Comparative Study of Chemical and Mechanical Surface Treatment Effects on The Shear Bond Strength of Polyether-Ether-Ketone to Veneering Resin

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ABSTRACT

Purpose: To assess the shear bond strength of composite resin to polyether ether ketone (PEEK) after mechanical and chemical surface treatments. Materials and Methods: A total of 48 PEEK discs were fabricated and divided equally into four surface treatment groups (n = 12 each): (1) airborne particle abrasion with 50-µm alumina particles at 2 MPa pressure for 10 seconds; (2) 98% sulfuric acid etching for 1 minute; (3) airborne particle abrasion and sulfuric acid etching; and (4) no surface treatment. Specimens were conditioned, then Gradia
composite veneer (GC) was applied to the PEEK surfaces and polymerized. Bond strength was measured with shear bond test using a universal testing machine. One-way analysis of variance and Tukey post hoc tests were applied for statistical analysis. **Results:** The mean shear bond strength values of the sulfuric acid–etched group were higher than that of the airborne particle abrasion + acid etching, airborne particle abrasion, and control groups ($P < .05$). Mean shear bond strength values for the airborne particle abrasion + acid etching samples were higher than for the control and airborne particle abrasion groups ($P < .05$).

**Conclusion:** There was no significant difference between the samples treated with airborne particle abrasion and the control group. *Int J Prosthodont* 2021. doi: 10.11607/ijp.6938

**INTRODUCTION**

High-performance polyether-ether-ketone (PEEK) is a member of high-performance semi-crystalline thermoplastic biomaterial, which is a subgroup of polyaryl-ether-ketones (PAEK). This methacrylate-free polymer comprises of an aromatic linear chain, connected by ether and ketone groups. The aromatic rings of PEEK ensure that the polymer is unaffected by oxidative attacks, mechanical forces and high temperature. Its notable mechanical properties, resistance to organic and inorganic chemicals and biocompatibility make polyether-ether-ketone attractive for medicine and dental field.

PEEK is a material that has been widely used in medical applications and is now getting attention in dentistry. There are some aesthetic problems related to its grayish-white color and low translucency which restrict the application of PEEK for full-coverage monolithic restorations. For this reason, additional dental composites for veneering are still necessary to obtain satisfactory esthetics. Furthermore, the use of PEEK in prosthetic dentistry has also been limited by its hydrophobic, chemically inert nature in addition to the resistance of PEEK surface to modifications by various chemical and mechanical treatments.
In order to successfully use of PEEK in dental applications requiring long term stability, processes for achieving durable bonding between PEEK and veneer composite resins must be demonstrated.5,6,7

The main requirement for durable bonding is that the adhesive material spreads on the surface of the adherent or substrate. Adequate spreading will only occur if the surface free energy of the adherent is higher than that of the adhesive. Typically, the surface energy of adhesives is higher than that for untreated PEEK, which results in poor bonding properties. Since changing the surface energy of the adhesive is difficult, several attempts have been made to increase the surface energy of PEEK by using different surface treatment methods, in which plasma and laser treatments were tested.6,8 Their results showed that the polar element of the surface free energy of PEEK is much increased by surface treatment.

The current study aimed to evaluate the shear bond strength between a veneering composite and a PEEK core material as a function of mechanical and chemical surface treatments. The null hypothesis was that pre-treatment by either chemical and/or mechanical means would lead to possible bonding of a composite resin to PEEK. Our secondary null hypothesis states that the micro-roughness of PEEK surfaces is the main factor for ensuring durable bonding of a veneering composite to PEEK.

