

Article



# Influence of Alternative and Conventional Surface Treatments on the Bonding Mechanism between PEEK and Veneering Resin for Dental Application

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**Abstract:** This study evaluated the influence of conventional and alternative surface treatments on wettability and the bond strength between polyether ether ketone (PEEK) and veneering resin. PEEK samples were randomly divided into five groups: sandblasting, tribochemical silica coating, etching with 98% sulfuric acid for 5 s, etching with 98% sulfuric acid for 30 s, and tribochemical silica coating plus heated silane. One of them was subjected to analysis by energy-dispersive X-ray spectroscopy (EDS) and ten were analyzed by goniometry (n = 5) and scanning electron microscopy (n = 5). Shear bond strength (SBS) was tested, and failure types were assessed. Data were analyzed using one-way ANOVA, followed by the Tukey and Duncan tests (all,  $\alpha = 5\%$ ). Treatment with sandblasting and silica coating had the lowest SBS means (4.2 MPa and 4.4 MPa respectively), while sulfuric acid for 5 s showed the highest mean value (12.6 MPa), followed by sulfuric acid for 30 s and tribochemical + heated silane. All failures were classified as adhesive. The lowest mean contact angle was found for the polished (control) and etched group with 98% sulfuric acid for 30 s (83.9°). Etching with 98% sulfuric acid for 5 s increased the SBS between resin and PEEK.

Keywords: polyether ether ketone; wettability; shear strength; sulfuric acid; airborne-particle abrasion

# 1. Introduction

Adhesion to high performance polymers (HPP) for industrial applications (automotive, aerospace, sterilizable surgical instrument sectors) does not represent a barrier for their use because manufacturers of industrial adhesives have successfully developed adhesive systems to bond them appropriately [1]. However, such adhesives used to be epoxy- or urethane-based, and therefore toxic and consequently not indicated for medical purposes [2]. Polyether ether ketone (PEEK) is an HPP from the poly(aryletherketones) (PAEKs) family, and has been used for medical applications since the early 2000s. There have been some attempts to develop biocompatible adhesives and also surface treatments including the sulphonation process to improve the cell adhesion and osteoinductive capacity of PAEKs [3–5]. More recently, these semi-crystalline thermoplastic polymers have attracted researchers and clinicians to investigate their application in dentistry due to their versatility in terms of the prosthesis manufacturing process (thermopressing, subtractive and additive manufacturing), excellent mechanical performance, required accuracy, and



Citation: Villefort, R.F.; Anami, L.C.; Campos, T.M.B.; Melo, R.M.; Valandro, L.F.; von Zeidler, S.L.V.; Bottino, M.A. Influence of Alternative and Conventional Surface Treatments on the Bonding Mechanism between PEEK and Veneering Resin for Dental Application. *Coatings* 2021, *11*, 719. https://doi.org/10.3390/coatings 11060719

Received: 19 May 2021 Accepted: 13 June 2021 Published: 16 June 2021

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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). also the necessary biological properties [6,7]. Their high resistance to physical agents (heat, gamma radiation, electron beam) enables them to pass through different sterilization processes without affecting the dimensional stability. Moreover, biocompatibility and resistance to chemical (organic and inorganic) agents has also been confirmed [8]. Thus, as an inert and non-allergenic biomaterial, PEEK has supplanted metal alloys in some types of medical prostheses and orthoses, including craniofacial prostheses [9].

It is desirable that alternative processing methods, as well as the biomaterials should be linked with the most appropriate procedure, controlling clinical and laboratory parameters to get the most out of our therapeutic plan, always respecting our patient's systemic condition [10]. Thus, oncologic patients who present intra- or extrabuccal sequelae after surgical resection of the tumor would especially benefit with this approach for two reasons: (i) the follow-up and recurrence control by diagnostic imaging, such as computed tomography, magnetic resonance imaging, and X-ray would be easier because radiolucent prostheses generate less artifacts than metal-based restorations; (ii) in case of tumor recurrence in which radiotherapy is indicated, there is no necessity of prosthesis removal because they are metal-free. Furthermore, PEEK has a similar elastic modulus to native bone which is desirable for maxillofacial prosthesis, and the biofilm formation over its surface is lower than observed in ceramic and metallic alloy surfaces [11]. In vitro studies and short-term clinical reports have evaluated the use of PEEK in dentistry for: partial/total; fixed/removable, tooth-supported/implant-supported [12–16] and maxillofacial prosthesis, including palatal obturators [17]. Although the weight of the prosthesis does not represent a problem per se [18] regarding this last indication, a reduction in the prosthesis volume into the palatal defect by an implant-retained obturator and its higher stability can be considered a gain in the patient's quality of life [19]. Nevertheless, PEEK infrastructures should be veneered by lithium disilicate, veneering resins for laboratory use or polymethylmethacrylate to achieve desirable aesthetic requirements [20]. The bond strength between the veneering material and PEEK infrastructure must be strong enough to resist the adverse buccal environment which is subject to cyclic loading, different temperatures, and moisture [21].

PEEK polymer has very low or no solubility in ordinary solvents at room temperature due to its high chemical resistance. Two conventional etching methods very often used in dentistry are thus not efficient to pretreat the PEEK surface. Phosphoric acid does not chemically attack PEEK, even at 80% concentration [22]. Furthermore, 10% hydrofluoric acid is also not able to etch PEEK [23]. Doing so would require the use of 40% hydrofluoric acid. On the other hand, according to the manufacturer, it is possible to obtain a chemical etch with sulfuric acid in concentrations higher than 40%. In fact, concentrated sulfuric acid (98% which is equivalent to 18 mol/L) is capable of promoting the swelling process of PEEK at room temperature [24,25]. The polymer solubilization involves phenomena related to intermolecular interaction. In addition, the polymer dissolution process has two steps: the first is polymer swelling, and the second is the molecule mobility. The swelling is the critical point of the solvent absorption, increasing the mass and specific volume, where the sum of both enthalpy and entropy contributions are equal. The swelling and subsequent immersion in water produces a three-dimensional pore and a nanostructured network on the PEEK surface [26].

Surface treatments, as well as material processing, have a significant effect on different characteristics of the materials, such as wettability, friction coefficient, and adhesion [27,28]. It has been shown that wettability, a fundamental phenomenon in adhesion, is governed by both chemical and surface morphology resulting from the processing of materials [29].

Conventional sandblasting is the customary option among the surface treatment methods for a thermoplastic material, and is economically justifiable [29–31]. This is one of the two conventional methods for surface treatment currently recommended by the dental PEEK manufactures, which are: (i) sandblasting the PEEK surface with 110 µm or 50 µm in the same way it is used for metal framework sandblasting; (ii) a tribochemical silica coating, commercially known as Rocatec<sup>TM</sup> (3M ESPE, St. Paul, MN, USA) Alternatively, PEEK surface modifications by both chemical and physical agents have been investigated,

such as 98% sulfuric acid etching [32,33], piranha solution (mixture of sulfuric acid and hydrogen peroxide) [34], hydrofluoric acid etching [23], and treatments with inert gas plasma, and argon plasma [23,35]. Silane coupling agents (silanes), because of their good performance and biocompatibility, are the most broadly used coupling agents in dentistry. Hydrophobic silane monomers need to be dissolved in alcohol-water solvent and, activated by an addition of acid which makes the initially hydrophobic silane molecules hydrophilic, i.e., they will contain silanol, –Si–OH. Moreover, recent studies have showed that these agents influenced the bond strength of resin composites on air-abraded PEEK [36]. The possibility of substituting hydrofluoric acid etching by post-silanization heat treatment has been evaluated in studies of dental ceramics. This technique consists of accelerating the solvent by heating the surface immediately after the silane application at a temperature of 79 °C or 100 °C just for 1 min, depending on whether the solvent is alcohol or water, respectively [37,38]. According to Campos et al. [36], heating speeds up the condensation of the silane molecules and increases the interaction with the substrate, increasing the interaction at the adhesive interface [39].

As far as bonding to dental PEEK is concerned, sufficient data regarding an efficient protocol for adhesion between PEEK and veneering resin is not available in the literature. Furthermore, although dental PEEKs have a similar polymer structure, the type, size, and percentage of fibers added to the polymers may cause variations in bond strength. Thus, aiming to contribute to a better understanding of the adhesion mechanisms of dental PEEK, two conventional and three alternative surface treatments were performed and their influence on the bond strength of a light-cured resin for laboratory use to PEEK, as well, as on its wettability, were evaluated. The two null hypotheses were: there is no differences in shear bond related to the conventional or alternative surface treatments; the wettability of PEEK is not influenced by surface treatments.

#### 2. Materials and Methods

Trade names, manufacturers, lot number, and chemical composition of the materials used in this study are displayed in Table 1.

Trade Names	Manufacturers	Batch Number	Chemical Composition
Aluminum oxide	Polidental Ind. Com. Ltda	43126	45 $\mu$ m Aluminum oxide sand (extra-fine)
Rocatec Pre + Rocatec Plus	3M ESPE	1036301855	High-purity 110 μm aluminum oxide High-purity aluminium oxide 110 μm, modified with silicon dioxide (SiO <sub>2</sub> )
Sulfuric acid PA	F.Maia Ind. Com. Ltda	33860	98% H <sub>2</sub> SO <sub>4</sub>
RelyX <sup>™</sup> Ceramic Primer	3M ESPE	N 406345	Ethyl alcohol, water, methacryloxypropyltrimethoxysilane
Sinfony™ Opaquer Powder	3M ESPE	524838	Silane-treated quartz, calcium fluoride, titanium dioxide, lauroyl peroxide, isobutylmalonyl-N,N'-dicyclohexyl-sulfamide, silane treated silica, c.i. pigment yellow 42, iron hydroxide oxide
Sinfony™ Activator Liquid	3M ESPE	518926	Dicyclopentyldimethylene diacrylate, methyl methacrylate, monoacrylate acetate, vinyl acetate polymer, phosphine oxide, N,N-dibutylphenylethylamine hydrochloride
Sinfony™	3M ESPE	523076	Silane-treated glass powder, diurethane dimethacrylate, dicyclopentyldimethylene diacrylate, silane-treated silica, glass ionomer filler, 2-hydroxyethyl methacrylate

Table 1. Material specifications.

One unit of Juvora Dental Disc<sup>™</sup> (Juvora Ltd., Lancashire, UK) was machined in industrial milling by using numerical control software (CNC) under cooling to obtain 61 samples in dimensions of 12 × 6 × 3 mm<sup>3</sup>. A total of 50 samples were embedded in Araldite 1109 BR XGY epoxy resin activated with Araldur HY BR 951 (Huntsman Advanced Materials, Huntsman Química Brasil Ltda., São Paulo, Brazil) at a proportion of 100:12 and polished with P600 grit silicon carbide paper (Sic) using an automatic polishing machine (EcoMet<sup>™</sup>/AutoMet 250<sup>™</sup>, Buehler, Lake Bluff, IL, USA) for 60 s under 25 N pressure and water cooling. After obtaining standardized surfaces, the samples were immersed in acetone and subjected to an ultrasonic bath for 10 min. The distribution of embedded/non-embedded PEEK samples in different groups according to its final destination is summarized in Figure 1.



**Figure 1.** Schematic representation of the distribution of embedded/non-embedded PEEK samples in different groups according to its final destination: Shear bond strength (SBS) testing, goniometry, micromorphological analysis (SEM) or spectroscopy (EDS).

#### 2.1. PEEK Surface Treatments

First, 50 PEEK specimens were randomly divided into five groups (10 samples per group), which were then subjected to different surface treatments before application of the veneering resin, as described in detail in Table 2 and summarized below:

- TBS Group (control): microblasting sand with 110 μ Al<sub>2</sub>O<sub>3</sub> particles (Rocatec<sup>TM</sup> Pre) followed by tribochemical coating of the microblasted surface with silica-modified 110 μ aluminium oxide (Rocatec<sup>TM</sup> Plus)
- (2) ALO Group: sandblasting with  $45 \mu Al_2O_3$  particles.
- (3) SA5 Group: etching with 98% sulfuric acid for 5 s and rinse in running water for 1 min.
- (4) SA30 Group: etching with 98% sulfuric acid for 30 s and rinse in running water for 1 min.
- (5) TBS-H Group: microblasting sand with 110 μ Al<sub>2</sub>O<sub>3</sub> particles followed by silica coating and heated in an oven at 79 °C for 60 s after RelyX<sup>TM</sup> Ceramic Primer application.

Procedures	Materials	Techniques	Tools	Specifications	Time
Surface treatments	Rocatec <sup>™</sup> Pre + Plus	(Pre) Microblasting sand	Rocatec <sup>™</sup> Jr	1 cm distance, 2.8 bar	15 s
		(Plus) Silica coating	Rocatec <sup>™</sup> Jr	1 cm distance, 2.8 bar	15 s
	Aluminum oxide	Sandblasting	Rocatec <sup>TM</sup> Jr	1 cm distance, 2.8 bar	15 s
	98% sulfuric acid	Swelling	Petri dish	Contact the sample surface with H <sub>2</sub> SO <sub>4</sub> PA	5 or 30 s
Silanization	RelyX ceramic primer	Brushing	#1 brush	Homogeneous layer Wait for drying	5 min
Opacification	Sinfony™ Opaquer Powder + Sinfony™ Activator Liquid	Mixing and brushing	Plastic spatula Ceramic mixing plate	1:1 liquid—powder proportion Spatulation to cream consistency	45 s
		Photopolymerization	Halogen light	Two cycles	5 s
Veneering resin application		Incremental layers	#1 brush	Homogeneous layer	
		Individual layer photopolymerization	Halogen light	Two cycles	5 s
		Final photopolymerization	Visio.Beta	Program #1	1 min of light followed by 14 min of light and vacuum

## 2.2. Resin Application

First, each pretreated sample received two silicone cylinders to delimit the adhesive area (Ø:3 mm) on the PEEK surface with an inner diameter of 3 mm and an outer diameter of 5 mm, which were perpendicularly positioned to the PEEK surface and fixed with heated wax (Figure 2A). Afterwards, the veneering system was applied over the adhesive area as follows: silane (RelyX<sup>TM</sup> Ceramic Primer, 3M ESPE) was applied using a fine tip brush. Opaque powder and liquid (Sinfony<sup>TM</sup> Opaquer Powder, Sinfony<sup>TM</sup> Activator Liquid, 3M ESPE) were subsequently mixed according to the manufacturer's instructions and a thin layer was applied. The opaque layer was polymerized with two cycles of 5 s of halogen light with a 450 nm wavelength (4000 JetLite Plus, J. Morita USA, Irvine, CA, USA). Silicone tubes were then manually filled with 1 mm-thick incremental layers of light-cured resin for laboratory use (Sinfony<sup>TM</sup>, 3M ESPE). Each layer was cured for two cycles of 5 s with the same halogen light (Figure 2B), and the final photopolymerization was carried out in Visio<sup>®</sup> Beta Vario equipment (3M ESPE) (Figure 2C). The samples were stored in distilled water at 37 °C for 24 h before being tested. Silicone cylinders were cut with scalpel blades and gently removed prior to shear bond strength (SBS) testing.



**Figure 2.** Sample preparation for shear bond testing. (**A**) Left: one PEEK sample embedded in epoxy resin. Right: two silicone cylinders perpendicularly positioned over pretreated PEEK delimiting the bonding area. (**B**) Successive layers of veneering system applied during the bonding procedure. (**C**) Set prepared for the final photopolymerization.

## 2.3. SBS Test and Failure Analysis

Shear bond strength was measured with a universal testing machine (EMIC DL 1000, São Jose dos Pinhais, Paraná, Brazil). The samples were positioned with the treated surface parallel to the loading device. A circular section of stainless steel wire (0.45 mm in diameter) was positioned as close as possible to the bonded area and the load was applied with a speed of 0.5 mm/min (Figure 3). The maximum load (in Newton) was measured before

debonding occurred. Next, the maximum load (in Newton) was divided by the area of the adhesive interface (in mm<sup>2</sup>) to calculate SBS (MPa).

The debonding areas were examined with a stereomicroscope at  $25 \times$  magnification (Zeiss Discovery V20, Zeiss, Oberkochen, Germany) by a single calibrated examiner and failures were classified.



