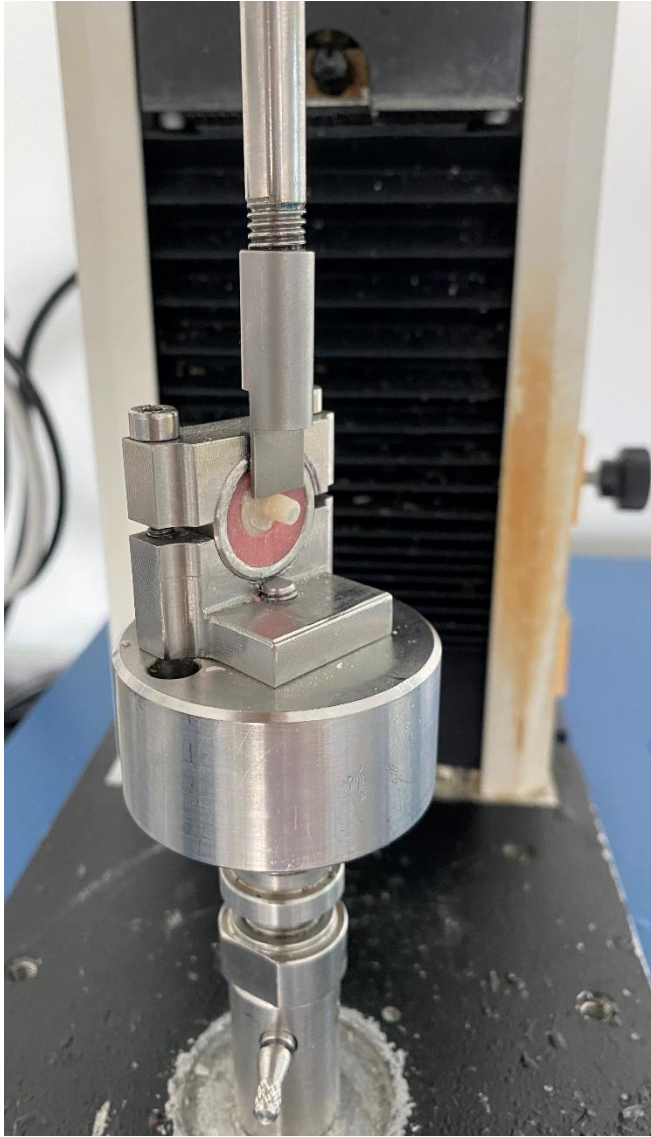


Figure 3.22. Illustration of measuring of shear bond strength.

3.3. Failure analysis

To calculate the debonded fractured interfaces of the discs, failure types (adhesive, cohesive or mixed) were examined under stereomicroscope (Leica, MZ10F, Germany) at a $\times 40$ magnification (Fig.3.23.). Three failure types were determined and defined:

- 1. Adhesive failure:** No composite remnants left on the sample surface.
- 2. Cohesive failure:** Fracture in the sample's surface or composite resin's surface
- 3. Mixed failure:** Resin remnants partially left on sample's surface and also part of the sample's surface was exposed.



Figure 3.23.Illustration of stereomicroscope. (Leica, MZ10F, Germany)

3.4. Statistical Evaluations

When effect size d (effect size):0.399 and SD (standard deviation):2 are taken for shear bond strength parameter as a result of power analysis using G*Power program the number of samples determined for power:0.80 and α :0.05 was determined as minimum $n=11$ for each group and 110 for ten groups.

Data were analyzed with IBM SPSS 22. Two-way analysis of variance was used to compare roughness according to material and surface treatment. Three-way analysis of variance was used to compare bond strength according to material, surface treatment and thermocycle application. Tukey HSD test was used for multiple comparisons. Analysis results were presented as mean and deviation. Chi-square test, Fisher's Exact Test, Continuity (yates) correction and Fisher Freeman Halton Exact Test were used to evaluate failure types. Significance level was taken as $p<0.05$.

4.RESULTS

4.1.Results of Surface Roughness Measurements

Table 4.1.Evaluation of the effect of material and surface treatment on surface roughness. (df:degree of freedom, F:analysis of variance)

Surface Roughness	Type III Sum of Squares	df	Mean Square	F	p
Material	0.368	1	0.368	705.874	0.000*
Surface Treatments	40.702	4	10.176	19521.73	0.000*
Material *Surface Treatments	1.189	4	0.297	570.387	0.000*

Two-Way ANOVA Test

*p<0.05

There is a statistically significant difference between the materials in terms of surface roughness averages (p:0.000; p<0.05).

There is a statistically significant difference between surface treatments in terms of surface roughness averages (p:0.000; p<0.05).

The combined effect of material and surface treatments on surface roughness was statistically significant (p:0.000; p<0.05). The material and the surface treatment together affect the surface roughness. Detailed interpretations of the mentioned results can be seen in Table 4.1.

Table 4.2.Evaluation of surface roughness (Ra) (µm) according to material and surface treatments.

	PEEK	PEKKTON
	Mean±SD	Mean±SD
Control	0.118±0.006 ^{Aa}	0.099±0.007 ^{Ab}
50 µm Air Abrasion	0.470±0.030 ^{Ba}	0.801±0.027 ^{Bb}
110 µm Air Abrasion	1.325±0.034 ^{Ca}	1.252±0.027 ^{Cb}
3M Cojet	0.526±0.012 ^{Da}	0.566±0.010 ^{Db}
98% Sulfuric Acid Etching	0.175±0.023 ^{Ea}	0.287±0.029 ^{Eb}

Two-Way ANOVA Test

*Different capital letters in the columns indicate the difference between the surface treatments, and different lower case letters in the rows show the differences between the materials.

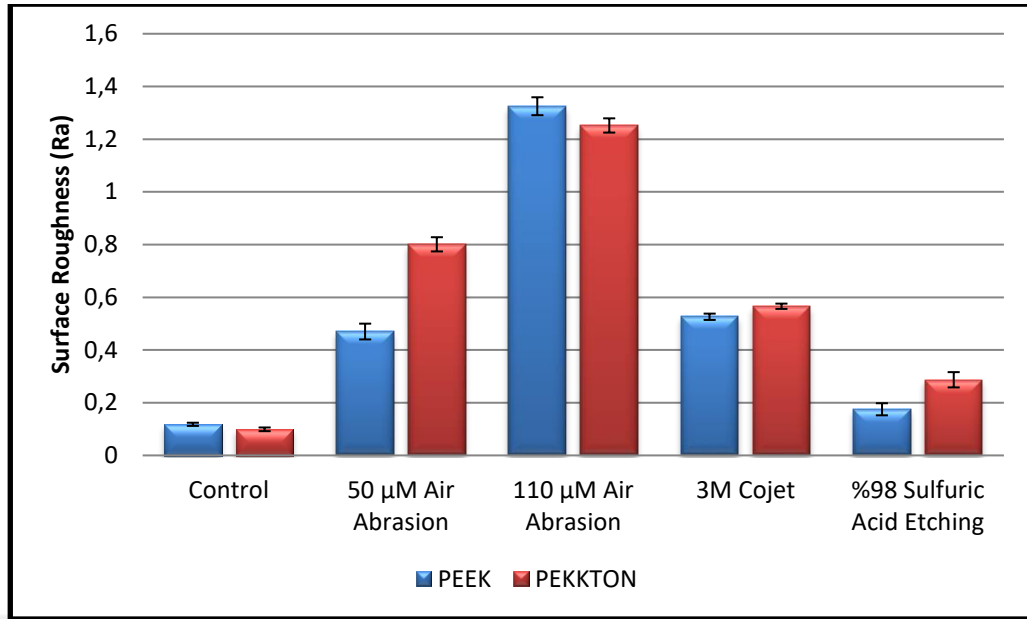


Figure 4.1. Evaluation of surface roughness (Ra) (µm) according to material and surface treatments.

In the PEEK groups; there is a statistically significant difference between surface treatments in terms of roughness averages ($p:0.000$; $p<0.05$). As a result of the post hoc Tukey HSD test performed to determine the significance; surface roughness of 110 µm air abrasion group was significantly higher than all other groups ($p:0.000$; $p<0.05$). The surface roughness of the 3M Cojet group is significantly higher than the control, 50 µm air abrasion and 98% sulfuric acid etching groups ($p:0.000$; $p<0.05$). The surface roughness of 50 µm air abrasion group is significantly higher than control, and 98% sulfuric acid etching groups ($p:0.000$; $p<0.05$). Surface roughness of 98% sulfuric acid etching group was significantly higher than control group ($p:0.000$; $p<0.05$).

In the PEKKTON groups; there is a statistically significant difference between surface treatments in terms of roughness averages ($p:0.000$; $p<0.05$). As a result of the post hoc Tukey HSD test performed to determine the significance; surface roughness of 110 µm air abrasion group was significantly higher than all other groups ($p:0.000$; $p<0.05$). The surface roughness of 50 µm air abrasion group is significantly higher than control, 3M Cojet and 98% sulfuric acid etching groups ($p:0.000$; $p<0.05$). The surface roughness of the 3M Cojet group is significantly higher than the control and 98% sulfuric acid etching groups ($p:0.000$; $p<0.05$). Surface roughness of 98% sulfuric acid etching group was significantly higher than control group ($p:0.000$; $p<0.05$).