MATERIALS AND METHODS
The materials utilized in the present study along with their specifications, chemical composition, batch number, and manufacturers are listed in Table 1. Forty-eight discs were manually sectioned out of PEEK blank (KETRON CLASSIX LCG PEEK, Invisibo, Germany) using a diamond-cutting disc (BUEHLER, ISOMET 1000, Germany) with dimensions of 2 mm thickness and 8 mm diameter. The bonding surface of each cylinder was polished with the polishing device (PHOENIX BETA, BUEHLER, Germany) under water-cooling with a series of silicon carbide papers (600 grit, 800 grit, 1200 grit). A surface
profilometer (Perthometer M1, MAHR, Germany) was used to determine the roughness (Ra) of the disc’s surface. Polished samples were cleaned in ultrasonic water bath for 5 minutes then equally divided into four groups (n=12) according to the received surface treatment as follows:

Group #1: This group acted as the control group and the discs did not receive any surface treatment.

Group #2: Disc surfaces were subjected to air abrasion (Basic Master, RENFERT, Germany) using 50 µm alumina oxide particles (Al2O3) at 2 MPa of pressure for 10 s and 10 mm distance between the nozzle and the specimen surface at right angles.

Group #3: Disc surfaces were subjected to 98% sulfuric acid etching for one minute. After etching, the specimens were washed carefully with distilled water, then dried at room temperature.

Group #4: Disc surfaces were subjected to air abrasion by 50 µm Al2O3 particles at 2 MPa pressure for 10 s perpendicular to the disc surface with 10 mm distance, and then were etched with 98% sulfuric acid for one minute. After etching, the discs were cleaned carefully with distilled water then air-dried at room temperature.

For scanning electron microscopy (SEM) analysis (FEI Philips XL30 ESEM-FEG), an additional five discs from each group were produced. The specimens were ultrasonically cleaned and coated with platinum layer. Then the surface morphology was evaluated. Before the application of adhesive system, all discs were washed in an ultrasonic water bath (ALEX, JAPAN) for 5 min then air-dried at room temperature. The average surface roughness (Ra) of PEEK discs was assessed by an atomic force microscope (AFM) (QUESANT, INSTRUMENT COOPERATION, UNIVERSAL SPM, USA) in non-contact mode. For all groups, the AFM image of samples was performed in a 10×10 µm scanning area. Data analysis software was utilized for 3D topographical data analysis. After the surface roughness
measurement, an adhesive system (Visio.link, Bredent, Senden, Germany, LOT # 164371) was spread over the bonding surfaces of the samples and immediately polymerized using light-curing machine (OPTILUX) for 90 seconds.

To ensure reproducibility, a cylindrically shaped acrylic mold with two parts was used (Figure 1). The PEEK discs were fixed in the corresponding holes of the lower part. The other one with height of 4 mm and an inner diameter of 4 mm was used to define the veneering area. The specimens were inserted into that mold, and a veneering composite of Gradia (GC corporate, GC Dental Product Group, Japan, LOT # 151124D) was applied to the specimens in two increments with 2 mm thickness for each increment. The increment was cured for 45 s by a curing light (OPTILUX). After polymerization, the veneered specimens were separated from the acrylic mold and immersed in distilled water for 24 h at 37 °C.

Samples were stabilized in an acrylic mold by Type 4 stone, for sitting in an accurate horizontal plane (Figure 2). Shear bond strength was calculated using a universal testing machine (INSTRON, USA). The maximum load before the separation of the resin composite from the PEEK surface was measured as the load at failure. Shear bond strength (SBS) was then measured using this formula: SBS (MPa) = Load (N) / area (mm²).

One-way ANOVA testing was applied to analyze the shear bond strength of the different surface conditioning methods. Afterwards, Tukey’s test was used for pairwise comparisons. The statistical significance level was adjusted at p<0.05.

RESULTS
The mean (±SD) bond strength of the veneering composite to the PEEK discs was 5.39±1.36 MPa in the control group, 6.43±1.05 MPa in the air abrasion group, 13.43±1.42 MPa in the sulfuric acid etching group, and 11.72±1.69 MPa in the air abrasion and sulfuric acid etching group, as evident in Table 2. One-way ANOVA test presented that, the variance in shear bond strength of the veneering composite to the PEEK discs was statistically significant.
between the groups (P < .05). The sulfuric acid etching group demonstrated SBS averages significantly higher than those of air abrasion, air abrasion and acid etching, and control groups (P < .05). SBS averages of the air abrasion and acid etching group were significantly superior to the air abrasion and control groups (P < .05). Whereas no significant statistical difference was encountered between shear bond strength averages for the control and air abrasion groups (P > .05).

The mean surface roughness values are listed in Table 3. The two-way ANOVA tests showed significant statistical differences between groups in terms of surface roughening averages (P: .000, P < .05). Surface roughness averages for the air abrasion group were significantly higher than the air abrasion and acid etching, sulfuric acid etching, and control groups (P < .05). SR averages of the control group were significantly lower than air abrasion and acid etching and sulfuric acid etching groups (P < .05). The air abrasion and acid etching and sulfuric acid etching groups presented no significant difference between them in term of surface roughness (P > .05).

**AFM evaluation**

The characteristics of PEEK surfaces after different surface treatments as determined by AFM are shown in Figure 3. As expected, the surfaces of the control group were comparatively smooth, with irregular ridges from the polishing process (Figure 3A). Air abrasion with alumina particles produced craters with large dimensions (Figure 3B). The sulfuric acid etching group exhibited smooth surface with some subsurface corrosion (Figure 3C). Air abrasion and sulfuric acid etching of PEEK surfaces showed uniform pores and pits and exhibited a rougher surface than did the control group (Figure 3D).

**SEM analysis**

From SEM micrographs, a smooth superficial layer is evident for the control group (Figure 4A). Air-abraded samples showed irregular, rough surfaces consistent with the distribution of
alumina particles (Figure 4B), while a sponge-like, complex fiber network characterized the surface of acid-etched samples (Figure 4C). In the air abrasion and acid etching group, agglomeration of alumina particles was evident inside the pores throughout the entire surface (Figure 4D).

**DISCUSSION**

The application of PEEK as a framework for fixed partial dentures needs a permanently durable and stable bonding to veneering composite materials. This study assessed the influence of chemical and mechanical surface treatment methods on the shear bond strength between the veneering composite and PEEK. It was shown that the control group reported the lowest shear bond strength of the composite resin to the PEEK surface as compared to other surface treated groups. Therefore, the first null hypothesis was accepted, while the second hypothesis was rejected since surface roughness would have an additive influence on the bond strength, but no significant improvement was observed.

Surface roughening is significant for enhancing the bonding strength of dental plastic materials.\(^9\text{–}^{11}\) Only a few types of surface roughening techniques can be effectively used with PEEK because of its strength and hardness. In the present study the choice of mechanical surface treatment was based on previous studies which recommended the airborne particle abrasion as one of the best initial pretreatment options for PEEK surface.\(^9\text{–}^{12}\) On the other hand earlier studies revealed that, sulfuric acid etching of PEEK could established durable and stable bond strength.\(^9\text{,}^{10}\text{,}^{13}\) In contrast other acids, like hydrochloric acid or nitric acid did not produce any surface changes even at highest concentration.\(^9\text{,}^{10}\text{,}^{13}\)

The low surface energy of polymer is responsible for adhesive problems, especially for wetting and interaction between the two polymers.\(^14\) In the current study, acid etching significantly increased the bond strength between PEEK and composite resin by the alteration of the chemical characteristic of PEEK structure via removing organic remnants, attacking
the aromatic structures and breaking the functional ether and carbonyl groups between the benzene ring. This results in more functional carbon-oxygen groups available to bond the components of the adhesive system, thus the surface energy increases and diffusion of the adhesive system into PEEK surface porosities can occur. However, it should be noted that 98% sulfuric acid cannot be used chairside in the clinical setting due to its health hazards. It should be only applied in a laboratory setting under controlled conditions.

The selection of Visio.link adhesive was based on the PEEK manufacturer’s recommendation. Its ability to initiate adequate bonding between PEEK surfaces and different veneering composites was previously displayed. Earlier trials reported superior bonding performances with application of Visio.link as a conditioning material on various pre-treated PEEK surfaces. Visio.link contains methyl methacrylate (MMA), pentaerythritol triacrylate (PETIA) and dimethacrylate monomers. Thus, it can be supposed that MMA makes the PEEK surfaces to swell and that the dimethacrylate monomers supply connection between the composite resin and two carboxyl groups as binding sites. However MMA is not sufficient for appropriate bonding. In the current study, the adhesive system in the control group without an additional pre-treatment showed low bond strength values. Therefore, it is likely that few shares of dimethacrylate and PETIA in Visio.link, result in the improvement of shear bond strength.

It is critical to mention that shear bond strength of unconditioned polished PEEK was not examined here. According to previous investigation, it is not possible to attain durable bonding between a veneering resin and an untreated PEEK surface. In the present study, the mechanical treatments were less effective than the chemical treatment. This is in agreement with earlier studies where etched PEEK surface presented the highest bond strength between resin material and PEEK compared to the air abrasion group.
SEM analysis of PEEK surface treated with air abrasion showed a rough surface associated with alumina particles that stuck to the polymer and suggested to reduce the mechanical interlocking, resulting in a lower shear bond strength in comparison to sulfuric acid etching group. Airborne particle abrasion mechanically modifies the PEEK surface by increasing the surface area, while acid etching chemically enhances the functional features of the polyether-ether-ketone surface.\textsuperscript{20} Also, micro-topographical modification of PEEK surfaces by sulfuric acid etching improved the diffusion of the adhesive system into the pores. Formation of resin tags could act as an anchorage site, which provides micromechanical retention by interlocking, resulting in increased shear bond strength.

The outcomes of this study presented that air abrasion plus sulfuric acid etching resulted in lower bond strength between the composite resin and the PEEK surface compared to treatment with sulfuric acid etching alone. This result agrees with Pourkhalili et al.\textsuperscript{22} who explained it by the absence of synergy between these two methods to produce greater effect than their separate effects. However, based on the current SEM analysis, it could be explained due to the agglomeration of alumina particles on the PEEK surface following air abrasion leading to blocking of the pores formed by acid etching. Thereby the amount of bonding agent that was able to flow into the pores was reduced and the shear bond strength resulted in an overall reduction.

In shear bond strength test, the strength of the initial bonding was dependent on the roughness of the material. Nevertheless, based on the current results of AFM presented in Figure 3, the improvement in shear bond strength because of various surface treatments does not correlate with the surface roughness of PEEK. The surface was roughened more when exposed to airborne abrasion with Al\textsubscript{2}O\textsubscript{3}, while the greatest bond strength achieved with acid etched group. Moreover, the shear bond strength averages of air abrasion group were not significantly different from the control group. Further research is required to explain the
surface roughness as a variable parameter on bonding strength between PEEK and veneering composite. These data will help to improve the shear bond strength in the clinical application and thus achieve a lower failure probability and higher durability.

Bond strength can be examined by several test methods. These tests vary and involve tensile/micro-tensile (TBS/µTBS) bond strength test, shear/micro-shear (SBS/µSBS) bond strength test. The shear bond strength test was selected in the current study since this test is comparatively easy to perform, simple and can initiate shear stress, which is an important contributor to weakening and debonding of restorative materials. Also, the shear bond strength test is more suitable for assessing adhesive abilities of composite resin. Any modification in the surface treatment of the restorative materials may influence the shear strength, which is correlated to chemical and mechanical adhesion. This is supported by other recent studies investigating the effect of surface pre-treatments on shear bond strength between composite veneer and PEEK. From a methodological point of view, a limitation of the present study can be the absence of artificial aging by water storage for long-term or thermocycling. Specimens should undergo an artificial aging to obtain clinically relevant statements. Limitations should be considered as future research ideas.

CONCLUSION

The surface roughness did not show a clear effect on the bonding behavior of PEEK to the composite resin veneer. The surface morphology (shape and texture) was more important than surface topography (roughness) for improving the adhesion of veneers to PEEK. Air abrasion with alumina particles adversely affected the bonding strength of PEEK to the veneering composite.

ACKNOWLEDGEMENTS

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REFERENCES


Table 1: Material names, