



Effects of Hydroxyapatite Coating on Shear Bond Strength of Sulfonated Polyetheretherketone with Resin Composite and Fracture Strength of Implant-Supported Provisional Resin Composite Crowns on Sulfonated Hydroxyapatite Coated (SHAC) PEEK abutment

Thae Phyu Htay

A Thesis Submitted in Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Oral Health Sciences

Prince of Songkla University

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ABSTRACT

Objective: The study evaluates the effects of hydroxyapatite coating on shear bond and fracture strength of sulfonated polyetheretherketone and resin composites.

Methods: Shear bond strength (SBS) was assessed on 120 PEEK disks in five surface treatment groups: untreated PEEK as control, sandblasted with 50 μ m alumina (Sa PEEK), etched with 98% sulfuric acid for 1 min (S PEEK), hydroxyapatite-coated sulfonated (HA PEEK), and phosphoric acid-etched HA-coated (HAP PEEK). Scotchbond Universal Plus (Scb) and Single Bond Universal (Sib) adhesive application and bond with flowable resin composite were grouped into two (n=12). SBS was assessed after thermocycling for 5000 cycles at 5°C and 55°C (30 s dwell time and 10 s transfer time), analyzed using two-way and one-way ANOVA, and Tukey's HSD ($\alpha=0.05$). A light and scanning electron microscopes were used for the failure mode analysis. Surface roughness and contact angle for each treatment were also analyzed. To assess the fracture strength of implant-supported resin composite crowns, 30 customized PEEK abutments were sandblasted with 50 μ m aluminum (n=15) and coated with HA (n=15) following sulfonation. Scb universal adhesive was applied, and 3M bulk-fill resin composites were used to veneer these abutments in order to create crowns for the mandibular right first permanent molar. After 24 hours in distilled water at 37°C, all specimens were thermocycled for 1000 cycles at 5°C and 55°C (30 s rest time and 10 s transfer time) before being mechanically loaded for 120,000 cycles with

50 N using a chewing simulator at room temperature. A universal testing machine evaluated fracture strength, while a 3D surface profilometer determined failure mode. The Mann-Whitney U test ($\alpha = 0.05$) was utilized for statistical analysis.

Results: HA PEEK showed the largest SBS in both Scb and Sib, whereas untreated PEEK had the lowest. Only the S PEEK group showed a significantly higher SBS ($P < 0.05$) in Sib compared to Scb, indicating the bonding agent impact. Others showed predominantly adhesive failure, whereas HA and HAP PEEK displayed cohesive and mixed failures. After surface treatment, PEEK wettability increased except for Sa PEEK. This result also favor for the fracture strength of the HA group which was substantially higher ($1469.71 \text{ N} \pm 200.36$) than the Sa group ($1152.36 \text{ N} \pm 180.89$). Most failures of the fractured crowns were adhesive and included irreparable fractures of the crown.

Conclusion: Integrating sulfonation with HA coating is a powerful strategy for significantly enhancing bonding strength between PEEK and resin composites and increasing fracture strength.

Keywords : .Polyether ether ketone · Shear bond strength · Fracture Strength
Sulfonation · Hydroxyapatite coating

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LIST OF ABBREVIATIONS AND SYMBOLS

PEEK	- Polyetheretherketone
PAEKs	- Polyaryletherketones
PEKK	- Polyetherketoneketone
HA	- Hydroxyapatite
EP	- Emergence profile
EA	- Emergence angle
CAD	- Computer-aided design
CAM	- Computer-aided milling
PEMA	- Polyethyl methacrylate
PMMA	- Polymethyl methacrylate
MMA	- Methyl methacrylate
DMA	- Di-methacrylate
PETIA	- Pentaerythritol triacrylate
MDP	- 10-methacryloyloxydecyl dihydrogen phosphate
SEM	- Scanning electron microscope
EDS	- Energy-dispersive X-ray spectroscopy
SSS	- Socket seal surgery
PFM	- Porcelain fused metal
AH	- Anatomic healer or anatomic healing abutment
LCU	- Light curing unit
LED	- Light-emitting diode
TiO ₂	- Titanium dioxide
SBS	- Shear Bond Strength

LIST OF ABBREVIATIONS AND SYMBOLS (CONTINUE)

Al₂O₃ - Aluminum oxide

Nd: YVO₄ - Neodymium-doped yttrium orthovanadate

RF - Radiofrequency

YSZ - Ytria-stabilized zirconia

TZ - Translucent zirconia

FTIR - Fourier Transform Infrared Spectroscopy

ATR - Attenuated total reflection

XRD - X-ray Diffraction

AFM - Atomic forced microscopy

TEM - Transmittance electron microscopy

TGA - Thermogravimetric analysis

DSC - Differential scanning calorimetry

Sa PEEK - 50 μ m alumina oxide sandblasted polyetheretherketone

S PEEK - Sulfonated polyetheretherketone

HA PEEK – 10% w/v hydroxyapatite coated sulfonated polyetheretherketone

HAP PEEK – 34% phosphoric acid etched 10% w/v hydroxyapatite coated sulfonated polyetheretherketone

Sib - Single bond universal

Scb - Scotchbond universal plus

CHAPTER 1

INTRODUCTION

1.1 Background information

Patient interest in dental implant therapy is increasing, with a research report from the United States estimating that the prevalence of such treatments may reach 23% by 2026 [1]. With the evolution of dental implant therapy, the emphasis in implant dentistry is changing from “survival” to “quality of survival.” Highly aesthetically pleasing restorations are becoming increasingly important for treatment success, and the anatomic emergence profile plays a major role in accomplishing this goal.

Conventional prefabricated healing abutments are circular and inadequate to form a natural emergence profile; therefore, it is difficult to maintain the peri-implant soft tissue profile [2]. Currently, there are no pre-manufactured implant components with anatomical emergence profiles that are appropriate for every anatomical circumstance. Liu et al. advised that the natural tooth dimensions and contours must be taken into account when planning an appropriate implant restoration design [3].

To create the correct emergence profile, gingival tissues must be gradually conditioned through progressively modified temporary restorations [4] or an emergence profile cast [5] or customized healing abutment [6] to mimic the soft tissue profile. Although implant healing abutments are used only temporarily, the emergence profile created by healing abutments can influence long-term peri-implant health [7]. There is also evidence that the use of customized abutments gave better results in terms of both soft and hard tissues [8]. Moreover, aesthetic and patient satisfaction factors that measure pain and pink aesthetic scores [9] than the use of standard abutments. The modified PEEK healing and temporary abutments are presently used widely using the CAD-CAM technique and applied to achieve a satisfying aesthetic result [10].

1.2 Problem Statement and Justification

Some various techniques and materials were applied for the fabrication of customized healing abutments, such as intraoral scanning and CAD/CAM, before implant placement [11] and during implant placement [12] using PMMA [11], PEEK [10], Titanium [13], and Zirconia [14]. Nonetheless, these techniques incur additional

costs and time for the fabrication of such healing abutments. The straightforward method of applying composite resin over a temporary abutment or a prefabricated healing abutment remains the simplest and most convenient approach.

Another way to create an emergence profile is during the delivery of the temporary prosthesis, and the duration of interim prosthesis application may take longer in full-mouth rehabilitation cases [15]. In addition, the long-term success of the implant prosthesis also depends on the longevity of the temporary prosthesis. The main concern is the detachment of the veneering material from the temporary abutments [16].

The dentists' knowledge about the various products and materials is becoming important for successful provisional prostheses [17]. Various types of provisional abutments, such as plastic, PEEK, and metal, are available, and previous researchers have investigated their durability [18, 19]. Among them, PEEK abutment is the first-line option because of its robust properties, such as its biocompatibility, ease of adjustment in chairside manipulation, and acceptable mechanical properties [20]. Moreover, PEEK abutments can be used as screw or cement-retained provisional abutment veneering with composite resin or cementing with provisional crowns. Nonetheless, bonding between PEEK and composite resin is still challenging because of its inert surface polarity, poor wettability, and resistance to surface changes.

Surface treatment methods for PEEK investigated by various researchers are plasma surface treatment [18], airborne particle abrasion [19], laser surface treatment [20], and usage of chemical agents: sulphuric acid etching [21], pinhead acid etching [22], vinyl sulfonic acid etching [23] and hydrofluoric acid etching [24].

The main issue in utilizing PEEK as a temporary abutment or customized healing abutment for establishing the emergence profile is the bonding interface between PEEK and resin composite. Furthermore, when utilized as a temporary abutment for long-term provisional restorations, more than two years in some cases, it must be capable of withstanding masticatory forces [21].

Prior studies have demonstrated that the fracture resistance of PEEK temporary abutments is comparable to that of conventional temporary metal abutments [19, 22]. However, the failure mode usually found in these studies is detachment from the veneering resin or the titanium base. Strength, elastic modulus, and bonding efficiency of implant-prosthetic abutments to veneering or crown materials determine the survival

rate of the temporary prostheses in the mouth [17]. Although temporary abutments are used only for a short duration, they have to be able to withstand the occlusal forces during function [17].

Therefore, this study tested the effect of hydroxyapatite coating on the shear bond strength of sulfonated polyetheretherketone and resin composite, focusing on both shear bond and fracture strength.

The null hypotheses tested for the part 1 study were: (1) there were no significant differences in wettability, surface roughness (Ra), and SBS among the various surface treatment groups, and (2) the different silane containing bonding agents utilized has no effect on the SBS in any of the surface treatment groups.

The null hypothesis for the part 2 study posits that there will be no significant difference in fracture strength among the various surface treatment groups of PEEK veneered with resin composite for implant-supported provisional crown

CHAPTER 2

REVIEW OF LITERATURE

2.1 Various Methods to Create Anatomic Emergence Profile

1. Cervical Contouring Concept [23]
2. Dynamic compression technique [24]
3. Immediate Temporization [25]
4. Anatomical Healing Abutment [26]

2.1.1 Cervical Contouring Concept

Bichacho, N., & Landsberg, C. J. proposed this concept in 1994 as a modified prosthetic technique comprising four steps in clinical and laboratory procedures, including the reshaping of the gingival profile. A case report was provided to exemplify the procedures following the introduction of a modified regenerative technique known as "socket seal surgery" (SSS) [23].

2.1.2 Dynamic compression technique

Wittneben, J.G. et al., 2013, recommended the creation of the emergence profile through the dynamic compression technique utilizing temporary restorations in the esthetic zone. This involves applying pressure to initially mold the soft tissue, subsequently positioning it, and gradually diminishing the cervical and interdental space to facilitate soft tissue fill [24].

2.1.3 Immediate Temporization

The adoption of a temporary restoration that is shaped to resemble the cervical morphology of the removed tooth at the time of immediate implant insertion may offer a platform to encourage soft tissue healing around the implant [25].

2.1.4 Anatomical Healing Abutment

The anatomic healing abutment, or anatomic healer (AH), idea was proposed by Pelekanos, S., & Vergoullis, I. (2023) and outlines the clinical guidelines for the design and manufacture of anatomical healing abutments for both immediate and delayed implant placements [26].

2.2 Materials Used for Customized Healing Abutment and Temporary Abutment

Customized healing abutments can be fabricated using polyetheretherketone (PEEK), titanium, polymethyl methacrylate (PMMA), zirconia, and resin composite, which are made up of only these materials or in combinations of these materials [7].

2.2.1 Polyetheretherketone (PEEK)

The repeating unit structure of PEEK is $-O-C_6H_4-O-C_6H_4-CO-C_6H_4-$ and the scientific name of PEEK is poly (Oxy-1,4 - phenylene -oxy - 1, 4- phenylene carbonyl - 1, 4 - phenylene) [27]. It has the advantages of high-temperature resistance, chemical and radiation and fatigue resistance, high impact strength, good wear resistance and flame retardant, excellent electrical properties, and so applied in electronic, medical, machinery, aerospace, and automotive fields and has become an indispensable key material in various fields [28].

In dentistry, PEEK healing abutments have positive effects on the soft tissue's healing pattern, favouring for an appropriate prosthetic emergence profile [29]. Despite PEEK's better qualities, chairside fabrication of pure PEEK customized healing abutments is limited because CAD/CAM technology is needed to fabricate customized PEEK healing abutments. PEEK-customized healing abutments can be created virtually utilizing dental implant software prior to implant surgery and implanted following implant insertion [11].

To use as chairside fabrication, a temporary PEEK cylindrical abutment was used with a flowable composite to guide the shape of the tooth socket. However, in that study, the researchers also mentioned the drawback of its inert surface, which causes poor bonding to dental materials [17].

In addition, PEEK temporary abutments are currently of great interest because of their ease of adjustment at the chairside. According to the review paper on implant abutments, there is a dearth of research on the PEEK abutment's durability. However, the results indicate that more investigation is required to completely comprehend its long-term performance and possible benefits over conventional materials. This information gap emphasizes the significance of continuing research to assess PEEK abutments' dependability and effectiveness in clinical situations [30].

2.2.2 Polymethyl methacrylate (PMMA)

Self-cured PMMA may provide ease of chairside manipulation but may limit the manufacturing of customized healing abutments due to its poor qualities, including

low wear and fracture resistance [31]. Several researchers tested the utilization of CAD/CAM PMMA as a customized healing abutment for socket closure following: immediate [12] and delayed implant placement [11, 32].

An implant-supported crown with a temporary plastic abutment produced a satisfactory aesthetic outcome and adequate oral function, according to a case study [33]. Other researchers, however, examined how the type of framework abutment—plastic, plastic with a foundation of cobalt chrome, and titanium—affects the provisional crowns supported by implants. They demonstrated that while the plastic abutments cannot endanger the implant, they can only tolerate stress for three months [18].

2.2.3 Resin Composite

Two types of resin composites were employed to fabricate customized healing abutments: flowable [34], and packable materials. Studies have shown that resin composite can be applied to various materials, such as PEEK or titanium interim abutments, to shape the extraction socket for quick implant placement. When a resin composite bonds with other materials to form the emergence profile zone, the cured composite offers a clear three-dimensional picture of the soft tissue profile around the implant. There are various advantages to adopting an anatomic harmony abutment for both immediate and conventional implant placement [35]. The fracture strength of three types of provisional implant abutments, veneered with composite resin restorations at four distinct places in the maxillary regions, was evaluated for use as implant-supported provisional single crowns [19].

2.2.4 Zirconia

In Weigl P., 2019 study, prefabricated zirconia healing abutments were compared to conventional titanium healing abutments. A major drawback in the use of zirconia healing abutment is that subsequent modifications of these abutments can lead to the propagation of tensile stresses, and another factor is the high cost of using CAD CAM fabrication of zirconia healing abutment [15].

The utilization of zirconia as an implant abutment should be restricted to scenarios involving minimal occlusal load and high aesthetic requirements [36].

2.2.5 Titanium

Customized titanium healing abutments require the use of CAD/CAM implant software and have been proven to have a better prognosis than the use of conventional healing abutments [14, 37].

Titanium alloy temporary abutments are commonly utilized in the fabrication of implant-supported provisional restorations, employing either traditional or CAD/CAM PMMA materials, resin composites, or temporary resin substances for the crowns [19, 37, 38].

2.3. Literature of Shear Bond Strength (SBS) of PEEK to Resin Composite

Surface pretreatment of PEEK with sandblasting with 50 or 110 μm alumina or the Rocatec system did not give any adhesion with the universal resin cement RelyX Unicem (3M ESPE). However, the utilization of an adhesive (Heliobond) and the composite resin (Tetric) led to SBS values ranging from 11.5 ± 3.2 MPa (silicate coating) to 13.5 ± 2.4 MPa (sandblasting 50 μm). The maximum bonding strengths were achieved for both resin systems when the PEEK was chemically pretreated with 98% sulfuric acid. [39].

Stawarczyk et al. in 2013 reported that the highest SBS values were achieved in the sulphuric acid surface treatment for the 1-minute group than in air abrasion (50 or 100 μm) and silica coating groups. They concluded that acid etching should be applied when PEEK is used as a substructure material veneered with composite resin material. [40].