**Figure 3.** Schematic representation of the SBS test. Set prepared for the test in which was employed an orthodontic-looped wire to stress the bonding interface at the universal testing machine (EMIC).

## 2.4. Contact Angle and Micromorphological Analysis

Five samples not embedded in resin underwent goniometry testing. One specimen did not receive any surface treatment and was used as control. The other specimens were subjected to the same surface treatments tested (except for the TBS-H group) (Figure 1). An optical tensiometer (TL 1000 Theta Lite Attension, Biolin Scientific, Lichfield, Staffordshire, UK) was used to measure the average contact angle of five different areas per sample with the sessile drop technique (grade 3 distilled water at room temperature). A graduated syringe (gastight Syringes #1001—1 mL, Hamilton, Reno, NV, USA) with hydrophobic needle deposited a drop and the average contact angle was then calculated after waiting for 10 s (OneAttension, Biolin Scientific) following the acquisition of 15 images/s for 30 s.

Next, five PEEK samples were sputter-coated with gold (EMITECH SC7620, Quorum Technologies Ltd., Laughton, UK) and subjected to scanning electron microscopy in high vacuum (IN-SPECT S50, FEI, Brno, Czech Republic) operating at 15 kV and at a working distance of about 12 mm to evaluate topographic changes after different surface treatments. Magnification ranged between  $5000 \times$  and  $10,000 \times$ .

## 2.5. Energy-Dispersive X-ray Spectroscopy (EDS)

A treated specimen was evaluated in energy-dispersive X-ray spectroscopy (EDS) to confirm that all the sulfuric acid had been eliminated from the PEEK surface after treatment and washing in running water.

## 2.6. Data Analysis

The Kolmogorov-Smirnov and Shapiro-Wilk tests were performed to verify the normality distribution of data. The evaluation of significant differences between groups regarding SBS and contact angle were performed by one-way ANOVA, followed by the Tukey's and Duncan test respectively (all,  $\alpha = 5\%$ ).

## 3. Results

# 3.1. SBS Test and Failure Analysis

The Kolmogorov-Smirnov and Shapiro-Wilk tests indicated no violation in the assumption of normality, and the data of shear bond strength and contact angle were evaluated using one-way ANOVA, followed by the Tukey's or Duncan test (all,  $\alpha = 5\%$ ).

The average SBS between PEEK and veneering ranged from 4.20 MPa to 12.57 MPa. One-way ANOVA showed the influence of surface treatments on bond strength (p < 0.0001). According to the Tukey's test (Table 3), etching with sulfuric acid at 98% for 5 s (SA5) resulted in the highest average bond strength value. All failures were classified as adhesive (no resin remaining on the PEEK surface).

Table 3. SBS results. Mean and standard deviation (SD) of the shear bond strength (MPa).

Surface Treatment	Mean and SD (MPa) *		
Aluminum oxide (ALO)	$4.2 \pm 2^{d}$		
** Tribochemical silica coating (TBS)	$4.4\pm2$ $^{ m d}$		
Tribochemical silica coating + heated silane (TBS-H)	$6.5\pm2.3$ c		
Sulfuric acid 5 s (SA5)	$12.6\pm2$ a		
Sulfuric acid 30 s (SA30)	$10.3\pm2.9$ <sup>b</sup>		
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\* The characters <sup>a</sup>, <sup>b</sup>, <sup>c</sup>, and <sup>d</sup> represent homogeneous groups after Tukey's test. Similar letters mean not statistically difference, while different letters represent significant difference. \*\* Control group.

#### 3.2. Contact Angle Measurements

The contact angle was also influenced by surface treatments (p < 0.0001). The highest values were observed for the aluminum oxide sandblasted group (ALO), while untreated specimens (control) and those etched using 98% sulfuric acid for 30 s (SA30) showed the lowest values (Table 4).

**Table 4.** Contact angle measurements. Mean and standard deviation of the contact angle measurement of specimens with different surface treatments.

Surface Treatment	Mean and SD (°) *
** Control (CTL)	$88.9\pm 6.0~^{ m ab}$
Aluminum oxide (ALO)	$127.4\pm5.7~^{\rm d}$
Tribochemical silica coating (TBS)	$93.3\pm3.8~\mathrm{bc}$
Sulfuric acid 5 s (SA5)	$98.2\pm4.3$ c
Sulfuric acid 30 s (SA30)	$83.9\pm2.9$ <sup>a</sup>

\* The characters <sup>a</sup>, <sup>b</sup>, <sup>c</sup>, and <sup>d</sup> represent homogeneous groups after Duncan test. Similar letters mean not statistically difference, while different letters represent significant difference. \*\* Control group.

#### 3.3. Micromorphological Analysis

Topographic features observed in PEEK samples before and after surface treatment are shown in Figures 4–8. The SEM observations give only qualitative information on surface morphology, which are described as follow. In this study, PEEK samples were not exhaustively polishing until reach a smooth surface. Samples were polished with P600 grit carbon to obtain standardized surfaces, reducing bias. Thus, the control group presented grooves created by the milling process, as noted in the Figure 4. Airborne-particle abrasion promoted a stripping of the surface and increased surface roughness (Figure 5). Figure 6 shows the modifications on PEEK surface promoted by the tribochemical silica coating process: a rough surface impregnated by SiO<sub>2</sub>. The swelling and subsequent immersion in water produces a three-dimensional pore and a nanostructured network on the PEEK surface. It should be noted that deeper and bigger holes were formed on the PEEK surface



the longer the exposure time to sulfuric acid, which could be observed on the PEEK surface after sulfuric etching with two different exposure times (Figures 7 and 8).



**Figure 4.** Control group (CTL). No surface treatment: even after the polishing procedure was completed, the grooves created by the milling process remained apparent on the PEEK sample. Magnification:  $5000 \times$  and  $10,000 \times$ .





**Figure 5.** Aluminum oxide group (ALO). Stripping of the surface and roughness promoted by sandblasting with 45  $\mu$ m aluminum oxide. Magnification: 5000× and 10,000×.



**Figure 6.** Tribochemical silica coating group (TBS). A rough surface resulted from using the silica deposition technique, where the roughness previously created using aluminum oxide sandblasting was later coated with silica. Magnification:  $5000 \times$  and  $10,000 \times$ .



**Figure 7.** Sulfuric acid group (SA5). Surface etched with 98% sulfuric acid for 5 s, forming three-dimensional pores. It is noted that there is the presence of even deeper grooves from the milling process. Magnification:  $5000 \times$  and  $10,000 \times$ .



**Figure 8.** Sulfuric acid group (SA30). Surface etching with 98% sulfuric acid for 30 s promoted an increased surface degradation, where it is no longer possible to observe the milling grooves and the pores are larger and deeper. Magnification:  $5000 \times$  and  $10,000 \times$ .

# 3.4. Energy-Dispersive X-ray Spectroscopy (EDS)

The absence of sulfur (Figure 9) proved that the acid was completely removed with this cleaning protocol and did not represent a risk of manipulation, or the use of PEEK submitted to sulfuric acid etching.



Figure 9. EDS. (A) Ecthing 5 s. (B) Ecthing 30 s.

# 4. Discussion

Veneer adhesion problems between PEEK frameworks and resin are the main challenges for long-term success of hybrid polymer prosthesis with CAD/CAM infrastructure. The current study evaluated the influence of alternative and conventional surface treatments on bonding mechanisms between PEEK and a light-cured resin system for laboratory use. Alternative treatments resulted in higher SBS values than the conventional ones. Thus, the first null hypothesis was rejected. In fact, sandblasting (ALO group) and silica coating (TBS group) mean values were lower than 5 MPa, which is the minimum acceptable bonding strength of resin-based materials, according to ISO 10477 [40]. On the other hand, 98% sulfuric acid etching (SA5 and SA30 groups) achieved mean values between 10–12 MPa which is desirable in oral conditions to ensure long-lasting bonding between resin-based materials [41]. Considering that bonding is a complex phenomenon that depends on many parameters and the interaction of chemical, physical, and mechanical effects, and aiming to avoid undesirable changes in crucial parameters during the bonding process, we respected the manufacturer's protocols and instructions. The dental PEEK manufacturer used in the present study offers eight options of veneering resins, but only two surface treatments, with silica coating with Rocatec<sup>TM</sup> Pre+Plus being the treatment of choice for association with the Sinfony<sup>TM</sup> System. Thus, this treatment was taken as a control group in this study and alternative chemical treatments of the PEEK surface were tested. The use of Sinfony<sup>TM</sup> was based on its lower viscosity which allowed better bonding results presented by previous studies that used other PEEKs [32,42]. The use of halogen light and its wavelength and cycles were determined by the resin manufacturer and is in consonance with a study that evaluated the impact of dental light curing units [43].

Procedures related to surface modifications by physical agents such as pressure, distance and time were also determined according to the dental PEEK manufacturer. Regarding chemical agents, sulfuric acid is a common solvent that dissolves and also sulfonates PEEK at room temperature [44]. However, the purpose of surface treatment was not to dissolve the substrate, but rather an increase in roughness, wettability, and the number of reactive groups able to physically and chemically interact with the materials applied on the surface. Therefore, the surface treatments chosen for this study were tribochemical silica coating (control), sandblasting and etching with 98% sulfuric acid. The silica coating and sandblasting techniques are routinely used in dental laboratories and offices and offer no major risks to operators if personal protective equipment (PPE) is used properly. On the other hand, etching with sulfuric acid at 98%, although very often used in the industry, is not a competency of dental technicians and requires extra care in terms of material handling, storage, and disposal.

Degradation promoted by concentrated sulfuric acid on the PEEK surface is classified as severe. Thus, different exposure times to the acid were tested in this study with the intention of creating retentions capable of improving adhesion to the veneering resin without compromising the material's strength (avoiding cohesive failures). The best SBS results were obtained when the specimens were exposed to acid for 5 s. There were microscopic alterations of the PEEK surface as expected. The differences in SBS were significant between groups and no cohesive failure occurred. The fact that the higher exposure time to the acid led to higher degradation of PEEK surface is noteworthy, which probably resulted in weaker interfaces after resin bonding.

Other studies showed superior results for treatment with 98% sulfuric acid for 60 s but exhibited PEEK cohesive failure [19]. The longer the exposure to acid, the greater the depth of attack, and the greater the topographic alterations. Dissolution of the material forms irregular pores with different sizes and depths. Schmidlin et al. observed dissolution of the PEEK subsurface when attacked by 98% sulfuric acid, although they did not observe penetration of the veneering resin into the pores or the formation of tags [27]. In contrast, resin tags were found in the 80, 85, 90 and 98% sulfuric acid groups in another study in which cohesive failure mode within PEEK was found only in the 98% sulfuric acid group [25]. Zhou et al. also etched PEEK with sulfuric acid for 60 s and observed pore formation and dissolution of the material, but they did not observe any cohesive failures with any of the resin cements tested [23]. It is important to note that resin cements and veneering resins present differences in their properties and polarity.

A study which tested the effect of seven different exposure times to 98% sulfuric acid on the shear bond strength between PEEK and conventional or self-adhesive cements could not define a single protocol of acid exposure time for the different cement types. They found the best results with exposure times between 60 and 120 s [33]. Furthermore, different studies used different PEEK compositions that had a variable concentration and arrangements of reinforcing fibers and crystallinity, which influenced its wetting behavior and contact angle measurements [29,43].

In our study, we observed a significant difference in SBS values between the control TBS (4.4 MPa) and TBS-H (6.5 MPa) groups. The only difference between surface treatment in these groups was that the specimens in TBS-H group were heated for 1 min at a temperature of 79 °C. The silane agent used in this study presents alcohol (7080 wt.%) and water (20–30 wt.%)) as a solvent, and only 2 wt.% of methacryloxypropyltrimethoxysilane (TM-SPMA). Heating at 79 °C is sufficient to evaporate alcohol and prevent non-desirableeffect as a sub product in bonding. Moreover, according to Queiroz et al., heat acts as a catalyst to complete condensation reactions of the bonding, because it volatilizes the products of the silane reaction [37]. This method was tested in ceramic studies and improved adhesion to ceramic materials [37,38].

Methacryloxypropyltrimethoxysilane is characterized by two molecule ends of different polarity. The alkoxy groups of the silanol unit ((RO)<sub>3</sub>Si–) chemically bond with the silicatized surface. However, contrary to what we expected, the bond strengths of ALO ( $4.2 \pm 2$  MPa) and TBS ( $4.4 \pm 2$  MPa) were very similar. Along with sandblasting, silane heating is a technique which can be easily applied in prosthodontic laboratories with low risk of use, and therefore should be considered as a viable alternative to treat PEEK.

The suitable morphology can be defined as surface which have a maximums peaks until a level where the surface wetting remains satisfactory [29]. In the present study, sandblasting with alumina resulted in a higher mean contact angle than the mean of the untreated specimen. According to Kubiak et al., peaks and valleys created by airborneparticle abrasion may act as barriers to the spreading of liquids, increasing the contact angles [45]. Moreover, it was observed that sandblasting only promoted a stripping of the surface and increased surface roughness. However, it did not increase the reactive groups on the PEEK surface because there was no chemical reaction with the aromatic rings of the polymeric chain.

The contact angle values are related to the chemical groups present on the surface. These groups will lead to chemical interactions which are partly responsible for bonding. Another factor that is responsible for bonding is the physical modifications on the material surface morphology. This is mainly due to the mechanical interlocking between the materials as a result of the irregularities created after the treatment. It was observed that the mechanical interlocking plays a leading role in the enhancement of bond strength, and the efficiency of this phenomenon is highly linked to the surface morphology [29]. Such irregularities were probably formed in a fashion which enhanced bonding for the 98% sulfuric acid/5 s group.

The main limitation of the current study refers to the inherent problems of the SBS test (such as the difficulty in obtaining a perfectly perpendicular position of the specimen in relation to the adhesive surface and the impossibility of total absence of tensile forces), and the fact that we did not perform any kind of aging treatment. Moreover, the parameters of the surface topography were not analyzed in the current study and the quantitative surface analysis by using a profilometer to analyze 3D roughness parameters should be considered in further studies.

PEEK is a polymer whose surface hinders heat propagation. Thus, in order to minimize heat concentration while cutting it, a milling or drilling process must be done under proper cutting parameters (clearance angle, rake angle, cutting speed, and coolants) [46]. This is probably the reason for no data in the literature comprising microtensile bond strength tests involving PEEK.

Bonding strength between PEEK and veneering resin composite increases significantly when a surface pretreatment is administered in association with a bonding system [47]. Thus, future studies about adhesion to PEEK should consider the possibility of formulating sulfuric acid in gel form for ease of handling in dental clinics.

#### 5. Conclusions

The minimum acceptable bonding strength of resin-based materials was not achieved after sandblasting and tribochemical silica coating, which are the two conventional surface

treatments recommended by the dental PEEK manufacturer. The etching promoted by 98% sulfuric acid with a 5-second exposure time increased the shear bond strength between PEEK and indirect resin and reached a desirable value to ensure long-lasting bonding in oral conditions. However, handling this acid in the form presented in this work requires training and safety measures, and therefore heating the silane after silica coating could be the alternative treatment of choice for bonding PEEK and resin composite for the time being.

Author Contributions: Conceptualization, R.F.V., R.M.M. and L.F.V.; methodology, R.F.V., L.C.A. and T.M.B.C.; software, R.F.V. and L.C.A.; investigation, R.F.V., L.C.A. and T.M.B.C.; resources, M.A.B. and S.L.V.v.Z.; data curation, R.F.V., L.C.A. and T.M.B.C.; writing—original draft preparation, R.F.V. and L.C.A.; writing—review and editing, R.M.M., L.F.V., and S.L.V.v.Z.; visualization, R.F.V.; supervision, R.M.M. and M.A.B.; project administration, M.A.B. and L.F.V.; funding acquisition, R.F.V. and S.L.V.v.Z. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by CAPES/FAPES, Grant No. 10/2018 and The APC was funded by FAPES PROFIX 2018, Process No. 83574662.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This study was supported by CAPES/FAPES.

**Conflicts of Interest:** The authors declare no conflict of interest.

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