In the control group; the surface roughness of the PEEK group was significantly higher than the PEKKTON group ($p:0.000$; $p<0.05$).

In the 50 μm air abrasion group; the surface roughness of the PEKKTON group was significantly higher than the PEEK group ($p:0.000$; $p<0.05$).

In the 100 μm air abrasion group; the surface roughness of the PEEK group was significantly higher than the PEKKTON group ($p:0.000$; $p<0.05$).

In the 3M Cojet group; the surface roughness of the PEKKTON group was significantly higher than the PEEK group ($p:0.000$; $p<0.05$).

In the 98% sulfuric acid etching group; The surface roughness of the PEKKTON group was significantly higher than the PEEK group ($p:0.000$; $p<0.05$). Detailed interpretations of the mentioned results can be seen in Table 4.2. and Figure 4.1.

4.2.Evaluation of Scanning Electron Microscope (SEM) Images

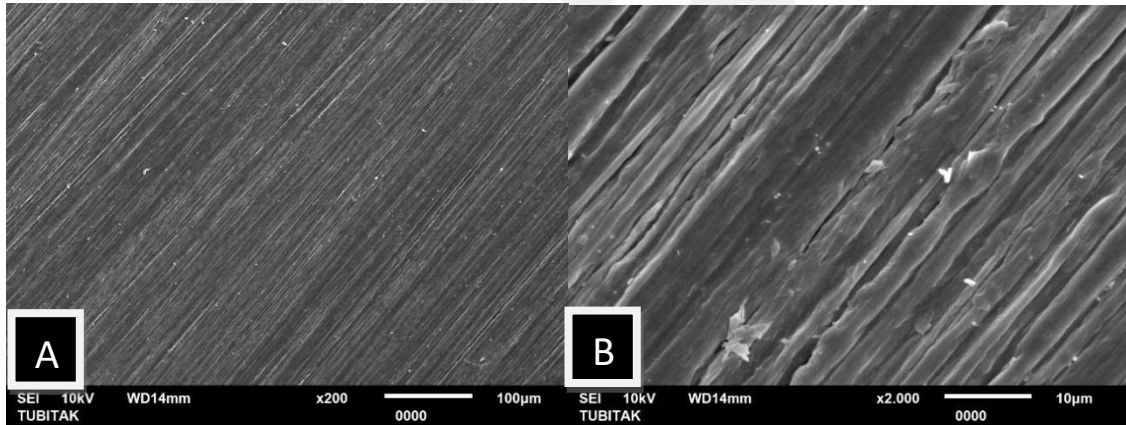


Figure 4.2.Scanning electron microscope images of PEEK control group (A: 200x magnification, B: 2000x magnification).

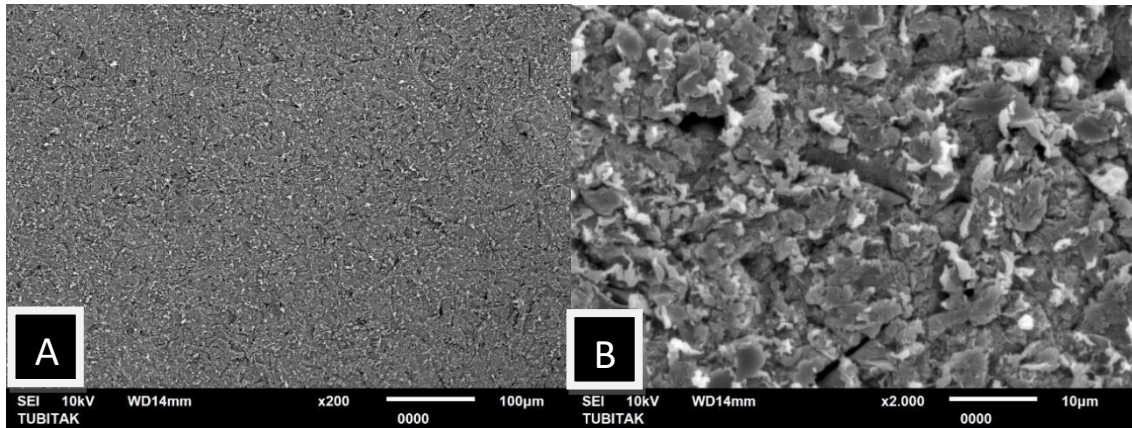


Figure 4.3.Scanning electron microscope images of PEEK 50 μm air abrasion group (A: 200x magnification, B: 2000x magnification).

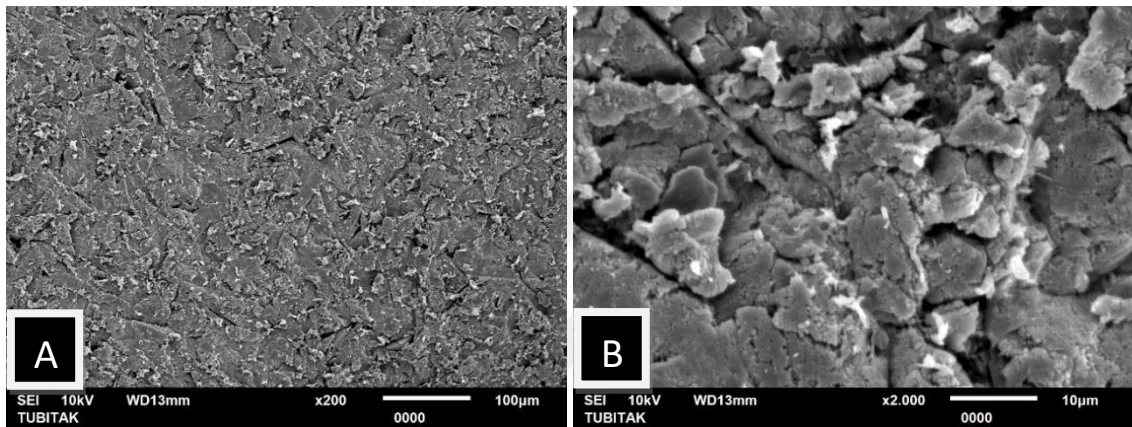


Figure 4.4.Scanning electron microscope images of PEEK 110 μm air abrasion group (A: 200x magnification, B: 2000x magnification).

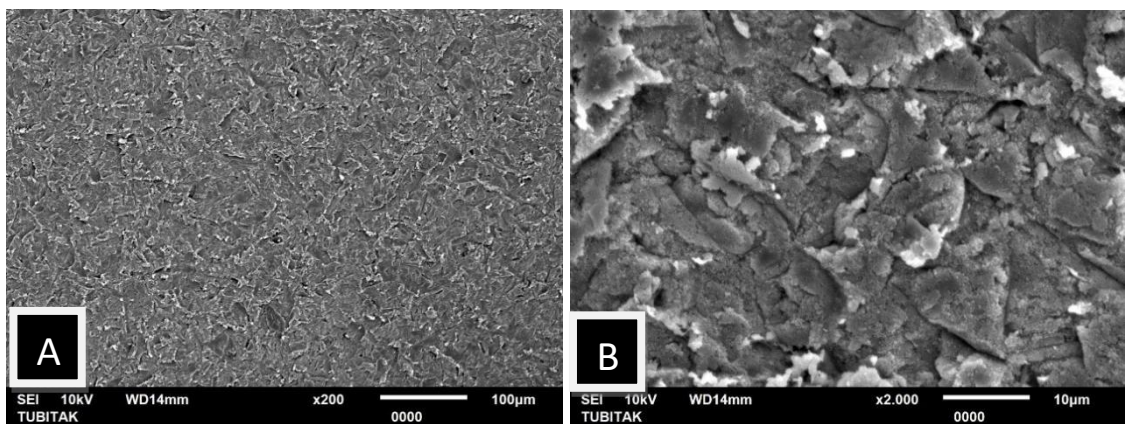


Figure 4.5.Scanning electron microscope images of PEEK 3M Cojet group (A: 200x magnification, B: 2000x magnification).

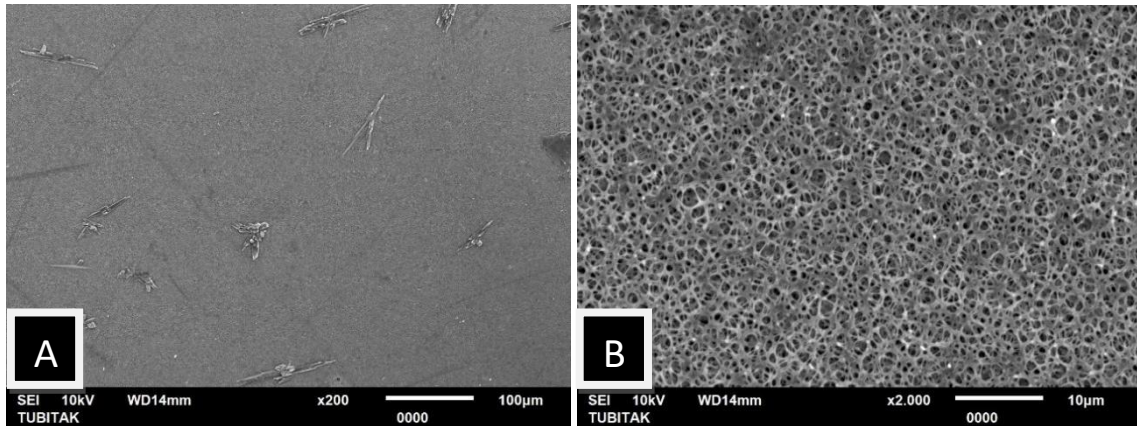


Figure 4.6.Scanning electron microscope images of PEEK 98% sulfuric acid etching group (A: 200x magnification, B: 2000x magnification).

SEM examinations revealed that the PEEK samples have uniform light scratches in the control group (Fig.4.2.), rougher irregular areas in the 50 µm air abrasion group (Fig.4.3.). These irregular rough areas increase in the 110 µm air abrasion group (Fig.4.4.). Irregular rough areas similar to the air abrasion groups are present in the 3M-Cojet group (Fig.4.5.), and in the 98% sulfuric acid etching group (Fig.4.6). There is a homogeneous smooth appearance at 200x magnification, and a homogeneous perforated appearance at 2000x magnification.

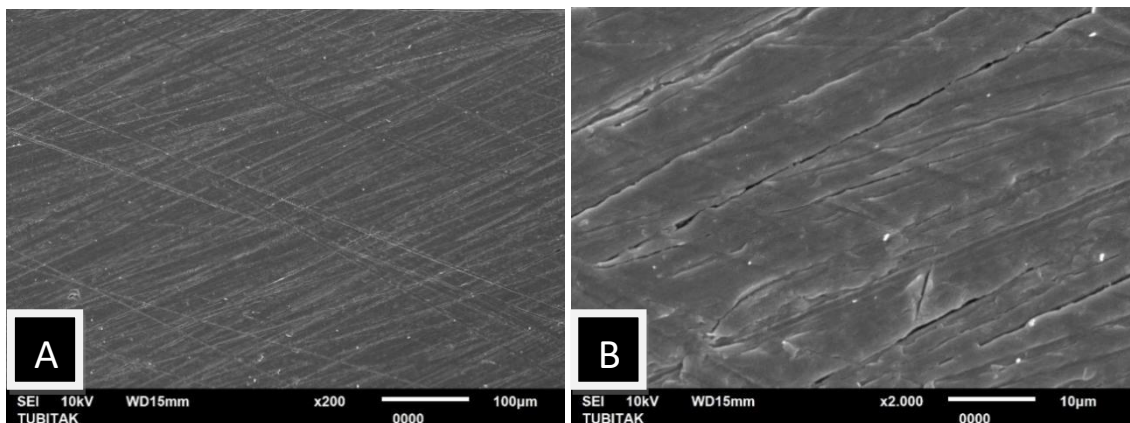


Figure 4.7.Scanning electron microscope images of PEKKTON control group (A: 200x magnification, B: 2000x magnification).

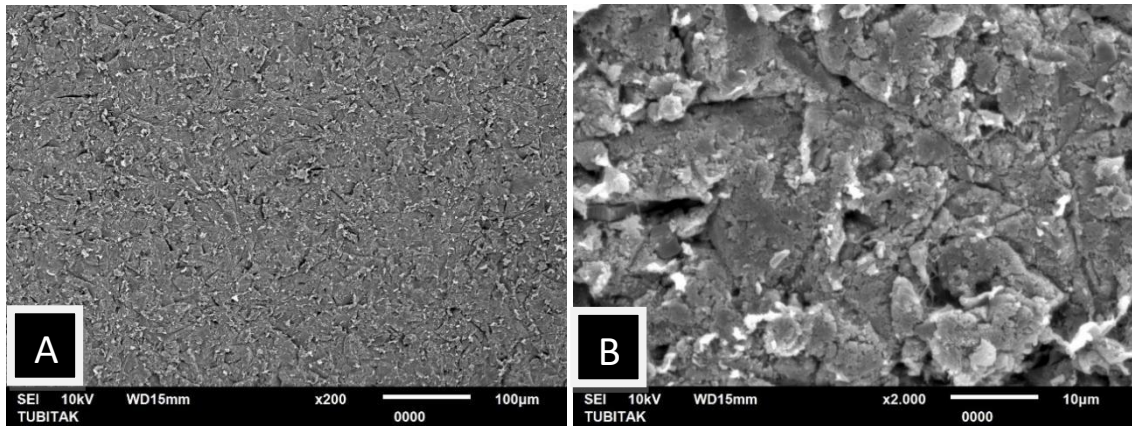


Figure 4.8.Scanning electron microscope images of PEKKTON 50 μm air abrasion group (A: 200x magnification, B: 2000x magnification).

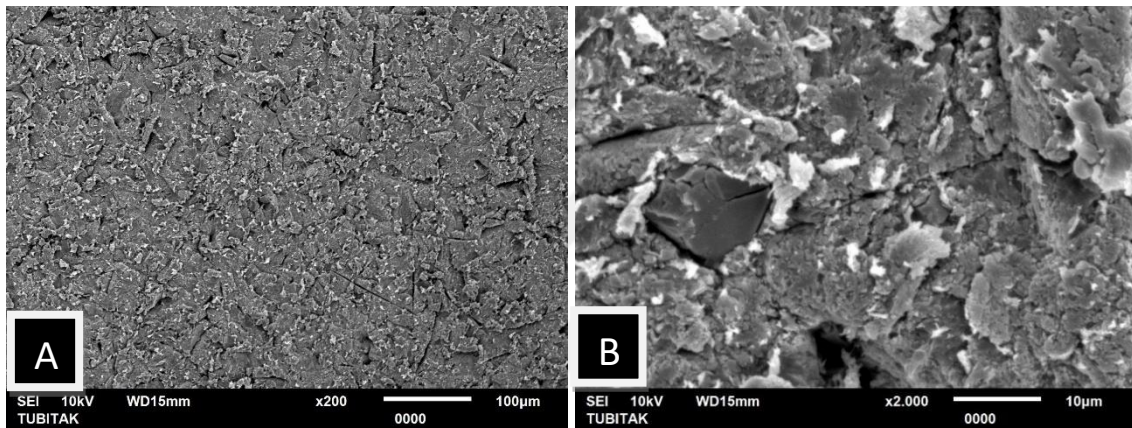


Figure 4.9.Scanning electron microscope images of PEKKTON 110 μm air abrasion group (A: 200x magnification, B: 2000x magnification).

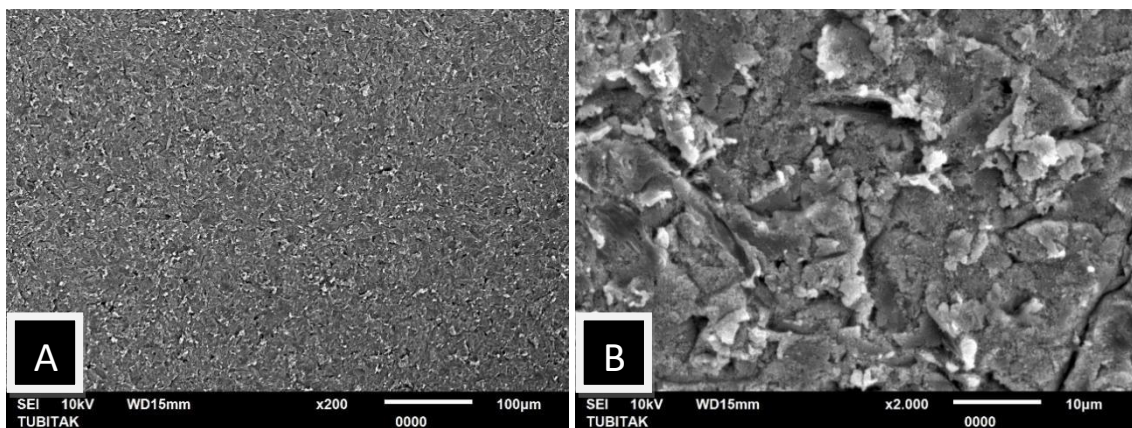


Figure 4.10.Scanning electron microscope images of PEKKTON 3M Cojet group (A: 200x magnification, B: 2000x magnification).

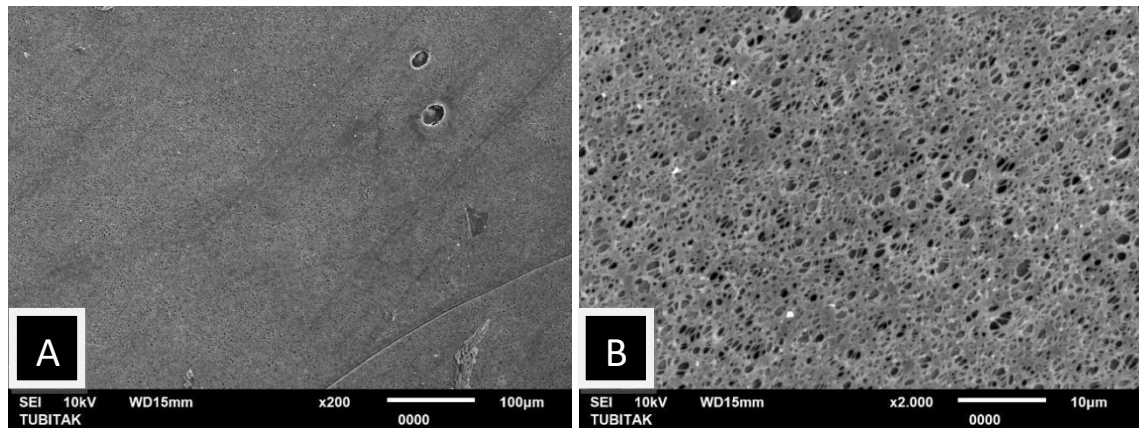


Figure 4.11.Scanning electron microscope images of PEKKTON 98% sulfuric acid etching group (A: 200x magnification, B: 2000x magnification).

SEM examinations revealed that the PEKKTON samples have irregular light scratches and grooves in the control group (Fig.4.7.), rougher irregular areas in the 50 µm air abrasion group (Fig.4.8.). These irregular rough areas increase in the 110 µm air abrasion group (Fig.4.9.), irregular rough areas similar to the air abrasion groups are present in the 3M-Cojet group (Fig.4.10.), and in the 98% sulfuric acid etching group (Fig.4.11.). There is a homogeneous smooth appearance at 200x magnification, and a homogeneous perforated appearance at 2000x magnification.

4.3.Results of Shear Bond Strength (SBS) Measurements

Table 4.3.Evaluation of the effect of material, thermocycle and surface treatments on shear bond strength.

	Type III				
	Sum Of				
	Squares	df	Mean Square	F	p
Material	162.894	1	162.894	112.848	0.000*
Thermocycle	1531.805	1	1531.805	1061.15	0.000*
Surface Treatment	1439.617	4	359.904	249.33	0.000*
Material*Thermocycle	50.354	1	50.354	34.884	0.000*
Material*Surface Treatment	326.52	4	81.63	56.551	0.000*
Thermocycle*Surface Treatment	119.387	4	29.847	20.677	0.000*
Material*Thermocycle*Surface Treatment	139.248	4	34.812	24.117	0.000*

Three-Way ANOVA Test

*p<0.05

There is a statistically significant difference between the materials in terms of shear bond strength averages ($p:0.000$; $p<0.05$).

There is a statistically significant difference between groups with and without thermocycle process in terms of shear bond strength averages ($p:0.000$; $p<0.05$).

There is a statistically significant difference between the surface treatments in terms of shear bond strength averages ($p:0.000$; $p<0.05$).

The combined effect of material and thermocycle treatment on shear bond strength was statistically significant ($p:0.000$; $p<0.05$). The material and the thermocycle together affect the shear bond strength.

The combined effect of material and surface treatments on shear bond strength was statistically significant ($p:0.000$; $p<0.05$). The material and surface treatment together affect the shear bond strength.

The combined effect of thermocycle process and surface treatments on shear bond strength was statistically significant ($p:0.000$; $p<0.05$). Thermocycle process and surface treatments together affect the shear bond strength.

The combined effect of material, thermocycle and surface treatments on shear bond strength was statistically significant ($p:0.000$; $p<0.05$). Material, thermocycle and surface treatments together affect shear bond strength. Detailed interpretations of the mentioned results can be seen in Table 4.3.

Table 4.4.Evaluation of shear bond strength (Mpa) according to material, thermocycle and surface treatments.

		SBS	
		Without Thermocycle	With Thermocycle
		Mean±SD	Mean±SD
PEEK	Control	6.786±0.803 ^{Aa}	3.380±0.927 ^{Ab}
	50 µm Air Abrasion	18.036±2.063 ^{Ba}	9.408±1.322 ^{Bb}
	110 µm Air Abrasion	16.513±1.311 ^{BDa}	7.696±1.356 ^{Cb}
	3M Cojet	14.012±1.238 ^{Ca}	10.582±0.831 ^{Bb}
	98% Sulfuric Acid Etching	16.257±1.088 ^{Da}	9.367±1.315 ^{Bb}
PEKKTON	Control	7.551±1.159 ^{Aa}	3.731±0.333 ^{Ab}
	50 µm Air Abrasion	8.795±1.333 ^{Aa}	6.570±1.107 ^{Bb}
	110 µm Air Abrasion	16.362±1.269 ^{Ba}	9.204±0.905 ^{Cb}
	3M Cojet	13.242±1.078 ^{Ca}	7.368±1.037 ^{Bb}
	98% Sulfuric Acid Etching	12.266±1.353 ^C	9.741±1.309 ^{Cb}

Two-Way ANOVA Test

* Different capital letters in the columns indicate the difference between surface treatments, and different lowercase letters in the rows indicate the difference between thermocycles.

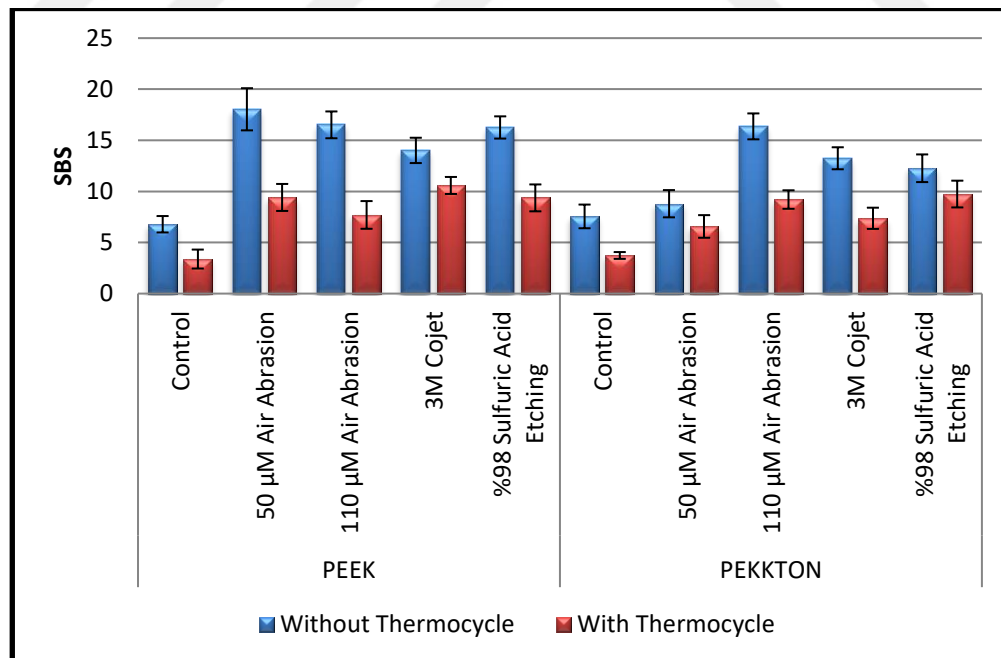


Figure 4.12.Evaluation of shear bond strength (Mpa) according to material, thermocycle and surface treatments.

4.3.1. Effect of thermocycle process on shear bond strength in PEEK material

When thermocycle process is not applied to PEEK material; there is a statistically significant difference between the surface treatments in terms of shear bond strength averages ($p:0.000$; $p<0.05$). As a result of the post hoc Tukey HSD test performed to determine the significance; shear bond strength of 50 μm air abrasion group was significantly higher than control ($p:0.000$), 3M Cojet ($p:0.000$) and 98% sulfuric acid etching ($p:0.029$) groups ($p<0.05$). The shear bond strength of the 110 μm air abrasion group was significantly higher than the control ($p:0.000$) and 3M Cojet ($p:0.000$) groups ($p<0.05$). The shear bond strength of the 98% sulfuric acid etching group was significantly higher than the control ($p:0.000$) and 3M Cojet ($p:0.003$) groups ($p<0.05$). The shear bond strength of the control group was significantly lower than all other groups ($p:0.000$; $p<0.05$). There was no significant difference between the other groups ($p>0.05$).

When thermocycle process is applied to PEEK material; there is a statistically significant difference between the surface treatments in terms of shear bond strength averages ($p:0.000$; $p<0.05$). As a result of the post hoc Tukey HSD test performed to determine the significance; the shear bond strength of the control group was significantly lower than all other groups ($p:0.000$; $p<0.05$). The shear bond strength of 110 μm air abrasion group is significantly lower than 50 μm air abrasion ($p:0.010$), 3M Cojet ($p:0.000$) and 98% sulfuric acid etching ($p:0.013$) groups ($p<0.05$). There was no significant difference in shear bond strength between 50 μm air abrasion, 3M Cojet and 98% sulfuric acid etching groups ($p>0.05$).

When surface treatment is not applied to PEEK material; the mean shear bond strength of the thermocycled samples was significantly lower than the non-thermocycled samples ($p:0.000$; $p<0.05$).

When 50 μm air abrasion is applied to PEEK material; the mean shear bond strength of the thermocycled samples was significantly lower than the non-thermocycled samples ($p:0.000$; $p<0.05$).

When 110 μm air abrasion is applied to PEEK material; the mean shear bond strength of the thermocycled samples was significantly lower than the non-thermocycled samples ($p:0.000$; $p<0.05$).

When 3M Cojet is applied to PEEK material; the mean shear bond strength of the thermocycled samples was significantly lower than the non-thermocycled samples ($p:0.000$; $p<0.05$).

When 98% Sulfuric Acid Etching is applied to PEEK material; the mean shear bond strength of the thermocycled samples was significantly lower than the non-thermocycled samples ($p:0.000$; $p<0.05$). Detailed interpretations of the mentioned results can be seen in Table 4.4. and Figure 4.12.

4.3.2.Effect of thermocycle process on shear bond strength in PEKKTON material

When thermocycle process is not applied to PEKKTON material; there is a statistically significant difference between the surface treatments in terms of shear bond strength averages ($p:0.000$; $p<0.05$). As a result of the post hoc Tukey HSD test performed to determine the significance; the shear bond strength of 110 μm air abrasion group is significantly higher than control, 50 μm air abrasion, 3M Cojet and 98% sulfuric acid etching groups ($p:0.000$; $p<0.05$). The shear bond strength of 3M Cojet and 98% sulfuric acid etching groups was significantly higher than that of control and 50 μm air abrasion groups ($p:0.000$; $p<0.05$). There was no significant difference between the other groups ($p>0.05$).

When thermocycle process is applied to PEKKTON material; there is a statistically significant difference between the surface treatments in terms of shear bond strength averages ($p:0.000$; $p<0.05$). As a result of the post hoc Tukey HSD test performed to determine the significance; the shear bond strength of the control group was significantly lower than all other groups ($p:0.000$; $p<0.05$). The shear bond strength of 110 μm air abrasion and 98% sulfuric acid etching groups is significantly higher than 50 μm air abrasion and 3M Cojet groups ($p:0.000$; $p<0.05$). There was no significant difference between the other groups ($p>0.05$).

When surface treatment is not applied to PEKKTON material; the mean shear bond strength of the thermocycled samples was significantly lower than the non-thermocycled samples ($p:0.000$; $p<0.05$).

When 50 μm air abrasion is applied to PEKKTON material; the mean shear bond strength of the thermocycled samples was significantly lower than the non-thermocycled samples ($p:0.000$; $p<0.05$).

When 110 μm air abrasion is applied to PEKKTON material; the mean shear bond strength of the thermocycled samples was significantly lower than the non-thermocycled samples ($p:0.000$; $p<0.05$).

When 3M Cojet is applied to PEKKTON material; the mean shear bond strength of the thermocycled samples was significantly lower than the non-thermocycled samples ($p:0.000$; $p<0.05$).

When 98% sulfuric acid etching is applied to PEKKTON material; the mean shear bond strength of the thermocycled samples was significantly lower than the non-thermocycled samples ($p:0.000$; $p<0.05$). Detailed interpretations of the mentioned results can be seen in Table 4.4. and Figure 4.12.

Table 4.5. Evaluation of shear bond strength (Mpa) according to material, thermocycle and surface treatments.

		SBS	
		PEEK	PEKKTON
		Mean $\pm$ SD	Mean $\pm$ SD
Without Thermocycle	Control	6.786 $\pm$ 0.803 ^a	7.551 $\pm$ 1.159 ^a
	50 μm Air Abrasion	18.036 $\pm$ 2.063 ^a	8.795 $\pm$ 1.333 ^b
	110 μm Air Abrasion	16.513 $\pm$ 1.311 ^a	16.362 $\pm$ 1.269 ^a
	3M Cojet	14.012 $\pm$ 1.238 ^a	13.242 $\pm$ 1.078 ^a
	98% Sulfuric Acid Etching	16.257 $\pm$ 1.088 ^a	12.266 $\pm$ 1.353 ^b
With Thermocycle	Control	3.380 $\pm$ 0.927 ^a	3.731 $\pm$ 0.333 ^a
	50 μm Air Abrasion	9.408 $\pm$ 1.322 ^a	6.570 $\pm$ 1.107 ^b
	110 μm Air Abrasion	7.696 $\pm$ 1.356 ^a	9.204 $\pm$ 0.905 ^b
	3M Cojet	10.582 $\pm$ 0.831 ^a	7.368 $\pm$ 1.037 ^b
	98% Sulfuric Acid Etching	9.367 $\pm$ 1.315 ^a	9.741 $\pm$ 1.309 ^a

Two-Way ANOVA Test

* Different lowercase letters in the lines indicate the difference between materials.

When thermocycle process is not applied to the control group; there was no statistically significant difference between PEEK and PEKKTON materials in terms of shear bond strength averages ($p:0.087$; $p>0.05$).

When thermocycle process is not applied to 50 μm air abrasion group; the shear bond strength of the PEEK group was significantly higher than the PEKKTON group ($p:0.000$; $p<0.05$).

When thermocycle process is not applied to 110 μm air abrasion group; there was no statistically significant difference between PEEK and PEKKTON materials in terms of shear bond strength averages ($p:0.786$; $p>0.05$).

When the thermocycle process is not applied to the 3M Cojet group; there was no statistically significant difference between PEEK and PEKKTON materials in terms of shear bond strength averages ($p:0.135$; $p>0.05$).

When the thermocycle process is not applied to the 98% sulfuric acid etching group; the shear bond strength of the PEEK group was significantly higher than the PEKKTON group ($p:0.000$; $p<0.05$).

When thermocycle process is applied to the control group; there was no statistically significant difference between PEEK and PEKKTON materials in terms of shear bond strength averages ($p:0.260$; $p>0.05$).

When thermocycle process is applied to 50 μm air abrasion group; the shear bond strength of the PEEK group was significantly higher than the PEKKTON group ($p:0.000$; $p<0.05$).

When thermocycle process is applied to 110 μm air abrasion group; the shear bond strength of the PEKKTON group was significantly higher than the PEEK group ($p:0.006$; $p<0.05$).

When the thermocycle process is applied to the 3M Cojet group; the shear bond strength of the PEEK group was significantly higher than the PEKKTON group ($p:0.000$; $p<0.05$).

When the thermocycle process is applied to the 98% sulfuric acid etching group; there was no statistically significant difference between PEEK and PEKKTON materials in terms of shear bond strength averages ($p:0.512$; $p>0.05$). Detailed interpretations of the mentioned results can be seen in Table 4.5.

4.4.Results of Failure Analysis

Table 4.6.Evaluation of failure types in PEEK samples.

PEEK	Failure	Control	50 μ m Air Abrasion	110 μ m Air Abrasion	3M Cojet	98% Sulfuric Acid Etching	p
		n (%)	n (%)	n (%)	n (%)	n (%)	
No	Adhesive	11 (100%) ^a	3 (27.3%) ^b	4 (36.4%) ^b	4 (36.4%) ^b	4 (36.4%) ^b	¹ 0.002*
Thermocycling	Mixed	0 (0%)	8 (72.7%)	7 (63.6%)	7 (63.6%)	7 (63.6%)	
	Cohesive	0 (0%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)	
Thermocycling	Adhesive	11 (100%) ^a	4 (36.4%) ^{bc}	3 (27.3%) ^{bc}	6 (54.5%) ^c	1 (9.1%) ^b	¹ 0.000*
	Mixed	0 (0%)	7 (63.6%)	8 (72.7%)	5 (45.5%)	10 (90.9%)	
	Cohesive	0 (0%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)	
P _{No T.C-T.C}		-	² 0,500	² 1,000	³ 0,669	² 0,311	

¹Chi-square test ²Fisher's Exact Test ³Continuity (yates) correction *p<0.05

* Different lowercase letters in the lines indicate the difference between groups.

When thermocycle is not applied to PEEK samples; there was a statistically significant difference between the groups in terms of failure types (p:0.002; p<0.05). Adhesive type failure was observed in all of the control group (100%), while this rate was significantly higher than the other groups (p<0.05). There was no significant difference between 50 μ m air abrasion, 110 μ m air abrasion, 3M Cojet and 98% sulfuric acid etching groups (p>0.05).

When thermocycling is applied to PEEK samples; there was a statistically significant difference between the groups in terms of failure types (p:0.000; p<0.05). Adhesive type failure was observed in all of the control group (100%), while this rate was significantly higher than the other groups (p<0.05). Adhesive type failure rate (54.5%) in 3M Cojet group was significantly higher than %98 sulfuric acid etching (9.1%) group (p<0.05). There was no significant difference between the other groups (p>0.05).

Adhesive type failure was observed in all samples with and without thermocycling in the control group.

In the 50 μ m air abrasion group, there was no significant difference in failure types between the thermocycled and non-thermocycled samples (p:0.500; p>0.05).

Mixed type failure was observed in 72.7% of the non-thermocycled samples and in 63.6% of the thermocycled samples.

In the 110 μm air abrasion group, there was no significant difference in failure types between thermocycled and non-thermocycled samples ($p:1.000$; $p>0.05$). Mixed type failure was observed in 63.6% of the non-thermocycled samples and in 72.7% of the thermocycled samples.

In the 3M Cojet group, there was no significant difference in failure types between thermocycled and non-thermocycled samples ($p:0.669$; $p>0.05$). Mixed type failure was observed in 63.6% of the non-thermocycled samples and in 45.5% of the thermocycled samples.

In the 98% sulfuric acid etching group, there was no significant difference in failure types between the thermocycled and non-thermocycled samples ($p:0.311$; $p>0.05$). Mixed type failure was observed in 63.6% of the non-thermocycled samples and in 90.9% of the thermocycled samples. Detailed interpretations of the mentioned results can be seen in Table 4.6.

Table 4.7. Evaluation of failure types in PEKKTON samples.

PEKKTON	Failure	Control	50 μm Air Abrasion	110 μm Air Abrasion	3M Cojet	98% Sulfuric Acid Etching	p
		n (%)	n (%)	n (%)	n (%)	n (%)	
No Thermocycling	Adhesive	11 (100%) ^a	5 (45.5%) ^b	6 (54.5%) ^b	4 (36.4%) ^b	7 (63.6%) ^b	¹ 0.015*
	Mixed	0 (0%)	6 (54.5%)	5 (45.5%)	7 (63.6%)	4 (36.4%)	
	Cohesive	0 (0%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)	
Thermocycling	Adhesive	11 (100%) ^a	5 (45.5%) ^{bc}	2 (18.2%) ^c	4 (36.4%) ^{bc}	7 (63.6%) ^b	² 0.001*
	Mixed	0 (0%)	6 (54.5%)	9 (81.8%)	7 (63.6%)	4 (36.4%)	
	Cohesive	0 (0%)	0 (0%)	0 (0%)	0 (0%)	0 (0%)	
P _{No T.C-T.C}		-	³ 1.000	⁴ 0.183	⁴ 1.000	⁴ 1.000	

¹Fisher Freeman Halton Exact Test ²Chi-square test ³Continuity (yates) correction ⁴Fisher's Exact Test

* $p<0.05$

* Different lowercase letters in the lines indicate the difference between groups.

When thermocycle is not applied to PEKKTON samples; there was a statistically significant difference between the groups in terms of failure types ($p:0.015$; $p<0.05$).

Adhesive type failure was observed in all of the control group (100%), while this rate was significantly higher than the other groups ($p < 0.05$). There was no significant difference between 50 μm air abrasion, 110 μm air abrasion, 3M Cojet and 98% sulfuric acid etching groups ($p > 0.05$).

When thermocycling is applied to PEKKTON samples; there was a statistically significant difference between the groups in terms of failure types ($p: 0.001$; $p < 0.05$). Adhesive type failure was observed in all of the control group (100%), while this rate was significantly higher than the other groups ($p < 0.05$). In the 98% sulfuric acid etching group, the adhesive type failure rate (63.6%) was significantly higher than the 110 μm air abrasion (18.2%) group ($p < 0.05$). There was no significant difference between the other groups ($p > 0.05$).

Adhesive type failure was observed in all samples with and without thermocycling in the control group.

In the 50 μm air abrasion group, there was no significant difference in failure types between thermocycled and non-thermocycled samples ($p: 1.000$; $p > 0.05$). Mixed type failure was observed in 54.5% of the samples that were and were not applied thermocycled.

In the 110 μm air abrasion group, there was no significant difference in failure types between the thermocycled and non-thermocycled samples ($p: 0.183$; $p > 0.05$). Mixed type failure was observed in 45.5% of the non-thermocycled samples and in 81.8% of the thermocycled samples.

In the 3M Cojet group, there was no significant difference in failure types between thermocycled and non-thermocycled samples ($p: 1.000$; $p > 0.05$). Mixed type failure was observed in 63.6% of the samples that were and were not applied thermocycled.

In the 98% sulfuric acid etching group, there was no significant difference in failure types between thermocycled and non-thermocycled samples ($p: 1.000$; $p > 0.05$). Adhesive type failure was observed in 63.6% of the samples that were and were not applied thermocycled. Detailed interpretations of the mentioned results can be seen in Table 4.7.

Stereomicroscope images of randomly selected samples with adhesive and mixed failures were shown in Figure 4.13.

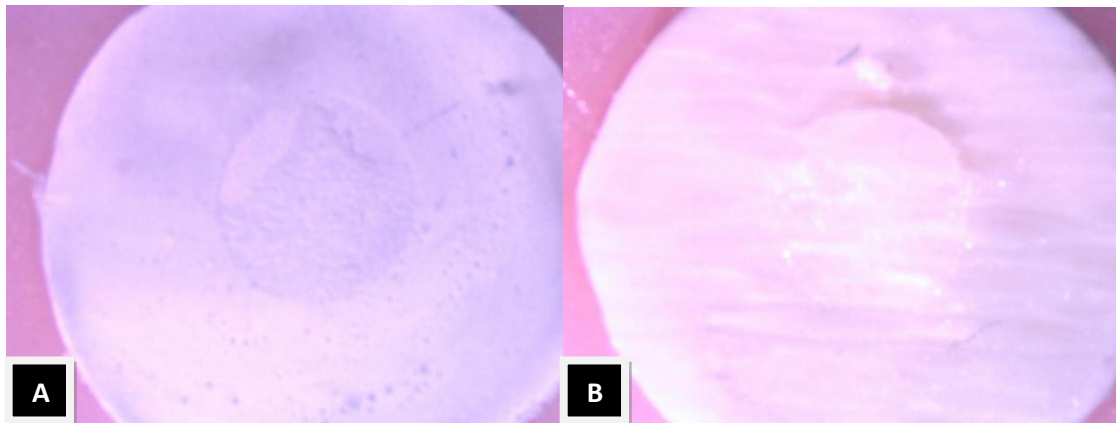


Figure 4.13. Stereomicroscope images of samples. (**A:** sample with adhesive failure, **B:** sample with mixed failure)

5.DISCUSSION

High performance polymers are recognized as having superior physical and mechanical properties, in addition to a high level of biocompatibility, making them one of the most important materials in the field of dentistry. Polymers are used in the fabrication of a wide variety of removable appliances, restorations, and base materials for dentures (1,2).

Two of the most well-known members of thermoplastic polymers, PEEK and PEKKTON, are used in many areas in dentistry. There is a significant amount of interest, as well as ongoing research, in tissue-substitute materials that have mechanical properties similar to those of human bone. In this context, high performance polymers may assist in meeting the demands of patients for metal-free dental reconstructions due to their biocompatibility as well as their mechanical properties, which include resistance to heat and solvents, excellent electrical insulation, robust wear and fatigue resistances, and so on (15,156).

The use of these polymers as the framework material for fixed prostheses requires a bonding to veneering composite materials that is both permanently durable and stable. However, these polymers, which are considered inert substances, have trouble adhering to veneering composite materials due to the chemical composition of their molecules and their low surface energy(157). The primary objective of the vast majority of research efforts has been directed toward finding ways of improving the adhesive strength of veneering composites by increasing the low surface energy of PEEK and PEKKTON polymers.

In order to achieve a higher surface energy, researchers have experimented with a variety of surface treatments. Surface treatment methods can be divided into two distinct categories: mechanical and chemical. The mechanical and the chemical methods of treating surfaces are both considered to be very effective. Abrasion with airborne particles (such as silica or aluminum oxide), laser and plasma applications, bur grinding, are the types of mechanical treatment. Etching can be done with sulfuric acid and piranha solutions as part of the chemical treatments.

The most common and simplest method of mechanical surface treatment is air abrasion with Al_2O_3 . Surface roughness is increased by air abrasion, which also removes organic contaminants from the surface. This results in the formation of a new,

active surface layer (13). It also encourages the micromechanical interlocking of polymer-based dental materials and makes it possible for the bonding agent to better penetrate them. This leads to a micro-mechanical retention and, most likely, an increased surface bonding capacity (9,15). It was observed that the bond strength was increased in the studies where air abrasion with Al_2O_3 was applied to PEEK and PEKKTON surfaces (10–20). Schmidlin *et al.* (20) roughened PEEK surfaces by sandblasting with different particle sizes of Al_2O_3 (50 μm and 110 μm) and investigated the surface roughness and bond strength with composite resins. As a result of the study, they reported that the sandblasting of the PEEK surfaces with either 110 μm or 50 μm Al_2O_3 did not result in a statistically significant difference between the two treatments. Stawarczyk *et al.* (19) also roughened PEEK surfaces by sandblasting with different particle sizes of Al_2O_3 (50 μm and 110 μm) and reported that sandblasting the PEEK surfaces with 110 μm Al_2O_3 , compared to 50 μm Al_2O_3 created higher surface roughness values and the shear bond strength was statistically significantly increased. Therefore, only in these two studies, two different particle sizes were sandblasted with Al_2O_3 , but since these studies had different results, two different particle sizes were also included in the current study.

The application of a silica coating is yet another frequent way of mechanical treatment. In studies investigating the bond strength by applying a silica coating to PEEK and PEKKTON surfaces, an increase in surface roughness and higher bond strength values were observed compared to the untreated samples (12–14,18–20). Çulhaoğlu *et al.* treated PEEK surfaces with silica coating (3M Cojet) and investigated the surface roughness, wettability, and shear bond strengths to veneering resin. According to the findings of the research, surface roughness and bond strength values increased in samples that had been coated with silica. The samples applied silica coating have the most wettable surfaces. Stawarczyk *et al.* (19) treated PEEK surfaces with silica coating (3M Rocatec) and investigated the surface roughness and shear bond strength to composite resins. As a result of this study, they reported that silica coated PEEK samples have the highest surface roughness values and the shear bond strength was statistically significantly increased. According to the findings of the researches, two distinct approaches to applying a silica coating are effective. As a result, the application of a silica coating using 3M Cojet on PEEK and PEKKTON surfaces was favored in the current study.

Laser irradiation is also another method of mechanical treatment and different kinds of lasers have been studied like Er:YAG, Yb:PL. In studies where laser irradiation was used on PEEK and PEKKTON surfaces, it was seen that surface roughness was increased compared to untreated samples (12,13,18). Even though studies in which laser irradiation was used on PEEK and PEKKTON surfaces showed that the surface roughness increased significantly, laser irradiation was not used as a surface treatment in this study because it was not clear that it had a positive effect on wettability and bond strength.

Plasma treatment is also another method of mechanical treatment and different types of plasma has been studied like argon, non-thermal plasma. In studies where plasma treatment was applied on PEEK and PEKKTON surfaces, it was observed that surface roughness and bond strength were increased compared to untreated samples (10,11,15,156). Plasma treatment of PEEK and PEKKTON surfaces increases surface roughness and bond strength; nevertheless, it is not included as one of the surface treatments in this study since it is unable to demonstrate superiority over the surface treatments that are commonly used in the studies.

The most common method of chemical surface treatment is etching with sulfuric acid. Various percentages of sulfuric acid have been used in studies (70%, 80%, 85%, 90%, 98%). In researches where sulfuric acid etching was applied on PEEK and PEKKTON surfaces, it was observed that micro-topographical changes of PEEK and PEKKTON surfaces after sulfuric acid etching enhanced the penetration of the resin adhesive, resulting in the increased bond strength (8,14,15,17–21). Chaijareenont *et al.* (8) applied different concentrations of sulfuric acid (70%, 80%, 85%, 90%, 98%) to the PEEK surfaces and investigated surface roughness and shear bond strength. As a result of this study, they reported that the 98% sulfuric acid group revealed the highest surface roughness but was not significantly different from the 80, 85 and 90% sulfuric acid groups and 90 and 98% sulfuric acid groups have the highest shear bond strength values. Therefore, ideal sulfuric acid concentrations of 90 and 98% have been suggested to increase adhesion. In this investigation as well as following studies, researchers treated the surfaces of PEEK and PEKKTON with sulfuric acid for sixty seconds, and they got long-lasting bond strengths. Therefore, in the current study, 98% sulfuric acid was applied to PEEK and PEKKTON surfaces for 60 seconds.

Etching with piranha solution is also another method of chemical treatment. The piranha solution is a mixture of 98% sulfuric acid (H_2SO_4) and 30% hydrogen peroxide (H_2O_2) in a 10:3 ratio. Studies that used piranha solution demonstrated that piranha etching considerably improved the strength of the bonds between PEEK/PEKKTON and dental adhesives by eliminating organic residues, enhancing surface polarity, and disrupting aromatic structures (9,17,22). Silthampitag *et al.* (17) treated PEEK surface with piranha solution and reported that piranha solution showed little effect on the roughness of PEEK and the shear bond strength of PEEK samples etched with piranha solution was lower than the samples that applied 98% sulfuric acid. According to the findings of the previous researches, piranha solution was not favored to be used in the current study. This was due to the fact that the increasing effect of piranha solution on bond strength was not discovered to be more than that of other surface treatments, and the fact that the preparation and use of piranha solution was very dangerous.

The poor adhesion of PEEK and PEKKTON was the primary focus of the research conducted on these two materials. Additionally, the researchers investigated how the surface topography, surface roughness, and bond strength of these materials changed after being subjected to a variety of surface treatments. According to the result of the current study, after applying surface treatments to the PEEK samples, air abrasion with 110 μm Al_2O_3 group ($Ra:1.325\pm0.034 \mu m$) showed higher surface roughness values than 3M Cojet group ($Ra:0.526\pm0.012 \mu m$), air abrasion with 50 μm Al_2O_3 group ($Ra:0.470\pm0.030 \mu m$), acid etched with 98% sulfuric acid group ($Ra:0.175\pm0.023 \mu m$) and control groups ($Ra:0.118\pm0.006 \mu m$). Çulhaoğlu *et al.* (18), Silthampitag *et al.* (17) and Çağlar *et al.* (12) applied various surface treatments to the PEEK surface and measured the surface roughness with a profilometer and examined the surface topography with SEM. Çulhaoğlu *et al.* (18) declared that surface roughness values of laser irradiated (Yb:Pl laser) group had the highest surface roughness values, followed by the sandblasted with 110 μm Al_2O_3 group. The groups treated with 3M Cojet, 98% sulfuric acid and acetone were not statistically significant from the control group and had the lowest surface roughness values. Silthampitag *et al.* (17) declared that surface roughness values of sandblasted with 50 μm Al_2O_3 group and etched with 98% sulfuric acid group had the highest surface roughness values. The group treated with piranha was not statistically significant from the control group and had the lowest surface roughness values. Schmidlin *et al.* (20) and Stawarczyk *et al.* (19) sandblasted the

PEEK surface with two different particle sizes (50 μm and 110 μm) and compared the surface roughness. Schmidlin *et al.* (20) used SEM to examine the surface topography and declared that sandblasted with a particle size of 50 μm group had an irregular surface, when compared to the group that had been sandblasted with particles that were 110 μm in size, it exhibited a surface pattern that was more pronounced and distributed. Stawarczyk *et al.* (19) used profilometer for surface roughness measurement and stated that sandblasted with 110 μm Al_2O_3 group had higher surface roughness values compared to the sandblasted with 50 μm Al_2O_3 group. In the most of researches, the surface roughness values of sandblasted samples were found to be higher than those of other treatments, as was the case in the current study. In addition to other studies, sandblasting with two different particle sizes was performed in the present study, and it was found that the surface roughness values of the 110 μm Al_2O_3 group were higher than those of the 50 μm Al_2O_3 group.

According to the result of the current study, after applying surface treatments to the PEKKTON samples, sandblasted with 110 μm Al_2O_3 group ($\text{Ra}:1.252\pm0.027$ μm) showed higher surface roughness values than sandblasted with 50 μm Al_2O_3 group ($\text{Ra}:0.801\pm0.027$ μm), 3M Cojet group ($\text{Ra}:0.566\pm0.010$ μm), acid etched with 98% sulfuric acid group ($\text{Ra}:0.287\pm0.029$ μm) and control groups ($\text{Ra}:0.099\pm0.007$ μm). Fokas *et al.* (158), Lee *et al.* (14), Labriaga *et al.* (11), Sakihara *et al.* (21) applied various surface treatments to the PEKKTON surface and examined the surface roughness. Lee *et al.* (14) examined the surface roughness with profilometer and declared that sandblasted with 50 μm Al_2O_3 group had lower surface roughness values than 110 μm silica-coated group (3M Rocatec) and higher surface roughness values than 95% sulfuric acid etched group. Labriaga *et al.* declared that the 98% sulfuric acid etched group had higher surface roughness values than sandblasted with 110 μm Al_2O_3 group. Surface treatment of PEEK and PEKKTON materials may have different results in studies due to differences in the design of the procedures, such as changes in sandblasting particle sizes, different sandblasting equipment or application at different pressures, changes in the concentrations of sulfuric acid used, and different methods of measuring surface roughness.

According to the result of the current study, after applying surface treatments to the PEEK and PEKKTON samples, the highest surface roughness values were measured in the 110 μm Al_2O_3 ($\text{Ra}:1.325$ μm , $\text{Ra}:1.252$ μm) group, while the lowest

values were measured in the 98% sulfuric acid etched group (Ra:0.175 μm , Ra:0.287 μm) after the control group. Surface roughness values of 110 μm Al_2O_3 PEEK and PEKKTON samples were found to be higher in PEEK samples (Ra:1.325 μm) than in PEKKTON samples (Ra:1.252 μm). Surface roughness values of 98% sulfuric acid etched PEEK and PEKKTON samples were found to be lower in PEEK samples (Ra:0.175 μm) than in PEKKTON samples (Ra:0.287 μm). Since there is no study examining surface roughness to both PEEK and PEKKTON materials, a comparison of these two materials was made in the current study.

After surface treatments, there are various methods for determining the bond strength between the veneered composite and PEEK and PEKKTON materials. The most commonly used bond strength tests on these two polymer materials are shear (SBS) (8,10–15,17–21,156) and tensile (TBS) (9,10,158–161) tests. There are currently no standards for SBS and TBS testing of polymeric materials like PEEK and PEKKTON. The SBS test was conducted in accordance with ISO 10477, a technical specification issued by the international organization for standardization. In a study comparing the shear and tensile tests (10), it was shown that both test methods can be used to assess the impact of various surface treatment techniques on the bond strength between PAEK and veneering composites. However, the shear test may be preferred due to its simplicity in specimen preparation and rapid testing process. Additionally, unlike tensile tests, the shear test for PAEK materials may be standardized in accordance with ISO 10477. Therefore, the shear bond strength test was used in the current study.

In the studies, various adhesive agents were applied to the polymer surfaces after surface treatments in order to increase the bond strength between the PAEK polymers and the veneered composite. Studies have shown that the application of an adhesive agent clearly increased the bond strength (11–14,16,156). Methylmethacrylate (MMA) monomers are reported to be particularly effective for enhancing the bond strength of PAEK polymers to composite veneer. It has been found that the use of MMA-containing adhesive agents is more effective in increasing the bond strength (156). Therefore, Visio.link adhesive agent with MMA was used in the current study. With its PETIA component, it has the ability to modify the surface of PAEK polymers.

The thermocycle process is an important step in examining the bond strength between PAEK polymers and the veneered composite. By aging the samples with the thermocycle process, the long-term effectiveness of the adhesive bonding is examined (11,12,18,21,156). The bond strength may be affected by the thermal cycle procedure. The reduction in shear bond strength values after the thermocycling process is assumed to be due to moisture, mechanical stress, and volume changes brought on by temperature changes in the bonded areas (162). Since there is no standard procedure for thermocycle process; various cycle times were used in the studies. Since it is preferred in many studies (10,12,13,22), 5000 cycles were used in the current study, which is equivalent to 6 months of aging.

According to the results of the current study, the mean shear bond strength values of the veneering composite to PEEK surfaces was the highest in the air abrasion with 50 μm Al_2O_3 (18.036 ± 2.063 MPa) group followed by the air abrasion with 110 μm Al_2O_3 (16.513 ± 1.311 MPa) and etching with 98% sulfuric acid (16.257 ± 1.088 MPa) groups which did not differ significantly, 3M cojet (14.012 ± 1.238 MPa) group and control (6.786 ± 0.803 MPa) groups. Schmidlin et al. (20), in their study on PEEK samples, found that the shear bond strength values of the etching with 98% sulfuric acid group were higher than those of the air abrasion with 50 and 110 μm Al_2O_3 groups and the 110 μm silica coating group. They did not find a significant difference between sandblasting groups and 110 μm silica coating groups. In our study, the etching with 98% sulfuric acid group was found to be higher than the silica coating group, but we used silica with a particle size of 30 μm . Other results do not overlap with our study. The reason for this is that the adhesives used, the sandblasting method and the sandblasting device are different. In the study of Çağlar et al. (12) on PEEK samples, the shear bond strength values of the air abrasion with 50 μm Al_2O_3 group were found to be higher than the 30 μm silica coating group. The results of this study are consistent with our study. In the study of Stawarczyk et al. (19) on PEEK samples, the shear bond strength values of the etching with 98% sulfuric acid group were found to be higher than the air abrasion with 110 μm Al_2O_3 group and the 50 μm Al_2O_3 group, respectively. These results are not consistent with our study. The reason for this difference may be the variability of application methods.

According to the results of the current study, the mean shear bond strength values of the veneering composite to PEKKTON surfaces was the highest in the air

abrasion with 110 μm Al_2O_3 ($16,362 \pm 1.269$ MPa) group followed by 3M Cojet ($13,242 \pm 1.078$ MPa) and etching with 98% sulfuric acid ($12,266 \pm 1.353$ MPa) groups which did not differ significantly, air abrasion with 50 μm Al_2O_3 ($8,795 \pm 1.333$ MPa) and control ($7,551 \pm 1.159$ MPa) groups which also did not differ significantly. Lee et al. (14), in their study on PEKKTON samples, found that the shear bond strength values of the air abrasion with 50 μm Al_2O_3 group and 110 μm silica coating groups were higher than the 95% sulfuric acid group. These results are not consistent with our study. The reasons for this might be; ratio of the acid used, particle size of the silica, application method and the different adhesive used. There are not many studies on PEKKTON material. In future studies, the number of studies to increase the bond strength of PEKKTON material should be increased.

According to the results of the current study, the shear bond strength values of the thermocycled groups were found to be lower than the non-thermocycled groups. Findings of Labriaga et al. (11) confirm these results. In most of the studies (12,13,18,21), thermocycle treatment was applied to all groups in different cycles, and since there were no group that did not undergo thermocycled treatment, it was not revealed if thermocycling changed the bond strength or not. In order to evaluate the effect of the thermocycling, future studies should include samples with and without the thermocycling treatment together. Effects of the processes in different cycles should be examined and a method which can replicate oral environment better should be searched.

As a result of the treatments applied to PEEK and PEKKTON surfaces in this study, the roughness and shear bond strength values examined showed different results for the two materials, which may be due to the fact that these materials have different structural properties despite being from the same family. More studies should be done on the comparison of these two materials in future studies.

6.CONCLUSIONS

In this in vitro study, four different surface treatments were applied to both PEEK and PEKKTON surfaces and their effects on bond strength were investigated. There were some limitations of this study. With the test method applied to measure the bond strength, it is hard to achieve perfect replication of intraoral environment. There are various surface treatments available, and in this study, four of them, which can be easily applied in the clinical setting selected after results of previous studies reviewed. In future studies, research should be carried out to find a method that can much more increase the bond strength by including different surface treatments. The number of studies comparing PEEK and PEKKTON materials is few and more studies should be done on these two materials. In order to measure the bond strength, test methods that can better imitate the forces in the oral environment should be developed to achieve more detailed results.

In the current study, the conclusions can be summarised as follows:

1. Among the surface treatments applied to the PEEK and PEKKTON surfaces, the air abrasion with 110 μm Al_2O_3 groups had the highest surface roughness values ($p<0.05$).
2. When the groups within the PEEK samples were compared, ranking of the surface roughness values (Ra) from high to low was air abrasion with 110 μm Al_2O_3 > silica coating with 3M Cojet > air abrasion with 50 μm Al_2O_3 > acid etching with 98% sulfuric acid > control ($p<0.05$).
3. When the groups within the PEKKTON samples were compared, ranking of the surface roughness values (Ra) from high to low was air abrasion with 110 μm Al_2O_3 > air abrasion with 50 μm Al_2O_3 > silica coating with 3M Cojet > acid etching with 98% sulfuric acid > control ($p<0.05$).
4. Among the surface treatments applied to the PEEK surfaces, the air abrasion with 50 μm Al_2O_3 group had the highest shear bond strength values ($p<0.05$).
5. When the groups within the PEEK samples were compared, ranking of the shear bond strength values from high to low was air abrasion with 50 μm Al_2O_3 > air abrasion with 110 μm Al_2O_3 , acid etching with 98% sulfuric acid > silica coating with 3M Cojet > control ($p<0.05$).

6. In PEEK samples, there was no statistically significant difference between air abrasion with 110 μm Al_2O_3 and acid etching with 98% sulfuric acid methods in terms of shear bond strength values ($p>0.05$).
7. Among the surface treatments applied to the PEKKTON surfaces, the air abrasion with 110 μm Al_2O_3 group had the highest shear bond strength values ($p<0.05$).
8. When the groups within the PEKKTON samples were compared, ranking of the shear bond strength values from high to low was air abrasion with 110 μm Al_2O_3 > silica coating with 3M Cojet, acid etching with 98% sulfuric acid > air abrasion with 50 μm Al_2O_3 , control ($p<0.05$).
9. In PEKKTON samples, there was no statistically significant difference between silica coating with 3M Cojet and acid etching with 98% sulfuric acid methods in terms of shear bond strength values. Also, there was no statistically significant difference between air abrasion with 50 μm Al_2O_3 and control groups in terms of shear bond strength values ($p>0.05$).
10. The shear bond strength values of the thermocycled groups were found to be lower than the thermocycled groups.
11. In the failure analysis, adhesive or mixed failure was observed in all groups. While adhesive failure was most common in PEEK samples, mixed failure was observed in PEKKTON samples. Cohesive failure has never been observed. In other words, the veneered composite was either completely detached from the bonding point or partially separated from the PEEK/PEKKTON surface.

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8.CURRICULUM VITAE

Personal Informations

Name	BERK	Surname	AKSOY
Place of Birth		Date of Birth	
Nationality		TR ID Number	
E-mail		Phone number	

Education

Degree	Department	The name of the Institution Graduated From	Graduation year
Doctorate	Prosthetic Dentistry	Yeditepe University	2022
University	Dentistry	Marmara University	2016
High school	-	Fatin Rüştü Zorlu High School	2011

Languages	Grades (#)
English	56.2

Work Experience (Sort from present to past)

Position	Institute	Duration(Year-Year)
Dentist	Hospitadent	2022-
Dentist	Centerdent	2022-
Dentist	Alpi	2018-2018