When the visio.link adhesive system is polymerized for 90 seconds with a halogen light curing unit (LCU) rather than an LED LCU, it delivers effective and long-lasting bonding with various PEEK compositions. According to the findings of this study, various parameters such as different wavelength ranges and the presence of titanium dioxide (TiO_2) filler particles are expected to generate complicated effects that can influence the bonding capabilities of PEEK [41].

Scotchbond Universal and Adhese Universal are examples of universal adhesive systems that can be used instead of Visio. Link for appropriate bonding for PEEK because of comparable findings in terms of tensile bond strength and survival rates [42].

Three different patterns of laser ablation were designed and applied to the PEEK surface and compared with the sulphuric acid etching as surface treatment methods, and

the SBS of PEEK to dual-cure resin cement was tested. SEM images of the fractured specimens demonstrated that the resin cement could not flow properly to the retention holes ablated by laser. The shear bond strength of unfilled PEEK to resin cement was lower in the laser ablated group than the sulphuric acid etching group [43].

One study examined the effects of surface pretreatment with varying concentrations of sulfuric acid, etching 70, 80, 85, 90, and 98% sulfuric acid for 60 seconds on surface characteristics and bonding between Polyetheretherketone (PEEK) (Dentokeep) and a resin composite (Filtek™ Z350XT Flowable restorative) using Heliobond dental adhesive. 90 and 98% sulfuric acid etched PEEK achieved higher SBS values than the other groups [44]. The highest SBS values of PEEK to resin composites were recorded for grit-blasted PEEK modified by sulfuric acid treatment, combined with the use of methacrylate-based adhesives [45].

The SBS of PEEK is nearly the same as zirconia, although higher SBS was observed in the PEEK group. In that investigation, the PEEK group was treated with CRB-Ceraresin Bond (Shofu). A single application of Bond I CRB—Ceraresin Bond (Shofu) was applied and air dried for 10 seconds. Then, Bond II CRB—Ceraresin Bond (Shofu) was put in a single layer and lightly polymerized. Following that, the specimens were coated with Ceramage Indirect resin composite (Shofu, Dentin A2 shade). The zirconia group was treated with AZ Primer (Shofu, Kyoto, Japan) for 10s. The specimens were then coated with Ceramage Indirect resin composite (Shofu, Dentin A2 shade) [46].

The SBS of composite resin to PEEK under hypobaric and hyperbaric pressure changes in different PEEK surface treatments (sandblasted, acid-etched, and nontreated) was tested, and the result showed that the acid-etched PEEK had the highest SBS regardless of the environmental pressure variations, but bonding strengths were lower in all groups after changing environmental pressure [47].

Gouveia et al. 2022 tested the SBS of pressed and milled PEEK and PEKK to composite resin and concluded that they have similar SBS when the same surface treatment (airborne-particle abrasion with 110-µm aluminum oxide) and the bonding protocol using MMA and PETIA containing adhesive (visio. link) was utilized [48].

The impact of various surface treatments on the SBS of PAEEKs (PEEK and PEKK) on light-cure composite and lithium disilicate ceramic veneering materials was

assessed, and it was determined that 60 seconds of sulfuric acid solution (98%) etching is more effective on the PEEK polymer than PEKK. Sandblasting with 110 μm Al_2O_3 and tribochemical silica coating with 110 μm modified Al_2O_3 can greatly increase the SBS values of both polymers. The combined use of 98% sulfuric acid with sandblasting or tribochemical silica coating did not considerably enhance the SBS values [49].

2.4. Surface Treatment Methods of PEEK for Adhesive Bonding

Surface treatment methods for PEEK can be generally categorized as chemical and mechanical modifications. Chemical modifications can be sub-categorized as sulfonation (sulphuric acid etching) [44] And non-sulfonation, which includes plasma surface treatment [50] surface coating with hydroxyapatite [51] and using adhesive bonding agents containing methyl methacrylate (MMA), dimethylacrylate (DMA), pentaerythritol triacrylate (PETIA) [52] or 10- methacryloyloxydecyl dihydrogen phosphate (MDP) [53]. Mechanical modifications include airborne particle abrasion [53], and laser surface treatment [54].

The sulfonated poly(ether-ether-ketone) (SPEEK), a fluorine-free ionomer, is created by the chemical surface modification caused by PEEK sulfonation by immersion in concentrated sulfuric acid. Each repeat unit is made up of an aromatic backbone of 1,4-disubstituted phenyl groups separated by ether (-O-) and carbonyl (-CO-) linkages, with the $-\text{SO}_3\text{H}$ group typically bonded to the oxy-phenylene-oxy unit as illustrated in Figure 1 [55].

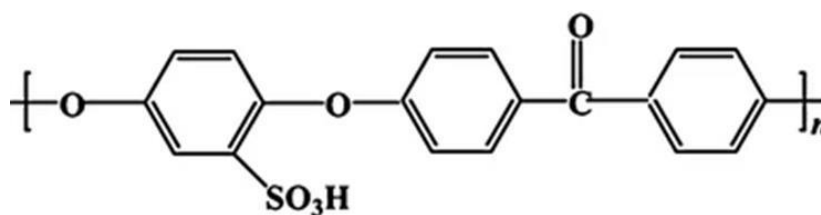


Figure 1 Sulfonated PEEK [55]

Aromatic polymers can be modified in a variety of ways through sulfonation, which also acts as a baseline for further modification. The ideal sulfonation period was determined to be 5 min due to its effective formation of a porous structure, comparatively low residual sulfuric acid content, and favorable cytocompatibility [56].

Sandblasting followed by a low-pressure plasma process using oxygen plasma for a duration of 35 min seems to be the most favorable surface treatment method to increase the shear bond strength between veneering composites with both filled and unfilled PEEK materials [57]. The combined use of air abrasion and surface treatment with low-pressure argon/oxygen plasma increased SBS significantly, especially on unfilled PEEK material. However, the usage of plasma surface treatment alone is not as effective as the use of sandblasting alone [50].

On SEM analysis, the surface treatment of PEEK with 50 μm particle size sandblasting revealed a more pronounced and distributed surface pattern than the 110 μm pre-treatment [39]. The shear bond strength between veneering composite resin and PEEK and PEKK polymers was strengthened by airborne-particle abrasion with 110- μm aluminum oxide; however, all specimens displayed 100% adhesive failures [48]. The 2020 meta-analysis noted that, of the many mechanical and chemical pretreatments used in the included studies of Gama L. T., only air abrasion was used with comparable methodology across investigations. Accordingly, a comparison of air abrasion applications showed that (50 μm alumina) enhanced SBS by an average of 4.90 MPa [58].

The surfaces of the PEEK (Vestakeep: PEEK + TiO_2) were irradiated with a Neodymium-doped yttrium orthovanadate (Nd: YVO₄) laser, and the luting agents used: Panavia V5, RelyX Ultimate Resin Cement, G-CEM Link Force, and SuperBond C&B were applied, and it was concluded that the SBS between the PEEK and resin-based luting cement was substantially increased by laser surface treatment [59].

2.5. Methods of Hydroxyapatite Coating PEEK

There are several commercial coating methods available for HA coating on PEEK. These methods include:

- Spin-coating [60],
- Aerosol deposition [61],
- Cold spraying [62],
- Radiofrequency magnetron sputtering [63]
- Dip coating after surface treatment with sandblasting [51] and
- Crystalline HA coating on PEEK via chemical deposition [64]

The PEEK implants were coated with nanoHA solution, which contained surfactants, organic solvents, and an aqueous solution of Calcium Nitrate ($\text{Ca}(\text{NO}_3)_2$) and Phosphoric acid (H_3PO_4). The spin coating method was applied, followed by a 10-minute drying period. The sample was then heat-treated at 300°C to enhance the adherence of the crystals to the PEEK surface. Using this technique, the implant surface developed a thin coating of crystalline HA [60].

The HA particles in the aerosol chamber were blasted with a carrier gas and deposited onto the PEEK substrate via a nozzle after the PEEK substrate was placed in the deposition chamber. Compressed air was employed as the carrier gas, and its flow rate was set at 20 L/min. The whole surface of the PEEK substrate was covered with a $5\text{ }\mu\text{m}$ thick HA coating, which was then hydrothermally treated for 20 hours at 190°C in an autoclave [61].

The cold spraying HA coating method was like the equipment used in the Aerosol deposition HA coating procedure. However, The spray particle had a short contact time with the preheated carrier gas and cooled quickly after being fired from the nozzle. The real temperature of the HA beads is only about half the preheating temperature ($200, 300, 400^\circ\text{C}$) of the carrier gas, as measured by thermocouples. To avoid heat damage to PEEK, the maximum localized heating of 400°C during the coating process was kept below 200°C [62].

The radiofrequency (RF) magnetron sputtering HA coating technique needs three steps. Before coating HA, the PEEK surface was treated by oxygen plasma activation. The yttria-stabilized zirconia (YSZ) coating layer was next deposited over 8 hours at 80 W RF power, followed by the HA coating layer, which was coated over 6 hours at 150 W RF power. The third step was post-deposition heat treatment using microwave annealing or hydrothermal annealing [63].

These HA coating methods need to modify the post-treatment heat method, and it can affect the crystallinity and chemical composition of HA. Moreover, another disadvantage is the detachment of the HA coating layer from the substrate [65].

HA-coated PEEK specimens were sandblasted with $110\text{-}\mu\text{m}$ Al_2O_3 at a pressure of 2 bar and a distance of 10 mm for 20s. The specimens were then air dried after being ultrasonically cleaned for five minutes using 96% ethanol. By mixing 1%, 3%, 5%, and 10% nanoHA powder into 60% ethanol for HAp coating solutions, four different

coating solutions were created using the sol-gel process. Dip Coating equipment was used to coat the solutions after HCl was added to bring their pH down to 8, and they had been mixed for four hours in a magnetic stirrer. After coating the samples at a rate of 10 cm min^{-1} immersion, they were removed from the solution and allowed to dry at room temperature for a day. The SBS was then measured [51].

The procedure for crystalline HA coating on PEEK by chemical deposition is that PEEK samples were sulfonated, and the $-\text{SO}_3\text{H}$ group was introduced and termed SPEEK. Deposition of HA particles was achieved chemically through immersion of the sulfonated PEEK in HA suspension. The HA particles that have the $-\text{OH}$ group on their surface were attached to the $-\text{SO}_3\text{H}$ group on the SPEEK layer due to the polarity property. EDX, FT-IR, and XRD analysis confirmed the deposition of HA particles, and analysis confirmed the chemical bonding of HA to SPEEK [64].

2.6. Mechanism Between Sulfonated PEEK with Hydroxyapatite

There are two assumptions for forming HA on sulfonated PEEK. The first one is the $-\text{OH}$ group on the HA surface connected to the $-\text{SO}_3\text{H}$ group on the sulfonated PEEK (S-PEEK) layer due to the polarity property (Figure 2). The formation of HA was confirmed by EDX, FTIR, and XRD analysis [64].

The second assumption is that the presence of the SO_3H functional group in polymers can enhance the nucleation of HA in simulated body fluid, just transforming the chemical composition and structure of the outer surface layer without altering the substrate bulk properties of polymers (Figure 3) [66].

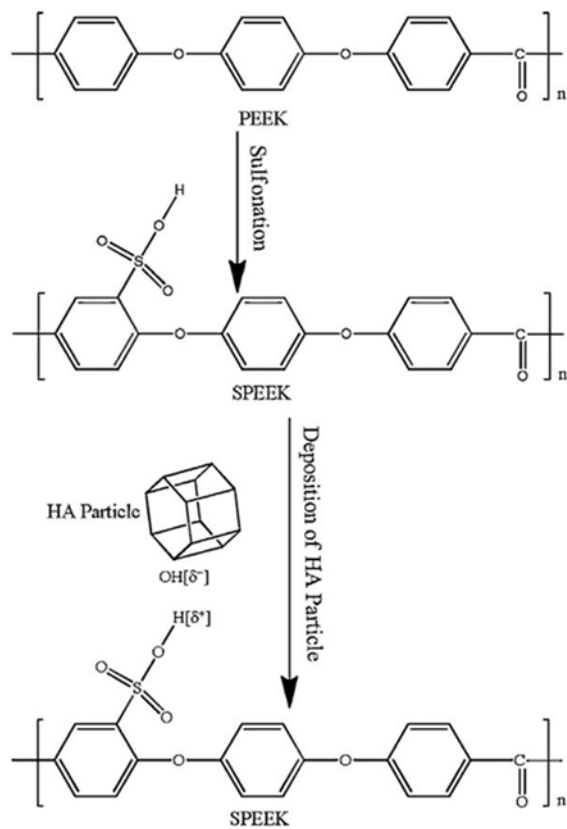


Figure 2 Schematic figure of deposition of HA on PEEK [64]

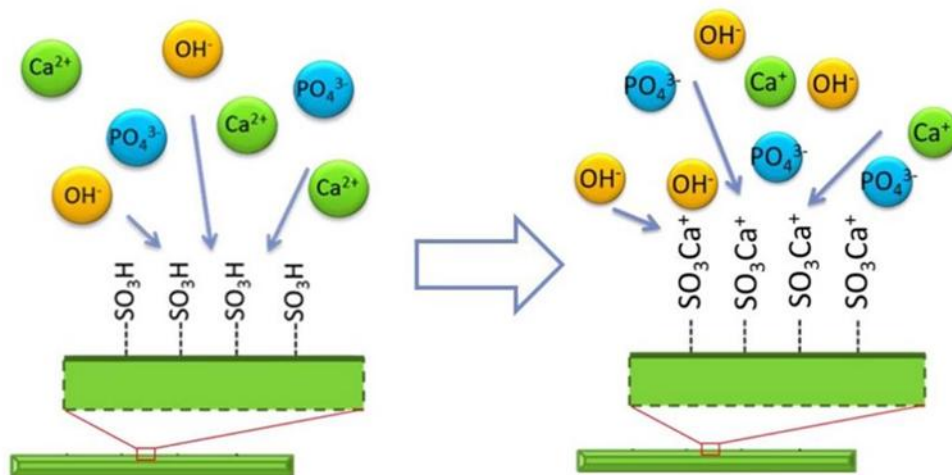


Figure 3 Mechanism of HA precipitation over sulfonated PEEK [67]

2.7. Analytical methods to confirm the Characterization of Hydroxyapatite

To characterize HA, the widely used analytical methods are X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR), atomic force microscopy (AFM), transmittance electron microscopy (TEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), etc. along with other instrumental techniques [67, 68].

Fourier Transform Infrared (FTIR)

IR analyses give the following information: (a) identity; (b) purity, whether uni- or multiphasic; (c) presence of functional groups (e.g., HPO_4^{2-} , CO_3^{2-} , PO_4^{3-} , $\text{P}_2\text{O}_7^{2-}$ organic component, etc.); (d) environment of the functional groups (lattice-bound or free state); (e) effect of the incorporation of one element on the vibration frequency of other functional groups (e.g., CO_3^{2-} or F- on the character and frequency of the vibration bands of the PO_4^{3-} or OH^-); (f) type of substitution (g) crystallinity: well crystallized, poorly crystallized or 'amorphous' (h) type and relative amount of constituent. [69].

Before HA coating, the formation of the sulfonic acid group $-\text{SO}_3\text{H}$ needs to be confirmed using FTIR analysis. The bands at 1010 cm^{-1} , 1380 cm^{-1} , 1450 cm^{-1} , and 1552 cm^{-1} , which correspond to sulfonic (SO_3H) groups, were observed in the FTIR spectra of the 3-min H_2SO_4 -etched PEEK [70].

The first functional group of HA that can be found in FTIR analysis is phosphate groups, which show the four fundamental vibrational modes (symmetric stretching, asymmetric stretching, symmetric bending, and asymmetric bending). Four different vibrational modes are expected to be exerted by phosphate ions, a sort of tetrahedral ion or molecule: ν_1 , ν_2 , ν_3 , and ν_4 . Bending vibration produced peaks in 465, 563, and 599 cm^{-1} wavenumbers, while three stretching modes of vibration were seen near 962, 1026, and 1087 cm^{-1} wavenumbers; these bands are also present in HA [68].

The second functional group of HA that can be detected in HA is the hydroxyl group, which can be found as the small peaks near the bands of 630 cm^{-1} and 3550 cm^{-1} [68]. Pure HA can be proved by the phosphate group and seen as peaks at 965 cm^{-1} (a single intense band) and 470 cm^{-1} between $1050\text{--}1095\text{ cm}^{-1}$ and $565\text{--}602\text{--}635\text{ cm}^{-1}$ (three

sites) for n1, n2, n3, and n4, respectively. The sharp band at 3570 cm^{-1} is due to hydroxyl stretching and is visible only in pure HA [71].

X-ray Diffraction (XRD)

X-ray diffraction (XRD) is applied to identify inorganic crystals, measure the degree of crystallinity, and determine the size of the crystal and crystalline orientation.[61] XRD analyses give information on the crystallographic properties, e.g., atomic arrangements of Ca^{2+} , PO_4^{3-} , and OH^- in HA [69].

The HA-coated samples after sulphuric acid treatment, PEEK was confirmed by the XRD analysis, and for HA-coated specimens, the spectrum shows “a slight intensity of peaks belonging to the (0 0 2) and (2 1 1) crystallographic planes of HA” [64].

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS, EDX)

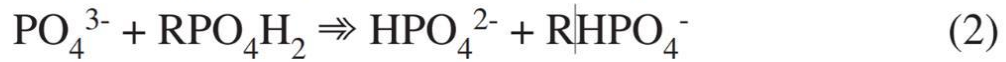
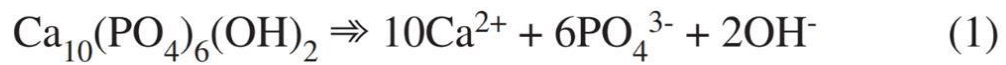
Scanning Electron Microscopy (SEM) analyses are useful in evaluating surface and crystal morphology [61, 63] Energy Dispersive X-ray Spectroscopy (EDS, EDX), together with SEM, can give certain information and surface composition of the samples that couldn't be identified properly with XRD. Moreover, how inorganic substrates were produced on the surface of the composite material with HA can be searched. [67].

In addition, the Ca/P molar ratio can be calculated from the data obtained from EDS analysis. The atomic weight of calcium is 40.078 g/mol, and phosphorus is 30.9738 g/mol. To calculate the molar ratio of Ca/P in hydroxyapatite from EDS analysis, the following formula is used:

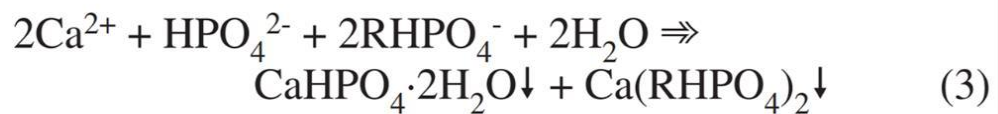
Ca/P molar ratio = (Ca weight% / Ca atomic weight) / (P weight% / P atomic weight) [72].

2.8. Bonding Mechanism Between Hydroxyapatite and MDP Containing Dental Adhesive Agents [73]

The following may then explain the mechanism of MDP adsorption, HA decalcification, and calcium salt deposition: MDP adsorption (RPO_4H_2 with R = 10-methacryloyloxydecyl group) in the aqueous solution causes the following decalcification reaction:



Co-precipitation of calcium salts with low solubility:



However, phosphoric acid etching of dental enamel before the use of the Scotchbond Universal Adhesive system improves bond strength instead of using adhesive only because the pH of the universal adhesive 2.7 is not enough to obtain an adequate etching pattern after Confocal Raman spectroscopy analysis [74].

Therefore, in this study, the shear bond strength of PEEK veneering with composite resin will be tested using MDP containing bonding agents and compared by applying five surface treatment methods, including:

1. No surface treatment as a negative control,
2. sandblasting with 50 μm aluminum oxide, and
3. 1-minute sulphuric acid etching as positive control,
4. The crystalline HA chemical deposition of the hydroxyapatite coating and
5. Phosphoric acid etching after hydroxyapatite coating surface treatments as innovative methods.

2.9. Fracture strength of PEEK abutments with various crown materials.

Implant-supported single provisional restorations in implant dentistry can be classified into cement-retained or screw-retained [75]. Among the various types of provisional abutment material, PEEK abutment is the first-line option because of its robust properties, such as its biocompatibility, ease of adjustment in chairside manipulation, and acceptable mechanical properties [20]. Moreover, PEEK abutments can be used as cement or screw-retained provisional abutment veneering with composite resin or cementing with provisional crowns. Although temporary abutments

are used only for a short duration, they have to be able to withstand the occlusal forces during function. [17].

The fracture strength and fatigue mode of two commercially available PEEK provisional implant abutments were compared with solid titanium provisional implant abutment veneering using Solidex resin composite for four distinct locations in the maxillary area. All abutment types were determined to be similar, except for the maxillary central incisor region. However, most of the failure types in PEEK abutments were adhesive failure, and cyclic loading was not applied in this study [19].

However, the fracture resistance of ceramic-reinforced PEEK implant abutment with the titanium base was compared with the titanium and zirconia implant abutment supporting lithium disilicate ceramic crowns for the maxillary central incisor. They concluded that the ceramic-reinforced PEEK could be an alternative to zirconia abutment for that region [76].

The marginal gap and fracture resistance of the PEEK (Bio HPP) framework were compared with the titanium framework veneered with the composite resin for implant-supported three-unit fixed dental prostheses. The fracture load of PEEK was 1518 ± 134 N, and they concluded that it is a suitable alternative to a metal framework to be veneered with resin composite [77].

Barbosa-Junior et al. also studied the mechanical fatigue analysis of customized hybrid abutments made of PEEK and yttria partially stabilized zirconia polycrystals (YZ) supporting two types of all-ceramic crowns made of translucent zirconia (TZ) and lithium disilicate (LD) crowns. According to that study, the mechanical fatigue performance of PEEK hybrid abutments can be compared with that of YZ abutments, regardless of the crown material [22].

When PEEK veneered with lithium disilicate crowns and resin composite crowns were observed for load-bearing capacity, it was found that both types met the necessary fracture strength (400 N) for any material to withstand occlusal force in the posterior region. However, the effect of the different surface treatments of PEEK veneered with lithium disilicate crowns was found. Also, in sandblasted PEEK veneered with resin composite crowns, all the failure specimens were due to the adhesive failure between PEEK and resin composite. Therefore, the researchers

recommended additional research on PEEK surface treatments to strengthen the bond between PEEK and the veneering material, using the aging conditions [78].

Recently, an *in vivo* study comparing a screw-retained PEEK abutment veneered with Cera.lign composite and a screw-retained porcelain-fused metal crown for short implants showed that the PEEK abutment had a better prognosis after 6 months in terms of stability and marginal bone loss [79].

One of PEEK's greatest advantages is that it can be reprocessed using a pressing procedure, and there is no discernible difference in strain value or fracture resistance between newly produced and reprocessed PEEK. The results of this observation proved that PEEK could be used for a posterior single-implant restoration and has a valuable benefit for “Green Dentistry” [80].

CHAPTER 3

RESEARCH METHODOLOGY

4.1 Study design

- Factorial design in vitro study for part 1
- Comparative experimental study for part 2

4.2 Study Population

Total 153 PEEK specimens: 120 PEEK specimens for shear bond strength test (n=12) in each surface treatment group for Single bond universal bonding agent (n=60) and for Scotchbond universal plus bonding agent (n=60) were used. 25 PEEK specimens for surface roughness and contact angle measurements (n=5 in each surface treatment group), and 3 PEEK specimens for surface characterization of hydroxyapatite coating confirmation (n=3): no surface treatment PEEK (n=1) for SEM, after sulphuric acid treatment (n=1) and after HA coating (n=1) were tested for SEM, EDS, FTIR and XRD analysis. One specimen from each surface treatment group (n=5) was analyzed for EDS mapping.

A total of 30 customized PEEK provisional crowns (N=30) were surface treated by (1) sandblasting (n=15) and (2) HA coating after sulfonation (n=15).

4.3 Study Area

Research Center Lab and Department of Prosthetic Dentistry at Faculty of Dentistry, The Office of Scientific Instrument and Testing (OSIT), and Department of Physics, Prince of Songkla University.

4.4 Study Period

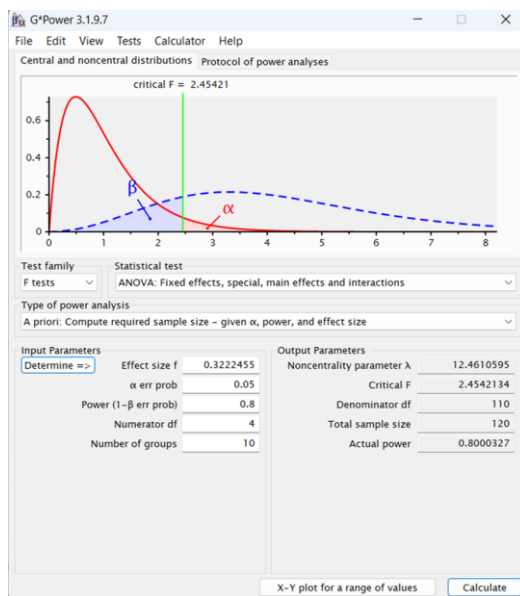
Starting from August 2022 to February 2025

4.5 Sample size determination

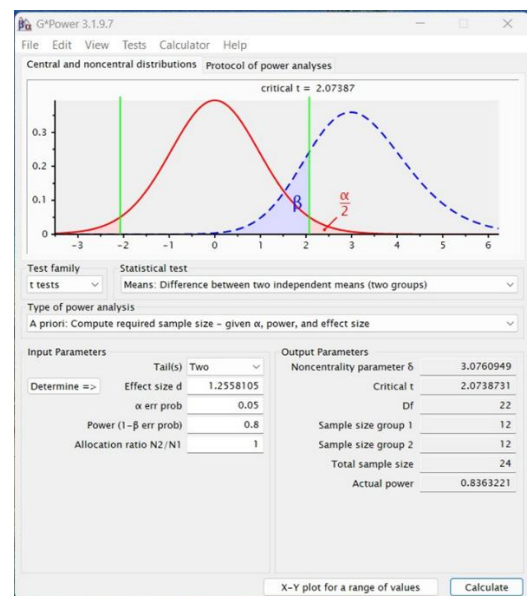
The sample size was calculated using the G* Power software (Version 3.1.9.7, University of Dusseldorf, Germany). The alpha value (α) of 0.05, a power value (β) of 0.2, and an effect size (f) of 0.322 were considered according to the pilot study results. The total number of groups was 10: Single bond universal bonding application contains 5 surface treatment groups, and Scotchbond universal plus bonding involves 5 surface

treatment groups. The numerator degree of freedom (df) was calculated depending on the factors: $(5-1) \times (2-1) = 4$. The minimum sample size of each subgroup was estimated to be 12 for the part 1 study.

For the part 2 study, the alpha value (α) of 0.05, a power value (β) of 0.2, and an effect size (f) of 0.8 were considered according to the pilot study result. The minimum required sample size was $n=12$.



(a)



(b)

Figure 4 G* Power sample size calculation (a) For part 1 study (b) For part 2 study

4.6 Sampling method and procedure

4.6.1 Sampling method

Simple random sampling method

4.6.2 Sampling procedure

The sample was selected conveniently and randomly.

4.7 Data collection tools and techniques/ research procedure

4.7.1 Data collection tools

The SBS and fracture strength of composite resin to PEEK were collected by using a universal testing machine. The values of surface roughness (Ra) of the specimens for each surface treatment group were examined using a 3D-surface Profilometer, and the contact angle was measured by the Contact Angle Goniometer (OCA 15plus, Data Physics) equipment.

4.7.2 Data collection technique

Quantitative data collection techniques – SBS was expressed in Mega-Pascals (MPa), and fracture strength was expressed in Newtons (N). Surface roughness was expressed as micrometers (μm), and contact angle was expressed in degrees.

Research Procedure

Sample preparation for Shear Bond Strength Test

The materials used in this study are described in detail in Table 1, and the mechanical properties of the V smile Dental PEEK Disc (yellow color) (HUNAN VSMILE BIOTECHNOLOGY CO., LTD, Changsha, China) (Lot No V 23101311) are prescribed in Table 2. The schematic figure of study design for part 1 is illustrated in Fig. 5. PEEK disc with the diameter of 98mm and the thickness of 16 mm was milled into the PEEK blocks with a dimension of $7 \times 7 \times 16$ mm by using the CAD-CAM and the PEEK blocks were cut into the PEEK specimens of $7 \times 7 \times 5$ mm with ISOMET 1000 Gravity-fed Precision Sectioning Machine (Buehler UK Ltd, England). The PEEK specimens were grounded with 600, 800, 1000, 1200, and 1500-grit silicon carbide paper (TOA, Samutprakarn, Thailand) with the speed of 400 rpm under running water to remove the abrasive particles from the sample surface by using Buehler Metaserv Grinder Polisher (Buehler UK Ltd, Coventry, England). After that, the specimens were ultrasonically cleaned with distilled water for 10 min twice, then dried using compressed air. The surface roughness of all the specimens was checked using 3 D Surface Profilometer (VR 6000, KEYENCE, America) with a cut-off value of $0.8 \mu\text{m}$ before applying the surface treatment methods and was standardized not more than $0.2 \mu\text{m}$.

Then, the PEEK specimens were assigned to five surface treatment groups, which received the following surface treatments ($n = 24$) for each group:

- The first group, as a control, did not receive any surface treatment. (PEEK)
- The second group was sandblasted with $50 \mu\text{m}$ aluminum oxide (Parkell Aluminum Oxide (50 microns)) at a 10 mm distance from the nozzle to the specimen at an angle of 45° for 20 seconds with 2 bar pressure [81], and the specimen surface was ultrasonically cleaned with deionized water for 10 minutes and then air-dried with compressed air for 20 seconds. (Sa PEEK)
- The third group specimens were treated by a drop of $\sim 10 \mu\text{L}$ of concentrated sulphuric acid (94-97%) (EMSURE® ISO (Merck KGaA, Frankfurter Str. 250, 26 D-64271

DARMSTADT, Germany) using a micropipette for one minute at ambient temperature. The specimens were then rinsed with deionized water for 10 min until no traces of acid remained. [70] (S-PEEK)

- The fourth group of surface treatment was immersion of the specimens in 10 mL of concentrated sulphuric acid (98%) for 3 min at room temperature. The specimens were then rinsed with deionized water at ambient temperature until no traces of acid remained, and the sulfonated PEEK specimens were dried overnight at room temperature. Subsequently, hydroxyapatite will be coated over S PEEK, and this group was named HA PEEK. The HA coating procedure was explained in detail in the following. (HA PEEK)
- The same surface treatment as in the fourth group was applied in the fifth group, and in addition, 34% phosphoric acid etching (3M™ Scotchbond™ Universal Etchant - Etching Gel, 41263, Seefeld, Germany) for 15 sec was used before bonding and rinsed with deionized water for 10 seconds. (HAP PEEK)

Hydroxyapatite coating

The fourth and fifth groups of sulfonated specimens were dried overnight, and the S PEEK specimens were placed in a 10% wt/v hydroxyapatite 289396 (Sigma Aldrich, USA) suspension in water for 5 hours and stirred continuously with a magnetic stirrer (IKA Mild Steel C Mag HS 7 Digital Magnetic Stirrer, model number - CMAG HS7) with a speed control scale of 1.5.

To get a 10% wt/v hydroxyapatite suspension, 10 g of HA powder was weighed in a Mettler Toledo AE200 Analytical Balance and then mixed with 100 mL of deionized water.

Two specimens hanging with a plastic rope were placed in 100 mL of HA suspension for 5 hours and stirred with a magnetic stirrer. After completion of 5 hours, the specimens were removed, washed, and cleaned with deionized water to dispose of any HA particles that were not chemically connected to the specimens. The specimens will be dried at room temperature overnight.

Three additional specimens from HA PEEK: no surface treatment (n=1), after 3 min sulphuric acid immersion (n=1), and after HA coating (n=1) will be tested to confirm the sulfonic group forming and hydroxyapatite forming over sulfonated PEEK

and to compare the original PEEK by analyzing SEM, EDS, FTIR, XRD, and one specimen from each surface treatment group (n=1) was done for EDS mapping.

Shear bond strength testing (SBS)

Following the respective surface treatment, the specimens in each group were assigned equally into two groups: the first group of specimens was applied Single bond universal adhesive (3 M, Seefeld, Germany), and the second group of specimens was applied Scotchbond universal plus adhesive (3 M, Seefeld, Germany).

The specimen was inserted into the stainless-steel mold holding with the screw jig (Fig. 6a). Then, a uniform thin layer of MDP containing adhesive material was applied with a disposable applicator and rubbed in for 20 seconds onto the PEEK specimens, direct a gentle stream of air over the liquid for about 5 seconds, and light cured for 10 seconds using LED LCU (3M™ Elipar™ DeepCure-L LED Curing Light, 3M ESPE, St. Paul, MN, USA) (1.47 mW/cm^2) (430-480 nm Wavelength).

Once the adhesive film had been cured, the mold was placed into the bonding clamp containing a white plastic button mold with a hole diameter of 3 mm and a 2 mm thickness. Resin composite (Filtek™ Z350XT Flowable restorative, 3M ESPE) was filled in the white plastic button mold and light-polymerized for 40 seconds. The screws on the bonding clamp were loosened and the specimen from the mold was removed using a packing instrument applying pressure directly downward onto the cured composite button until the specimen was released. Subsequently, all specimens were stored in distilled water at 37°C for 24 hours in the incubator. Then, thermocycling aging between 5°C ($\pm 2^\circ\text{C}$) and 55°C ($\pm 2^\circ\text{C}$) with a 30-s dwell time in each water bath and 10-s transfer time for 5000 cycles was done for all the specimens.

The SBS of resin composite to PEEK specimens for both bonding adhesive groups was tested by using a universal testing machine (AG-10KNX, Shimadzu Co., Kyoto, Japan). The mold connected with the PEEK specimen was connected to the device's holder, and a knife-edged chisel brake with a load of 250 newtons was directed to the bonding interface at a crosshead speed of 1 mm/min until failure occurred as shown in Fig. 6b. When the resin composite was separated from the PEEK surface, the load at failure was measured. SBS was expressed in Mega-Pascals (MPa), calculated by dividing the maximum value of the load at failure in newtons (N) by the bonding area in square millimeters (A).

Mode of failure analysis

After failure, shattered PEEK and resin composite specimens were examined under a light microscope (Olympus BX 60, Olympus; Tokyo, Japan) at 50X magnification. Scanning electron microscopy (SEM) was used to determine the kind of failure in one representative specimen from each surface treatment group. Failure modes were classified into three types: adhesive failure (80-100% failure at the interface between adhesive and PEEK), cohesive failure (80-100% failure within the HA coating, PEEK, or resin composite), and mixed failure is a combination of adhesive and cohesive failures.

Surface Characterization

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDS) analysis

Three specimens for HA coating confirmation were investigated using SEM (SU 3900, Hitachi, Hitachi High-Tech Corporation, Tokyo, Japan) coupled with EDS. EDS mapping was performed on one specimen from each surface treatment group.

Fourier Transform infrared spectroscopy analysis (FTIR)

FTIR analysis was performed on two specimens: 3 min sulfonated PEEK (n=1) and HA-coated sulfonated PEEK (n=1), using a Bruker ALPHA portable spectrometer (VERTEX 70, Bruker, Karlsruhe, Germany) with a single reflection diamond attenuated total reflection (ATR) module. FTIR analysis covered a frequency range of 4000 to 400 cm^{-1} , with a spectral resolution of 4 cm^{-1} .

X-ray Diffraction analysis (XRD)

XRD was performed on two specimens: 3 min sulfonated PEEK (n=1) and HA-coated PEEK (n=1) using a Diffractometer D5000 (Siemens, Karlsruhe, Germany) with a Cu X-ray tube operated at 40 kV and 30 mA to confirm the presence of the HA coating layer. Data was collected in the 2θ range of 20 to 80 degrees.

Surface roughness (Ra) and wettability analysis

Five extra specimens were generated from each surface treatment group to test wettability and Ra. Wettability was determined by measuring the water contact angle (CA) using the sessile drop method and digital image processing software. CA measurements were taken using a Contact Angle Goniometer (OCA 15plus, Data Physics Instruments GmbH, Germany) with a 3 μL drop of deionized water. Three

random surface points were assessed for each specimen, and angles were recorded following a 5-second exposure to the liquid (three measurements per specimen). Ra was measured using a 3D Surface Profilometer with a cut-off value of 0.8 μm at two points on each specimen. The mean Ra value was then calculated.

Sample Preparation for Fracture Strength and Failure Mode of Implant-Supported Provisional Resin Composite Crowns after sandblasted and Hydroxyapatite-Coated PEEK

The study procedure for part 2 is demonstrated in Figure 7. Straight cylindrical-shaped PEEK temporary abutments (5mm diameter and 3mm gingival height) for a 5.0mm Osteem implant with a regular connection were milled using computer-aided design/computer-aided machining (CAD/CAM) (Figures 8a and 8b). Figures 9a and 9b show the abutment's exact dimensions. Before the surface treatment, the abutments were linked to the lab analog to determine the level of surface treatment required. The portion of the cervical region that did not require surface treatment was covered with paper tape positioned 1 mm above the analog level (Figure 8a). Then they were divided into two surface treatment groups:

1. Sandblasting (Sa) [82] with 50 μm aluminum oxide with 2 bar pressure for 20 s and
2. Hydroxyapatite coating sulfonated PEEK (HA): At ambient temperature, the abutments were immersed in 98% concentrated sulfuric acid for 3 min up to 1 mm above the analog level that was marked before, then rinsed thoroughly with deionized water, and dried overnight. Subsequently, a 10% hydroxyapatite suspension was prepared by mixing 10 g of HA powder (Mettler Toledo AE200 Analytical Balance) with 100 mL of deionized water. Two abutments were simultaneously coated in a continuously stirred 100 mL hydroxyapatite suspension at a speed setting of 1.5 for 5 hours, utilizing an IKA Miled Steel C Mag HS 7 Digital Magnetic Stirrer. Post-coating abutments were rinsed with deionized water to eliminate unattached HA particles and subsequently dried overnight [64].

A thin layer of Scotchbond Universal Plus Adhesive (3M ESPE, St. Paul, MN, USA) was applied with a disposable applicator and gently rubbed onto the surface-treated PEEK abutments for 20 s. The specimens were dried with compressed air for

5s, followed by light curing for 20 s (10 s each on one side) using an LED light curing unit (3M™ Elipar™ DeepCure-L LED Curing Light, 3 M ESPE, St. Paul, MN, USA) operating at 1.47 mW/cm² (430-480 nm wavelength). Then, bulk fill restorative (3 M Filtek™ Bulk Fill Restorative) was veneered over the surface-treated PEEK abutments and light-polymerized for a total of 50 s (10 s each on occlusal, buccal, lingual, mesial, and distal surfaces). A clear vinyl polysiloxane mold (Exaclear, GC Corporation, Tokyo, Japan) filled in the plastic mold was made over the wax-contoured mandibular right first permanent molar (11.15 mm mesiodistally, 10.3 mm buccolingually, and 9.7 mm height occlusocervically) crown (Figure 8c) to control the thickness of the veneered material. The crowns affixed to the implant analogs were secured with screws and tightened using a manual torque wrench to a torque of 20 Ncm, followed by a re-tightening after 10 minutes. The screw access hole was sealed with Teflon tape and bulk-filled restorative composite, then light-cured for 10 s. The crowns were subsequently polished using a series of Sof-lex discs (3 M ESPE, St. Paul, MN, USA). The Osteem 4.0 mm diameter regular fixture lab analogs, affixed with provisional crowns, were subsequently encased in polymethylmethacrylate (GC, Unifast Trad, GC Corporation, Tokyo, Japan) within polyvinyl chloride rings (Figure 8c). The four specimens (Sa=2 and HA=2) were simultaneously tested, and eight iterations were conducted to achieve the necessary sample sizes. All specimens were maintained in distilled water at 37°C for 24 hours in the incubator.

The provisional resin composite crowns (n =15) in each group were thermocycled and aged for 1000 cycles at 5°C and 55°C with a dwell time of 30 s and transfer time of 10 s at each temperature [83]. The specimens were examined under a 3-D surface profilometer, and the survival specimens were continued to mechanical cyclic loading using the chewing simulator CS-4.8/CS-4.4 (CS 4.8, SD Mechatronic GmbH, Feldkirchen Westerham, Germany) at room temperature. The force was applied perpendicular to the middle of the crowns in the distilled water by a stainless-steel ball (6mm in diameter) [84] at room temperature with a chewing simulator (Figure 10a) at an axial 50 N load for 120,000 cycles (frequency of 1.1 Hz), which is equivalent to 6 months of chewing cycles [85]. The specimens were examined by post-cyclic loading, and the failed specimens were monitored and documented twice daily during the cyclic loading process. The specimens underwent re-examination using the 3-D profilometer.

Following cyclic loading, the survival specimens were centrally positioned within the apparatus to assess fracture resistance. The specimens underwent compressive loading using a universal testing machine (Lloyd LRX-Plus, Lloyd Instruments Ltd., Fareham Hants, UK) equipped with a 5 KN load cell at a crosshead speed of 1 mm/min. A load was applied perpendicularly to the occlusal surface of the crown using a 6 mm diameter stainless steel ball. An aluminum foil of minimal thickness was placed between the stainless-steel ball and the crown (see Figure 10 b) to attain a uniform stress distribution. The load necessary for failure was documented for each specimen [85].

The fractured specimens underwent visual analysis, and digital photographs were captured using a 3D Optical Profilometer (VR-6000 Series, KEYENCE INTERNATIONAL BELGIUM, Mechelen, Belgium) at low magnifications of 12x and 25x, as well as high magnification of 40x, to ascertain the failure type, location, and size. Following the analysis of all specimens' post-fracture testing, four distinct types of failures were identified: cohesive fracture of the composite resin restoration or PEEK abutments (CF), adhesive failure between the composite resin and the abutment (AF), screw loosening (SL), and deformation of the implant analog (DIA). Failure types were categorized into irreparable (Type 1: fracture of the crown $\geq 1/2$ or deformation of the analog) and reparable (Type 2: fracture of the crown $\leq 1/2$ or screw loosening) [19]. Another examiner conducted the fracture mode analysis to mitigate bias, with any discrepancies resolved based on the third author's recommendations.

Table 1 Materials used in this study

Material used	Manufacturer	Composition	Batch number
Polyetherether ketone	V smile Dental PEEK Disc (Yellow)	Polyetheretherketone and 12% Titanium dioxide pigment	V23101311
Hydroxyapatite	289396 (Sigma Aldrich, Merck KGaA, Darmstadt, Germany)	Ca ₁₀ (PO ₄) ₆ (OH) ₂	12167-74-7
Sulphuric acid	EMSURE® ISO, Merck, Darmstadt, Germany	98% Sulphuric acid	7664-93-9
Scotchbond Universal plus	Scotchbond Universal Plus Adhesive, 3M ESPE, St. Paul, MN, USA	10-MDP, HEMA, Optimized mixture of silanes, dimethacrylate, methacrylate modified polyalkenoic acid copolymer, Dual-cure accelerator, filler, ethanol, water, initiators	10425617
Single bond Universal	Single bond Universal Adhesive 3M ESPE, St. Paul, MN, USA	10-MDP, HEMA, silane, dimethacrylate, methacrylate modified polyalkenoic acid copolymer, filler, ethanol, water, initiators	31124A
Phosphoric acid etchant	Scotchbond Etchant, 3M ESPE, St. Paul, MN, USA	34% phosphoric acid water, poly (vinyl alcohol), amorphous silica thickener	6761579

Flowable resin composite	Filtek™ Z350XT, A3 Flowable restorative, 3M ESPE, St. Paul, MN, USA	Methacrylate resin monomers, BisGMA, TEGDMA, and Bis-EMA; dimethacrylate polymer; silica (75 nm) and zirconia (5–10 nm) nanofiller; approximately 65% wt filler load	9474385 9571262
Aluminium oxide	Parkell Aluminum Oxide (50 micron)	50 µm Aluminum oxide	D675
Bulk fill composite	Filtek One Bulk Fill Restorative (3M ESPE, St. Paul, MN, USA)	Bis-GMA, Bis-EMA, UDMA, procrylat resins, a combination of zirconia/silica and ytterbium trifluoride filler	11056929 11295231
Screw	OSSTEM IMPLANT Co., Ltd. Haeundae-gu, Busan, Korea	TS EbonyGold Abutment Screw Regular	CGS24D230
Clear Vinyl Polysiloxane	Exaclear (GC CORPORATION, Tokyo, Japan)	clear vinyl polysiloxane	2405131

Table 2 Mechanical Properties of V smile CAD/CAM PEEK

Technical Parameters					
Test Items	Standard Test	Test Conditions		Unit	Typical test data
Tensile Strength	ISO527	23℃		MPa	108
Elongation at break	ISO527	fracture 、 23℃		%	12
Bending strength	ISO178	23℃		MPa	170
Flexural modulus	ISO178	23℃		GPa	4.2
Izod impact strength	ISO180/A	a gap		KJm-2	6.5
Molding shrinkage	ISO294-4	Parallel to the direction of flow		%	1.10
		Perpendicular to the direction of flow		%	1.18
Thermal properties					
melting point	ISO11357	—		℃	343
glass transition temperature	ISO11357	—		℃	143
Fluidity					
Melt Index	ISO11443	380℃		g10min	10
Others					
density	ISO1183	crystallization		gcm-3	1.48

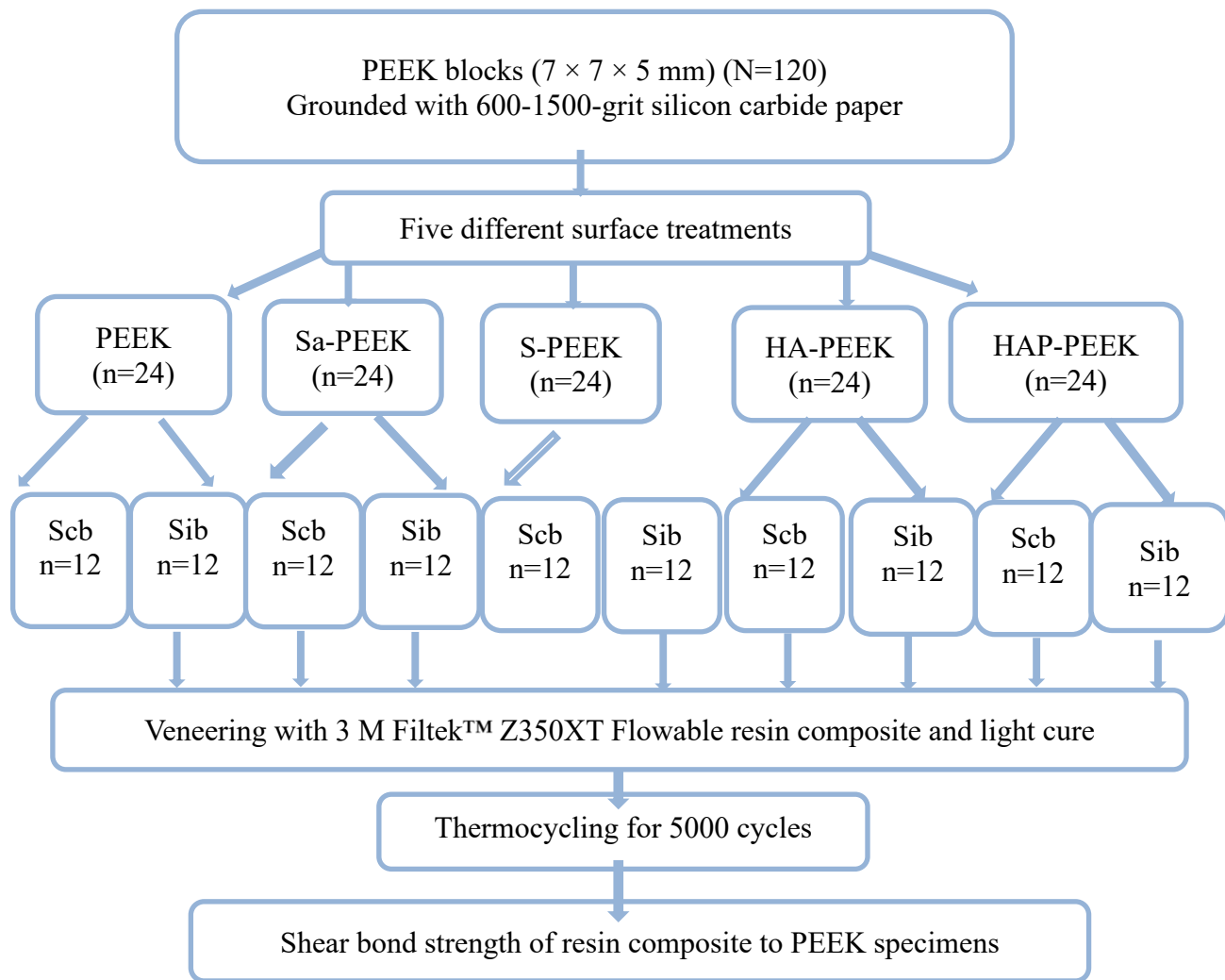


Figure 5 Schematic Figure of Study Design for Part 1

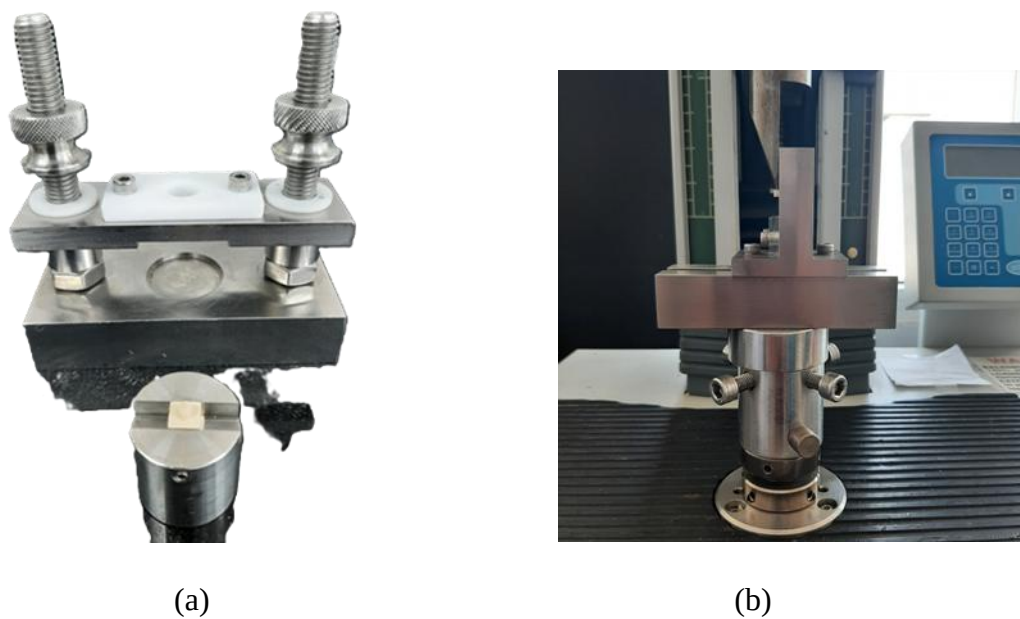


Figure 6 Setting up the specimen (a) in the stainless steel mold holding with the screw jig for bonding with resin composite (b) in the universal testing machine for shear bond strength test

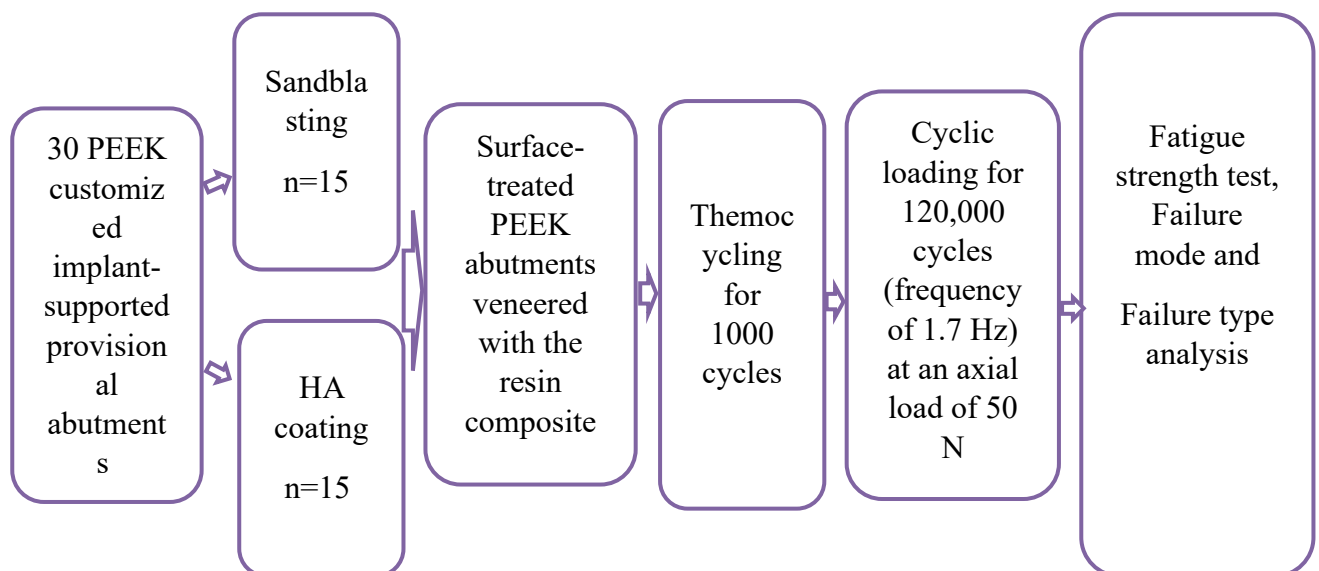


Figure 7 Schematic Figure of the Study Design for Part 2

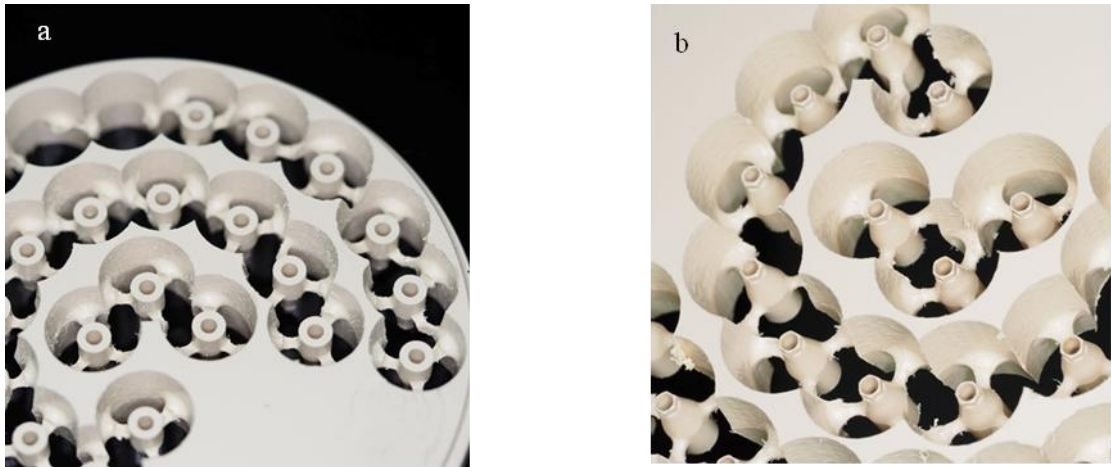


Figure 8 CAD/CAM milled PEEK temporary abutment (a) Occlusal view (b) Implant-abutment internal hexagonal connection

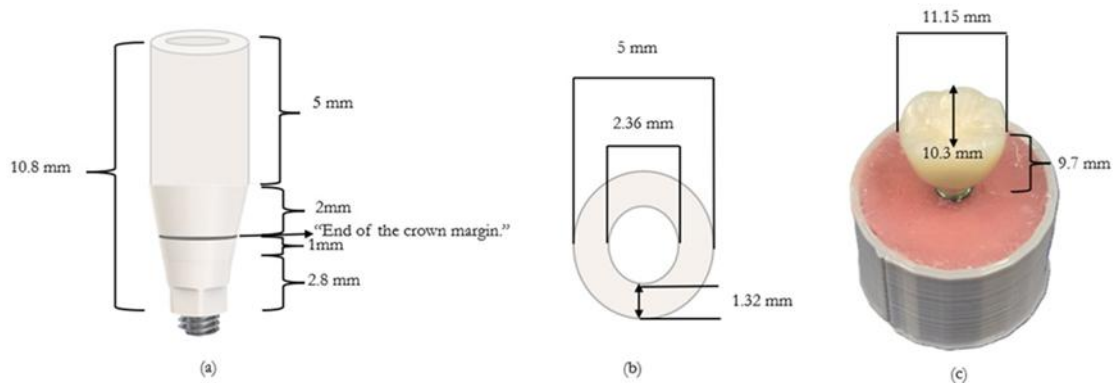


Figure 9 Schematic drawing of (a) the outer dimension of the PEEK temporary abutment, (b) the diameter of the temporary abutment, the screw access hole, and the thickness of the abutment, and (c) the dimension of the provisional resin composite crown for the first permanent mandibular first molar (mesiodistally, buccolingually, and occlusocervically).

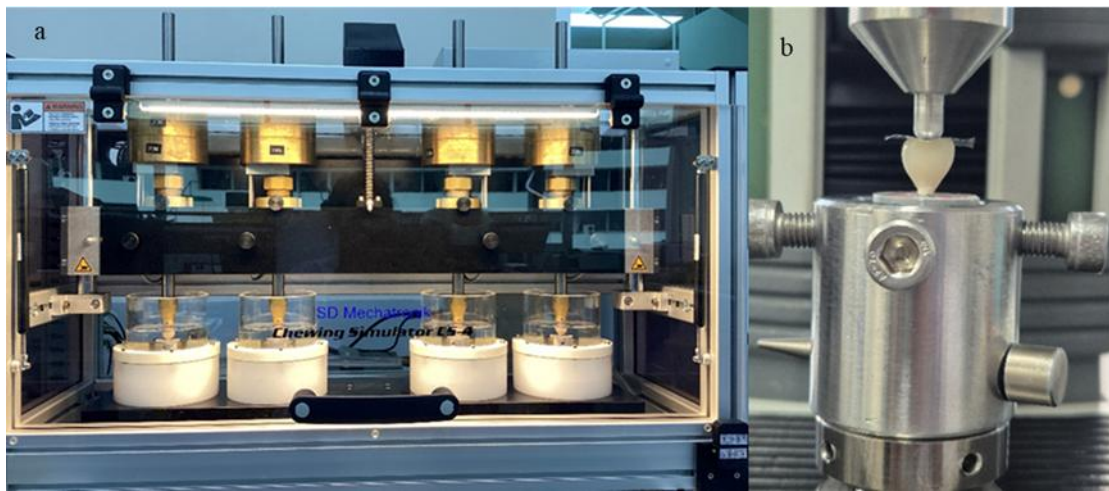


Figure 10 Setting up the specimens (a) in the chewing simulator for cyclic loading and (b) in the universal testing machine for fracture strength.

CHAPTER 4

RESULT

Hydroxyapatite coating confirmation

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray spectroscopy (EDS) analysis

The surface morphology of PEEK was analyzed and can be compared in SEM photos: no surface treatment PEEK (Figure 11a), after a 3-minutes immersion in sulfuric acid confirming sulfonation and the formation of sulfonic groups as porous surface (Figure 11b). Hydroxyapatite (HA) particles (Figure 11c) were then deposited onto the sulfonated PEEK substrate, covering the porous sulfonated PEEK and EDS revealing a calcium-to-phosphorus (Ca: P) molar ratio of 1.67, indicating successful HA deposition (Figures 12a and 12 b) [72].

Fourier-transform infrared spectroscopy (FTIR) analysis results

FTIR result, shown in Figure 3, further proved the attachment of sulfonic acid groups ($-\text{SO}_3\text{H}$) after sulfuric acid etching for 3 min, expressing a strong absorption band at 1160 cm^{-1} for aryl sulfonic acids and additional bands indicating the presence of specks of alkyl sulfonic acids [86]. Transmittance bands at 566 cm^{-1} for P–O stretching and 602 cm^{-1} for PO_4^{3-} bending confirmed HA presence, with stretching vibrations at 962 , 1033 , and 1091 cm^{-1} are also the indicators of the presence of the HA components (Figure 13) [67].

X-ray diffraction (XRD) analysis results

XRD confirmed the effective HA coating on the porous PEEK substrate by revealing high-intensity peaks at (002), (211), and (202) crystallographic planes at 25.89 , 31.74 , and 34.03 degrees, respectively (Figure 14) [67, 87]. Additionally, intense diffraction bands from rutile titanium dioxide pigments were observed, suggesting their presence in the material.

Chemical characterization for different surface treatments of PEEK

The surface compositions of various treatment procedures were assessed by EDS mapping, as indicated in Table 3. The purpose of this study was to compare and evaluate the shear bond strength of various surface treatments on polyetheretherketone (PEEK) and flowable resin composites. Despite the manufacturer's specification

indicating that titanium dioxide (TiO_2) constitutes 12% of the treatment, The EDS results revealed noteworthy disparities between the groups. Specifically, the PEEK and Sa PEEK groups had just trace levels of titanium. In contrast, the S PEEK group had a much larger amount of titanium, showing differences in the surface treatment's efficiency and composition.

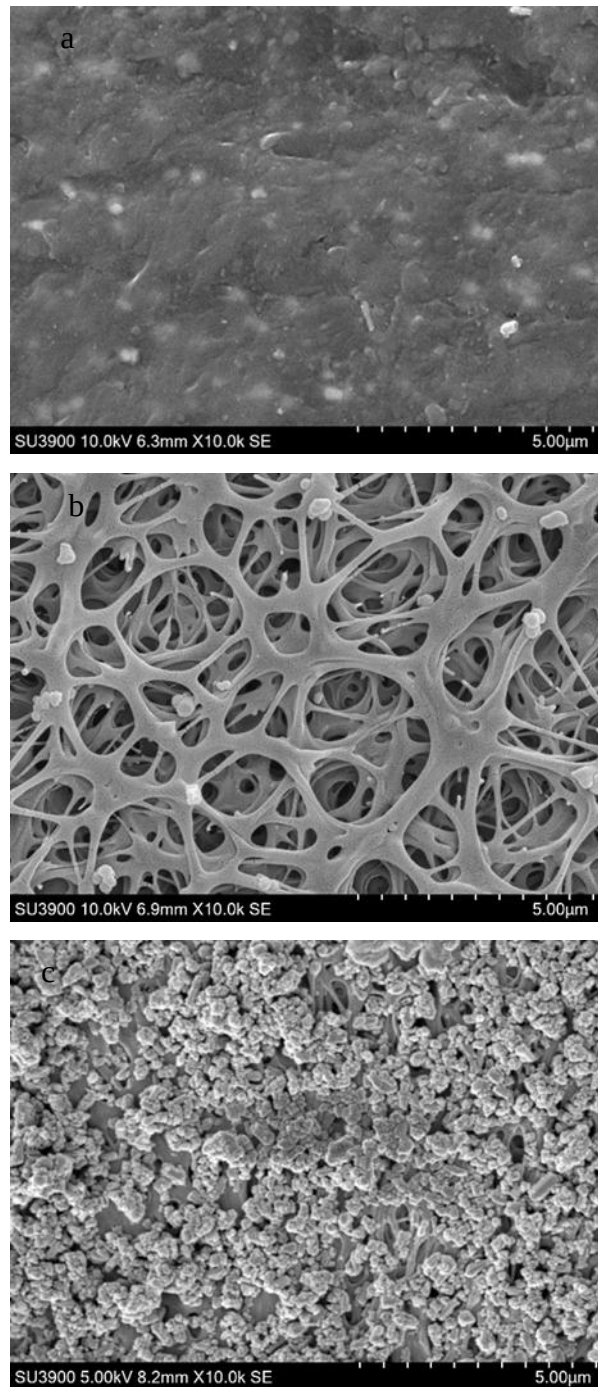


Figure 11 Scanning Electron Microscopy images of hydroxyapatite coating confirmation over PEEK. (a) no surface treatment PEEK (b) 3 minutes sulfonated PEEK, and (c) HA-coated sulfonated PEEK

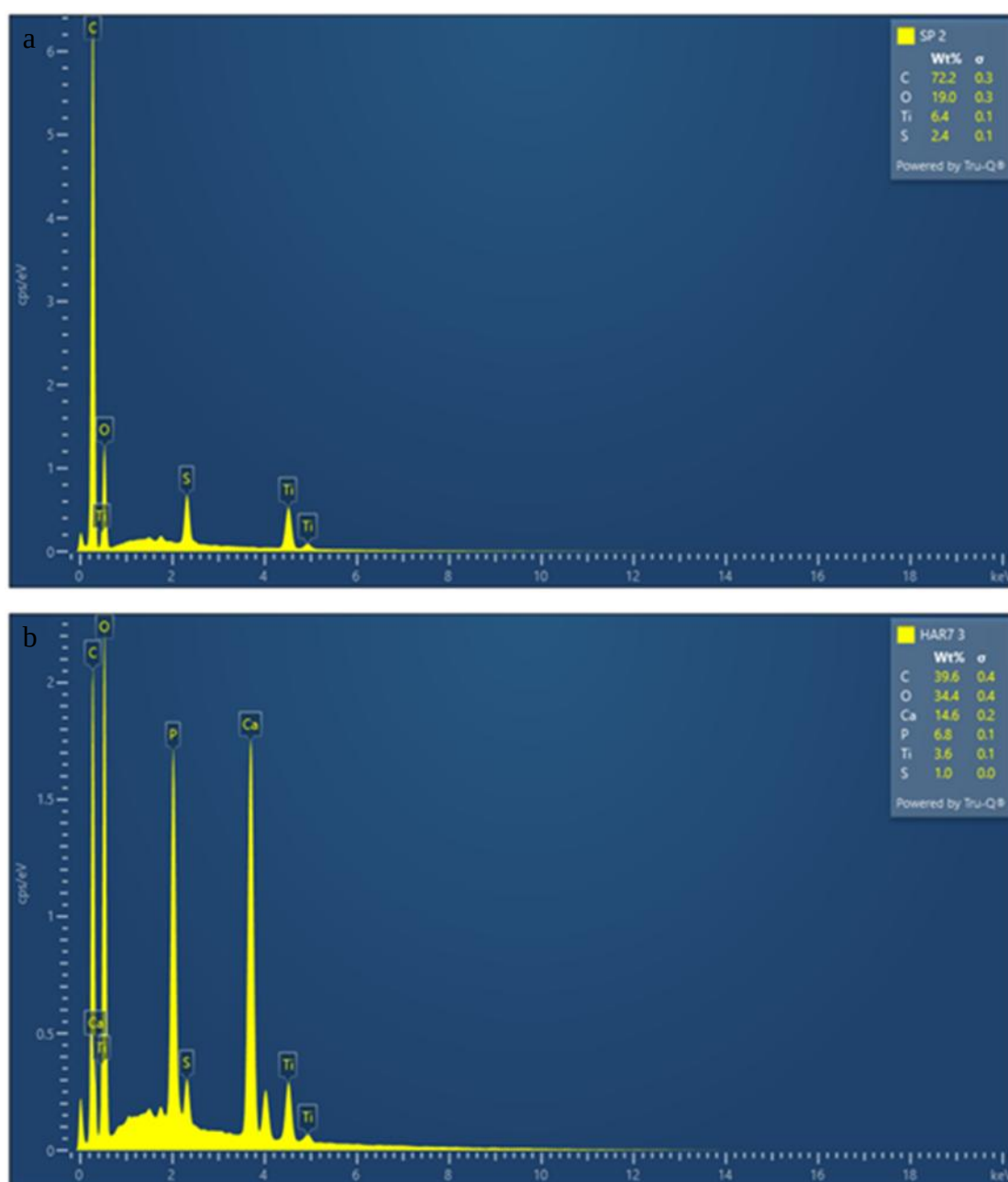


Figure 12 Energy-dispersive X-ray spectroscopy (EDS) analysis of (a) 3 min sulfonated PEEK, (b) HA-coated sulfonated PEEK

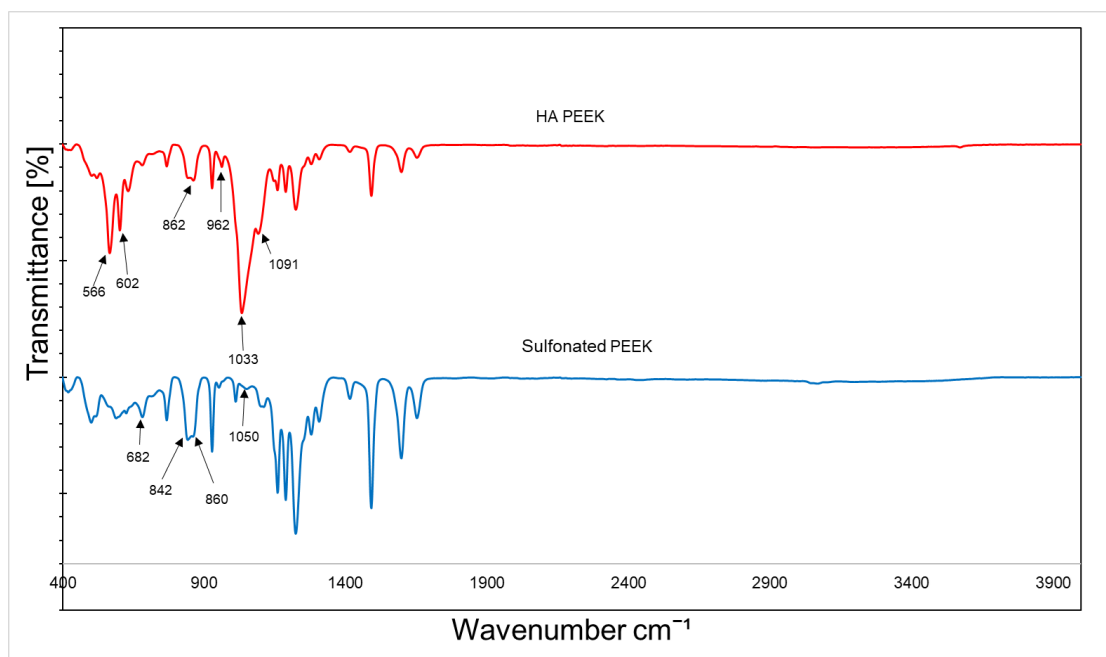


Figure 13 Fourier Transform Infrared Spectroscopy (FTIR) spectra of 3 min sulfonated PEEK and HA-coated sulfonated PEEK

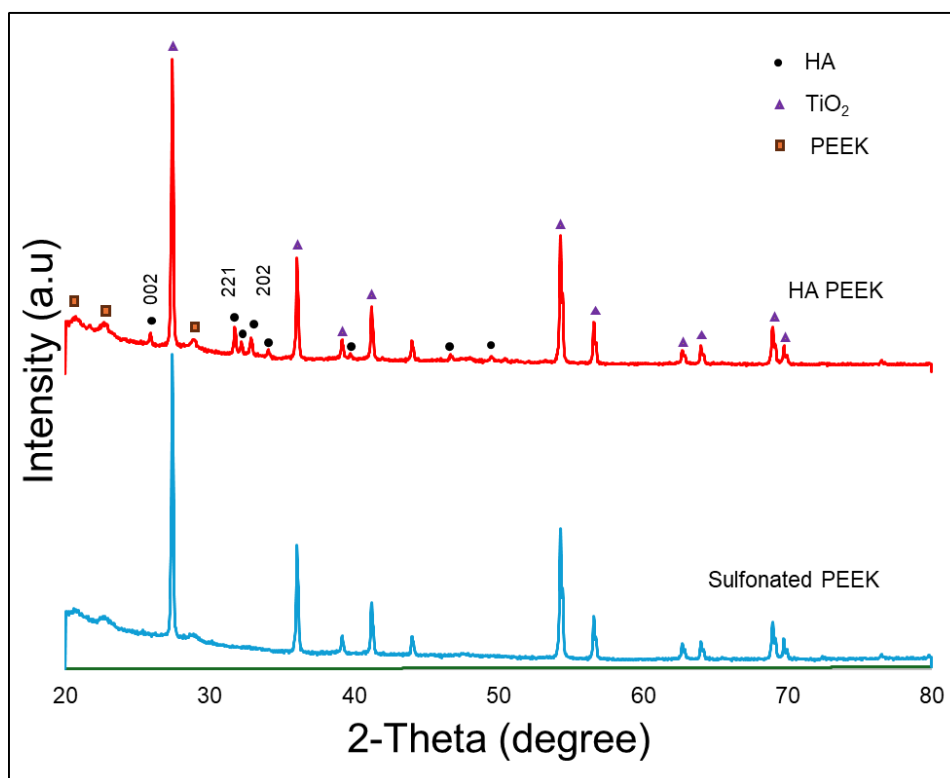


Figure 14 X-ray diffraction (XRD) spectra of 3 min sulfonated PEEK and HA-coated sulfonated PEEK

Table 3 Elemental compositions of various surface treatments of PEEK

Element	HA PEEK	HAP PEEK	S PEEK	Sa PEEK	PEEK
C	39.9	74	71.6	60.1	73.2
O	34.9	22.3	18.4	36.9	26.5
Ca	14.7	0.1			
P	7.3	0.1			
Ti	2.3	2.3	7.6	0.2	0.3
S	0.8	1.1	2.4		
Al				2.8	
Si		0.1			

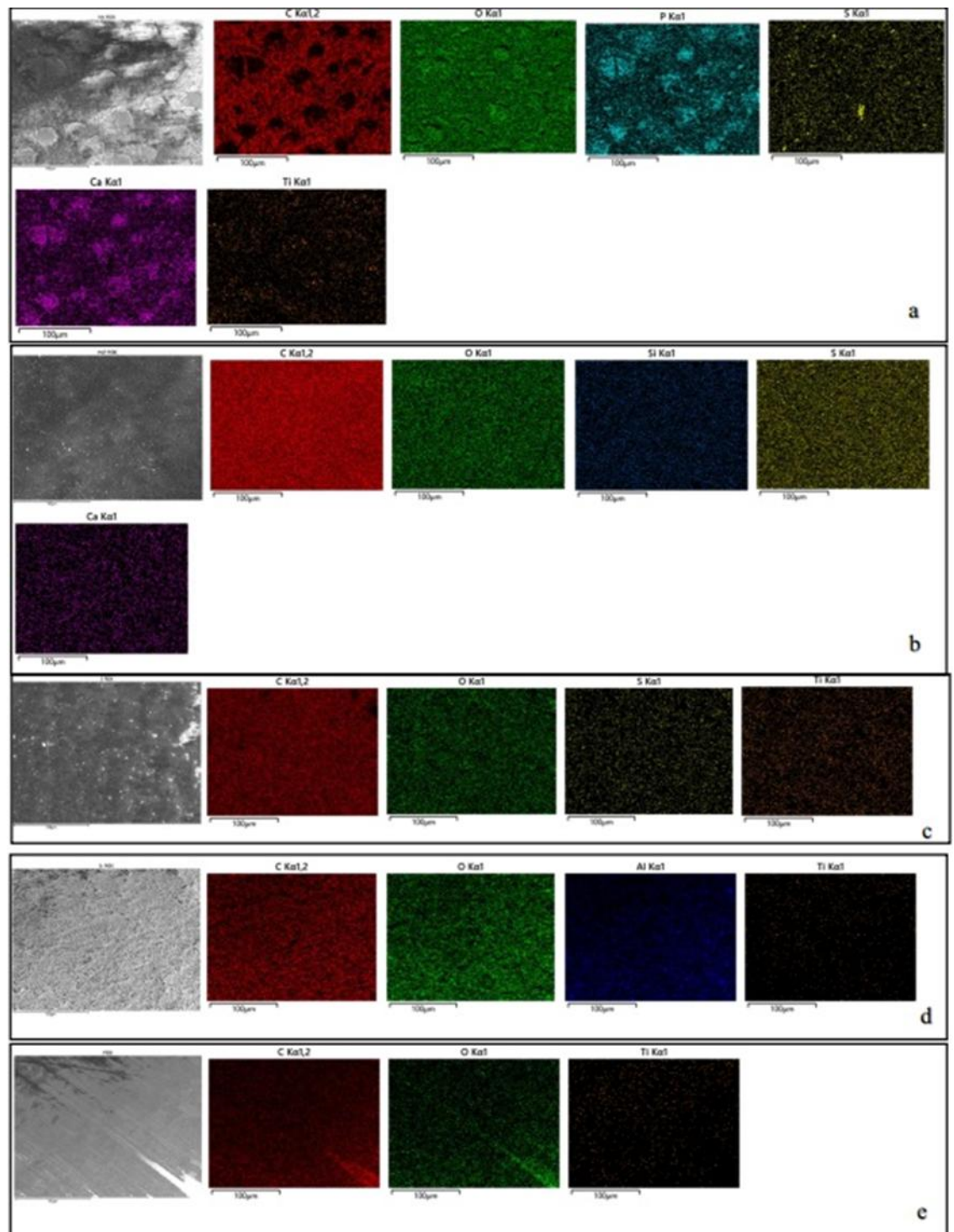


Figure 15 Energy-dispersive X-ray spectroscopy (EDS) maps of different pre-surface treatments (a) HA PEEK, (b) HAP PEEK, (c) S PEEK, (d) Sa PEEK and (e) PEEK

Shear bond strength test

In the Scb group, HA PEEK showed the highest SBS, followed by HAP PEEK, Sa PEEK, S PEEK, and PEEK. There was no significant difference between the HA PEEK and HAP PEEK groups, or between the S PEEK and PEEK groups. Sa PEEK showed much lower SBS than HA PEEK and HAP PEEK, but significantly greater SBS than no surface treatment PEEK and S PEEK.

In the Sib group, the highest SBS was discovered in the HA PEEK group, similar to the Scb group, followed by HAP PEEK, S PEEK, Sa PEEK, and PEEK. In contrast to Scb, there is no significant difference in SBS between Sa PEEK and S PEEK, and both have significantly lower SBS than HA PEEK and HAP PEEK, but significantly greater SBS than no surface treatment PEEK.

In both the Scb and Sib groups, the HA treatment method (HA PEEK) produced the maximum shear bond strength (SBS), followed by the HAP PEEK surface treatment. Table 3 shows that the SBS of S PEEK in the Sib groups had considerably higher bond strength than the Scb groups ($p < 0.05$). In contrast, no significant difference in SBS was found between the PEEK and Sa PEEK groups within the Scb category as compared to the Sib group. These results indicate that the influence of various bonding agents was more noticeable in the S PEEK groups. The mean values of SBS and the effect of the different silane-containing universal bonding agents can be seen clearly in Figure 16 and Table 4.

Surface roughness (Ra) and wettability analysis

Table 5 shows that the roughness average (Ra) values for the HA PEEK and HAP PEEK groups were statistically significant when compared to the other surface treatments. Notably, the wettability of the HA PEEK group was the highest and statistically significant of any treatment group. Despite having higher Ra values than the untreated PEEK group, the Sa PEEK group had a higher CA value than the PEEK group. Figures 17a–e show the wettability of the different surface treatment groups. This demonstrates a complex link between surface roughness and wettability in the treated samples.

Failure mode analysis

According to the failure mode analysis, cohesive failures were most common in the HA PEEK and HAP PEEK groups under both Scb and Sib circumstances, as

illustrated in Figures 18c and d. In contrast, the remaining surface treatment groups primarily exhibited mixed failure modes, as seen in Fig. 18e. The other three surface treatment groups had nearly all broken specimens with adhesive failures, as shown in Figures 18a and 18b. Notably, the S PEEK group under Scb circumstances saw a few mixed failures, as seen in Figure 18f.

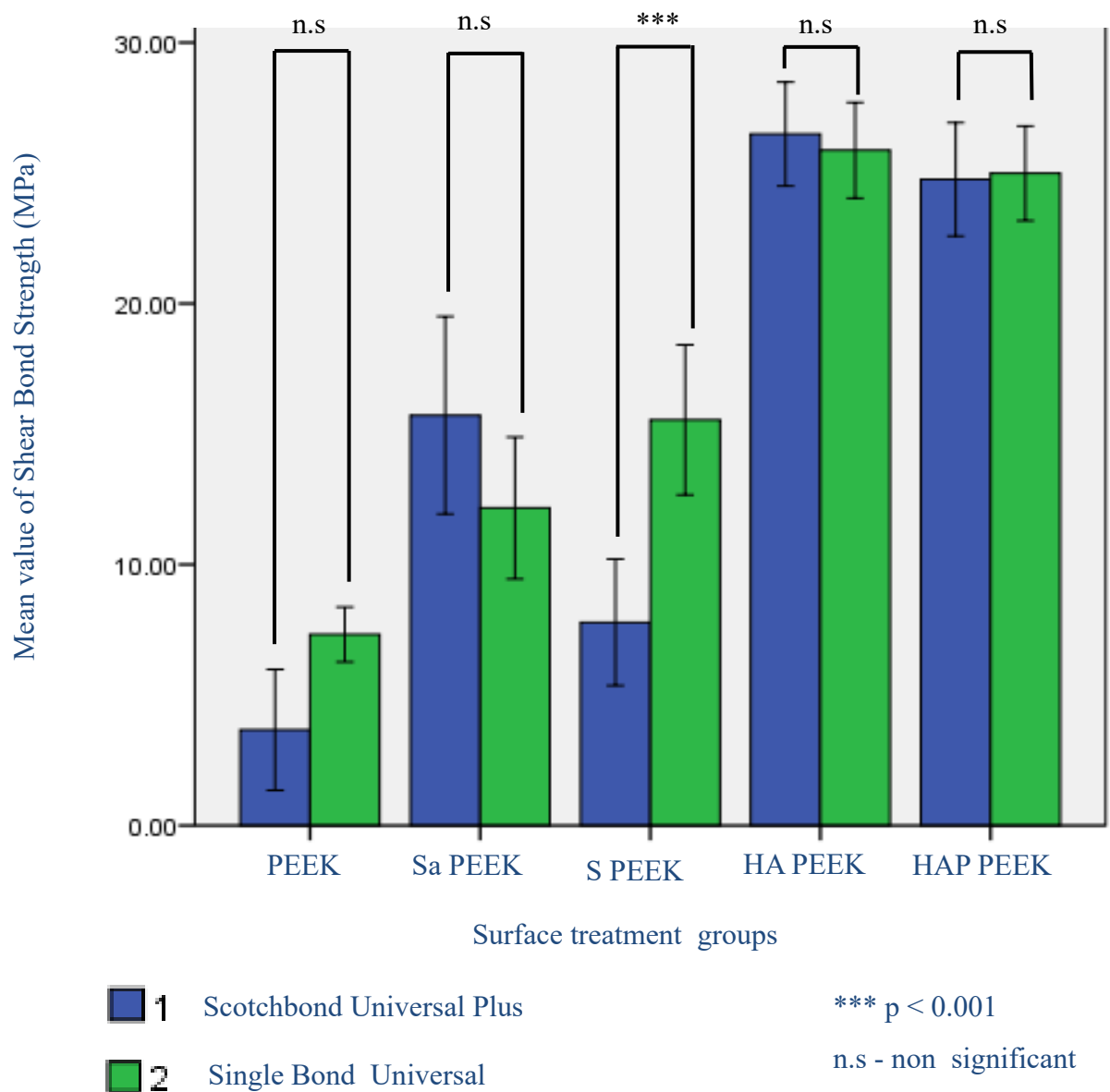


Figure 16 Bar chart diagram showing the mean value of shear bond strength of the different surface treatments groups of PEEK with flowable resin composite

Table 4 Shear bond strength and failure analysis results of various surface treatments with flowable resin composite

Types of bonding agents	Surface treatments	Shear bond strength [MPa] (SD) ^{e,f}	Failure analysis		
			Adhesive	Cohesive	Mixed
Scotchbond universal plus	PEEK	3.67 (3.64) ^{c, C}	100%	-	-
	Sa PEEK	15.72 (5.95) ^{b, B}	100%	-	-
	S PEEK	7.78 (3.81) ^{c, C}	66.67% (8)	-	33.33% (4)
	HA PEEK	26.49 (3.14) ^{a, A}	-	58.33% (7)	41.67% (5)
	HAP PEEK	24.76 (3.42) ^{a, A}	-	58.33% (7)	41.67% (5)
Single bond universal	PEEK	7.32 (1.66) ^{z, C}	100%	-	-
	Sa PEEK	12.17 (4.28) ^{y, B}	100%	-	-
	S PEEK	15.54 (4.53) ^{y, B}	100%	-	-
	HA PEEK	25.87 (2.89) ^{x, A}	-	50% (6)	50% (6)
	HAP PEEK	24.99 (2.85) ^{x, A}	-	58.33% (7)	41.67% (5)

^eDifferent lowercase letters in the same column indicate significant differences in various surface treatments using the same bonding agents.

^fDifferent uppercase letters in the same column indicate significant differences in the same surface treatments between Scotchbond and Single bond Universal adhesives.

Table 5 Surface roughness and Contact angle analysis results of different surface treatment groups

Examined parameters	Surface treatment groups				
	PEEK	Sa PEEK	S PEEK	HA PEEK	HAP PEEK
Water contact angle (Degree)	92.31° ^c ± 5.85 ^c	126.28° ^d ± 10.57 ^d	84.49° ^c ± 1.21 ^c	53.91° ^a ± 1.21 ^c	77.94° ^b ± 3.15°
Surface roughness (μm)	0.14 μm ^D ± 0.00 ^D	0.39 μm ^C ± 0.4 ^C	0.64 μm ^B ± 0.15 ^B	0.82 μm ^A ± 0.15 ^B	0.82 μm ^A ± 0.55 ^A
Different lowercase letters indicate significant differences in CA in various surface treatment groups. Different uppercase letters indicate significant differences in Ra in various surface treatment groups.					

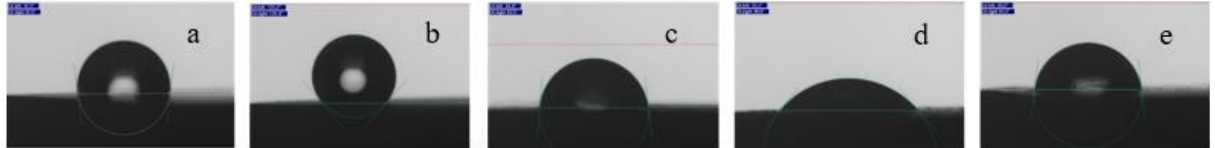


Figure 17 Contact angle analysis of (a) PEEK, (b) Sa PEEK, (c) S PEEK, (d) HA PEEK, and (e) HAP PEEK

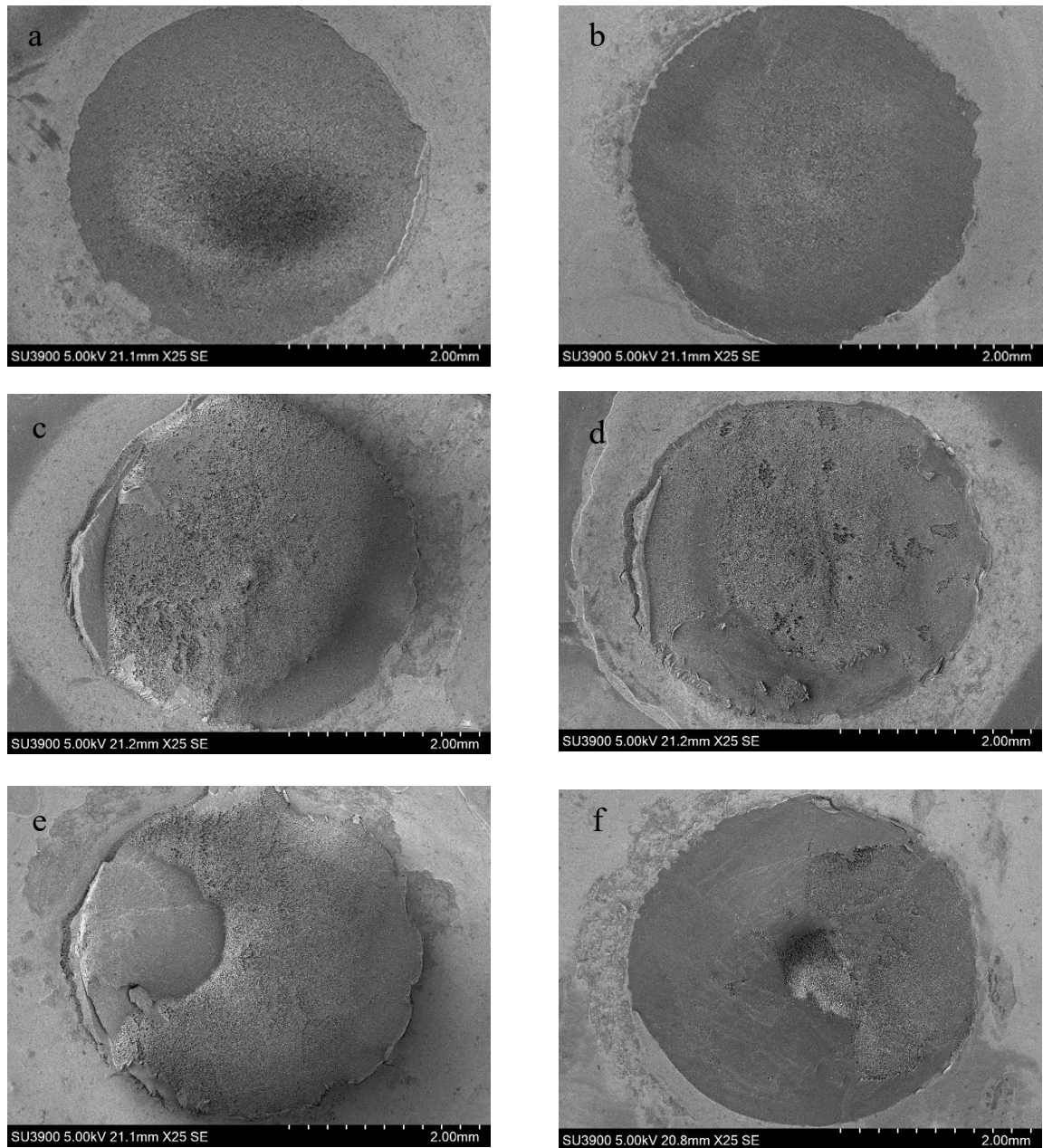


Figure 18 Scanning Electron Microscopy (SEM) images representing Adhesive failure pattern: (a) Si Sa PEEK and (b) Si S PEEK; Cohesive failure pattern: (c) Sc HAP PEEK and (d) Si HAP PEEK; and Mixed failure pattern: (e) Sc HA PEEK and (f) Sc S PEEK

Fracture strength tests

All specimens withstood the thermomechanical loading, although one from each group was accidentally damaged when calibrating the universal testing machine. As a result, the sample from each group (n=14) was assessed for fracture load and failure analysis. Table 6 shows the descriptive data for fracture load. A Mann-Whitney U test was used to compare the two groups (Sa and HA). Table 7 shows a significant difference between the groups, with HA having a higher mean rank than Sa, as demonstrated by a Mann-Whitney U statistic of 19.500 and a Wilcoxon W value of 124.500. The Z-value of -3.607 supports this conclusion, and the P value of 0.000 (asymptotic and exact) indicates a highly significant difference between the two groups.

The failure analysis results (Table 8) demonstrate that all of the specimens had adhesive failure (Figure 19a), with the exception of one specimen in the HA group that has cohesive failure (Figure 19b). Although the majority of the specimens in both groups had type 1 irreparable crown fracture (Figures 19c, 19d, and Table 8), roughly one-third of the implant-supported provisional crowns in both groups had type 2 reparable crown fracture (Figures 5e, 5f, and Table 8). No screw loosening or deformation of the analog was seen.

Table 6 Descriptive statistics of fracture load of HA PEEK and Sa PEEK

Surface Treatment	Mean	Median	Std. Deviation	Std. Error	Minimum	Maximum
Sa (n=14)	1152.36	1142	200.36	53.55	885	1643
HA (n=14)	1469.71	1409	180.89	48.34	1260	1830

Table 7 Comparison of the fracture load of HA PEEK and Sa PEEK using the Mann-Whitney test

Surface treatment groups	Mann-Whitney U value	Wilcoxon W value	Z value	P value
Sa and HA	19.5	124.5	-3.607	0.000

Table 8 Failure type and failure modes occurred in this study, classified according to the previous article ³

Failure type and failure mode	Sa	HA
Cohesive Failure (CF)	-	1
Adhesive Failure (AF)	14	13
Screw Loosening (SL)	-	-
Deformation of implant analog (DIA)	-	-
Irreparable Failure (Type 1)	11	10
Reparable Failure (Type 2)	3	4



Figure 19 (a) Specimen showing adhesive failure and abutment fracture from the Sa group, and (b) specimen showing cohesive failure from the HA group (c) Specimen showing Type 1 failure from the Sa PEEK group (occlusal view), and (d) specimen showing Type 1 failure from Sa PEEK group (profile view). (e) Specimen showing Type 2 failure from HA PEEK group (occlusal view), and (f) specimen showing Type 2 failure from HA PEEK group (profile

CHAPTER 5

DISCUSSION AND CONCLUSION

This in vitro study investigated various PEEK surface treatments to improve bond strength with resin composite, as well as the development of correct emergence profiles for customized PEEK healing abutments and fracture strength of implant-supported provisional resin composite crowns. Interim restorations usually last between two weeks to three months, however, they might last longer depending on the complexity of the implant treatment technique [15]. The HA PEEK group had the highest SBS values among the treated groups, followed by the HAP PEEK group in both Scb and Sib conditions, and outperformed the untreated PEEK, Sa PEEK, and S PEEK groups. Notably, Ra and wettability varied significantly among treatment groups. These findings resulted in a near-complete rejection of the first hypothesis, which stated that all surface treatments produced comparable bonding strengths. The second hypothesis, about the influence of bonding agents containing various silane components, was largely accepted, as evidenced by the performance of the S PEEK group. Furthermore, the fracture strength of this study sought to evaluate the fracture load and failure mode of implant-supported provisional resin composite crowns using hydroxyapatite-coated sulfonated PEEK abutments in comparison to conventional sandblasted PEEK abutments after 6 months of thermomechanical loading. The significant difference in fracture load between the two groups rejected the null hypothesis ($P < 0.05$).

According to previous studies, using bonding agents or resin cements in combination with chemical surface treatments like sulfuric acid etching or mechanical treatments like sandblasting can significantly increase the bond strength of resin composites to PEEK [54, 57]. These frequently acceptable surface treatments were used as positive controls to compare to untreated PEEK, which was designated as a negative control. HA-coated PEEK is widely employed in orthopedic and dental implant applications because of its biocompatibility (86-88) and antibacterial characteristics [88, 89]. The techniques available for HA coating encompass spin-coating, aerosol deposition, and dip coating. [60-63]. Many HA coating processes necessitate

modifications that involve post-treatment heat, which can negatively impact the crystallinity and chemical composition of the hydroxyapatite layer. Moreover, a significant disadvantage is the probable separation of the HA coating layer from the substrate [65]. Chemical deposition, sulfonation, has proven to be particularly effective in preserving PEEK's structural integrity while enhancing the functionality of the HA layer [64]. Additionally, methacryloyloxydecyl dihydrogen phosphate (MDP), which is present in common dental adhesives, forms a stable bond with calcium ions from the HA coating, improving the HA PEEK group's wettability and bonding strength [73, 90-92]. The findings of this investigation, which showed that HA PEEK had the highest SBS, confirm this hypothesis.

With the goal of obtaining micromechanical retention over HA PEEK, the SBS of the HAP PEEK group was also assessed, and the second-highest SBS value was discovered. However, because the SBS is lower than that of HA PEEK, phosphoric acid etching is not required over HA PEEK. This could be due to applying the adhesive for 20 seconds with the force of the microbrush in circular rubbing motion, which could destroy the etched pattern of HA [93]. The SBS of Sa PEEK in Scb and Sib is much lower than that of HA PEEK and HAP PEEK. This could be due to the embedding of alumina powder over the sandblasted PEEK surface, even after ultrasonic cleaning, which can interfere with the bonding process [94]. Nonetheless, the combination of sandblasting surface treatment and adhesives results in significantly higher SBS than without surface treatment PEEK because Scb and Sib contain polyalkenoic acid copolymer (Vitrebond), which promotes strong bond strength between Sa PEEK and resin composite [95]. Gama et al. proposed combining surface pretreatment to generate an efficient bond between PEEK and veneering resin composites. [58]. This is also corroborated by the study's findings, as the SBS in the Scb and Sib PEEK groups is less than the acceptable SBS of 9 MPa [92].

The interaction effect of different bonding agents on SBS can only be observed within the S PEEK group. Scb adhesive differs from Sib adhesive in that it contains an optimum blend of silane, a tiny quantity of transition metal salt as a dual cure accelerator, and radiopaque monomer resin instead of Bis-GMA, according to the manufacturer's specifications. In another investigation, the effect of 98% sulfuric acid surface treatment utilizing Heliobond (Bis-GMA 60%, TEGDMA 40%) without silane

revealed a considerably higher SBS than without using this adhesive to bond PEEK containing 20% TiO₂ with flowable resin composite [94]. Combining 3-(trimethoxysilyl) propyl methacrylate (γ -MPS) silane with sulfuric acid etching and plasma surface treatment can improve SBS in pure PEEK. However, silane had no appreciable effect when used alone with sulfuric acid etching and no surface treatment [96].

Even though silane is unable to enhance the SBS of PEEK following sulfuric acid etching, it has a detrimental effect on TiO₂ pigments that contain PEEK in this study. The SBS values of PEEK containing TiO₂ pigments were significantly influenced by the silane components of the Scb, which contains 3-(aminopropyl) triethoxy silane (APTES) alongside 3-methacryloxypropyl triethoxysilane (3-MPTES), and the Sib, which contains 3-methacryloxypropyl trimethoxysilane (3-MPTS) [97]. Increased TiO₂ concentrations in S PEEK compared to other surface treatments may result in reduced SBS when used with adhesives containing APTES [98]. In particular, agglomeration may happen when titanium nanoparticle concentrations are above ideal levels. This can impair proton conductivity and diminish hydrogen bonding capacities, which in turn can lead to decreased SBS values in the Scb SPEEK group. Additionally, the resin's capacity to enter deep grooves in the PEEK surface may be hindered by the sulfonic acid etching procedure, which would further reduce the bonding potential. [99]. Consequently, with no surface treatment PEEK and a lower SBS value than Sa PEEK in Scb, the SBS of S PEEK in the Scb group is not noteworthy. According to Kiliç M et al.'s study, the S PEEK group in Sib, however, has a substantially greater SBS than the Sa PEEK and PEEK groups [49].

Strong bonding between PEEK and veneering resin composites can be observed by the predominantly cohesive failures found in the Scb and Sib of HA PEEK and HAP PEEK, according to failure mode analysis. The other surface treatment groups' adhesive failures suggest the need for more extensive or sophisticated surface treatment. [74].

The CA, which indicates the adhesive bond's ability to adhere to the substrate, is a crucial parameter for assessing wettability [90]. PEEK with HA coating showed noticeably better wettability. The CA values dropped even while the Ra of the Sa PEEK increased. This suggests that the treated samples' Ra and wettability have a complicated relationship. This effect could be explained by PEEK's natural hydrophobicity [91]. Air

pockets may emerge between the adhesive and the substrate's surface if the adhesive does not completely wet the rough surface that has been sandblasted. These areas experience stress initiation under mechanical load and temperature variations, which might later result in bonding failures [90]. Therefore, compared to the HA PEEK and HAP PEEK groups, the SBS and wettability of Sa PEEK were noticeably lower for both Scb and Sib conditions.

Researchers investigated PEEK's mechanical strength using a variety of methods, including shear bond strength, tensile strength, biaxial flexural strength, fracture resistance, and stress distribution [80, 100-102]. The fracture load is a crucial parameter for evaluating the long-term durability of provisional restorations subjected to masticatory forces. The implant-supported interim restoration is critical to the final efficacy of the implant treatment. Clinicians' knowledge of the procedures, materials, and temporary implant components for short-, medium-, and long-term provisional prostheses is increasingly critical [103]. Temporary restorations ordinarily last 2 weeks to 3 months; however, they may occasionally last for a longer duration, depending on the complexity of the reconstructive or surgical implant surgery. [15]. As a result, depending on the complexity of the situation, they must withstand occlusal forces during the transition from the surgical to the prosthetic phase. [19]. Fracture of temporary restorations is a common issue that causes discomfort and incurs costs for patients and operators. [104]. The second part of this study aimed to compare the fracture load and failure mode of implant-supported provisional resin composite crowns with hydroxyapatite-coated sulfonated PEEK abutments to regular sandblasted PEEK abutments after 6 months of thermomechanical loading. The considerable fracture load between the two groups refuted the null hypothesis ($P < 0.05$).

A recent in-vivo study comparing a screw-retained PEEK abutment veneered with Cera.lign composite with a screw-retained porcelain-fused metal crown for short implants discovered that the PEEK abutment had a superior prognosis in terms of marginal bone loss and stability after 6 months [79]. Thus, provisional PEEK abutments are anticipated to have unique advantages over other temporary abutments. Furthermore, the reprocessed PEEK crown displayed fracture resistance and successfully distributed load among dental implants and the surrounding bone, comparable to a zirconia crown and a new process PEEK [80]. The findings of this

observation indicated that PEEK is appropriate for a posterior single-implant repair and provides considerable benefits for "Green Dentistry" in our environment.

The average maximum voluntary bite force (MVBF) varies based on gender and facial structure. The largest MVBF reported is 771.50 N; however, one study indicates that the peak biting force surpasses 900 N. [105, 106]. The previous research employed thermocycling aging before cyclic loading for 1000 cycles (30 s dwell time and 10 s transfer time) at temperatures of 5°C and 55°C [83]. Cyclic loading parameters were defined to replicate six months of usage. [85, 107]. The investigation found that the mean fatigue load in Sa is $1152.36 \text{ N} \pm 200.36$ and in HA is $1469.71 \text{ N} \pm 180.89$, as shown in Table 2. Both values exceed the MVBF, even after thermomechanical loading. However, the fracture strength of the HA groups is much greater than that of the Sa groups. This contradicts the study's conclusions that PEEK surface pre-treatment and veneering material do not impact the fracture load of veneered fixed dental prosthesis (FDP) [108]. This may arise from the different surface pre-treatment methods utilized in this study.

The minimum fracture load in the Sa group is 885 N (Table 2), indicating that the MVBF may exceed this value in some situations. The HA group's peak fracture load was 1830 N (Table 2), and the specimen failed cohesively (Figure 5 b). In situations with parafunctional behaviors, such as bruxism and clenching, the maximum voluntary clenching force exceeds 1181 N [109]. The minimal fracture load in the HA group is 1260 N (Table 2), indicating that HA-coated surface pre-treatment may provide significant benefits to patients with parafunctional behaviors.

Gupta et al. emphasized the importance of the bonding interface in measuring the load-bearing capacity of fixed dental prosthesis (FDPs) during the fracture analysis of PEEK samples [78]. The printed molars (VarseoSmile Temp A3, BEGO) have a fracture strength of $1189.50 \text{ N} \pm 250.85$ for implant-supported screw-retained molar crowns. The study found that the milled molar (VitaCAD Temp mono-color, Vita) had a fracture strength of $1817.50 \text{ N} \pm 258.22$, which exceeded the fracture strength established in this research. However, the study did not account for aging circumstances [110]. Therefore, implant-supported provisional resin composite crowns made on hydroxyapatite-coated sulfonated PEEK abutments may function similarly to temporary crowns that are milled and printed under aging conditions. When a load is

applied perpendicular to the central fossa and progresses down the PEEK abutment surface, shear stresses may cause the fractured veneering composite [78]. These assumptions demonstrate that enhanced bonding properties may withstand cyclic stress, resulting in higher fracture strength, which is directly related to each other [111, 112]. According to this analysis, adhesive failures are the main cause of failure in both groups; however, the HA group's fracture load is noticeably greater than the Sa group's. This could be because hydroxyapatite-coated sulfonated PEEK has a higher shear bond strength and performs well even after thermocycling, but sandblasting can weaken bonds over time since PEEK is hydrophobic [101]. The outcomes of this study also proved these findings. If the adhesive fails to properly wet the hydrophobic sandblasting surface, air pockets may form between the adhesive and the rough sandblasted PEEK, potentially leading to stress initiation in these locations after temperature and mechanical variations [101].

PEEK demonstrated higher fracture strength, indicating that it should be considered as a long-term provisional material, according to Mendes, J.M. et al.'s investigation of the fracture strength of three temporary CAD/CAM materials (PEEK, PMMA, and resin composite) [113]. Additionally, the pH of saliva may affect the fatigue strength of some implant-supported bis-acrylic resin provisional crown materials [114]. Bulk fill restorative materials showed promising outcomes in terms of appearance, functionality, and biological factors throughout a five-year clinical trial. [115]. In addition, comparison of veneered PEEK frameworks using either CAD-milled composite or lithium disilicate, manual veneering of PEEK frameworks with traditional composite, and using a 1 mm-thick PEEK framework may yield better results [116]. Due to this, the veneering material for the PEEK abutment in this investigation was a 1.32 mm-thick, and was veneered with bulk-fill restorative composite.

Furthermore, more elastic materials, such as PEEK, absorb greater chewing stress than less elastic materials, such as zirconia. Stress absorption reduces micromovements between components and wear on mating surfaces, which decreases screw loosening [117]. This study pointed out the features of PEEK materials as a possible explanation for the lack of screw loosening and deformation in the implant analog. Type 1 failure occurs in about two-thirds of all specimens in both groups (Table 3); however, all crowns are capable of withstanding typical bite forces. Surprisingly,

this study also identified abutment fractures. There were seven abutment fractures in the Sa group, compared to three in the HA group. Following the abutment fracture, the results demonstrate that sandblasting may reduce the mechanical strength of the PEEK abutment when compared to HA coating treatments. As a result, the study of residual stress in PEEK after surface treatment deserves additional investigation.

Despite various limitations in this study, such as a lack of thorough biocompatibility testing and in vivo evaluations, the EDS analysis results offer good evidence for the safety of the materials utilized. Another constraint was that this test was only used to create the individualized healing abutment for a maximum of 6 months of use, with thermocycling performed 5000 times. Commercially available PEEK reinforced with carbon fiber, glass fiber, and ceramic, as well as pure PEEK free of TiO₂ pigments and other bonding agents that contain MDP but not silane, should be researched and compared. Future research could look at the long-term impact of these treatments on the mechanical properties and biocompatibility of HA-coated PEEK to help cement its therapeutic potential in clinical settings.

Hydroxyapatite-coated sulfonated PEEK (HA PEEK) had the greatest value for SBS, followed by HAP PEEK, regardless of bonding agent used. Although sandblasting surface treatment for PEEK achieved acceptable SBS results, it should be used with caution for long-term applications. APTES, including bonding agents, should not be employed with sulphuric acid etching surface treatment in TiO₂-containing PEEK. Without surface treatment, PEEK cannot offer enough SBS; thus, pre-surface preparation is essential before applying the adhesive. The HA coating on sulfonated PEEK provides a practical method for increasing SBS with flowable resin composites, which is crucial for the efficacy and durability of individualized healing abutments.

The second part of this study focuses on customized PEEK temporary abutments for medium and long-term use; therefore, fatigue strength is tested after 6 months of thermomechanical aging. More mechanical strength tests should be performed for long-term usage and clinical applications, such as the flexural strength test following surface treatment, the application of a titanium base, and biocompatibility assessments. According to the study's findings, both surface treatment groups can endure average masticatory biting forces. Implant-supported provisional resin composite crowns on hydroxyapatite-coated sulfonated PEEK abutments may be a

better option for people who display parafunctional behaviors and have been using provisional restorations for a long time.

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APPENDIX

APPENDIX



Human Research Ethics Committee
Faculty of Dentistry, Prince of Songkla University

Ref. PSU 109.1.6.3/67-0455

DATE 24 December 2024

REF: Non-Human Research

Dear: Assoc.Prof.Dr.Chaimongkon Peampring

EC Project No.	NH6712-026
The Project Entitled	Surface modification of polyether ether ketone(PEEK) via sulfonation and hydroxyapatite coating: Impact on shear bond strength with resin composites
Principal Investigator	Assoc.Prof.Dr.Chaimongkon Peampring
Affiliation	Department of Prosthetic Dentistry, Faculty of Dentistry, PSU
Co-Principal Investigator	Assoc.Prof.Dr.Putsadeeporn Thammajaruk and Dr.Thae Phyu Htay
Affiliation	Faculty of Dentistry, Prince of Songkla University

The submitted protocol has been reviewed by the Human Research Ethics Committee, Faculty of Dentistry, Prince of Songkla University.

The committee determined on 24 December 2024 that the submitted protocol met the criteria of the Non-Human Research

(Assoc.Prof. Chairat Charoemratrote)
Chairman of Human Research Ethics Committee
Faculty of Dentistry, Prince of Songkla University
Date 24 December 2024

VITAE

Name Miss Thae Phyu Htay

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1. Surface modification of polyether ether ketone (PEEK) via sulfonation and hydroxyapatite coating: impact on shear bond strength with resin composite
2. Fracture Strength and Failure Mode of Implant-Supported Provisional Resin Composite Crowns on Hydroxyapatite-Coated Sulfonated PEEK Abutments Following Thermomechanical Loading
3. Oral presentation with the title of “Shear Bond Strength of Resin Composite to Polyetheretherketone used in Fabrication Healing Abutments with Various SurfaceTreatments” in 7th Bangkok International Symposium of Implant Dentistry 2024.

4. Participating in Research Day 2025 as oral presentation with the title of “Shear Bond Strength of Resin Composite to Polyetheretherketone used in Fabrication Healing Abutments with Various SurfaceTreatments”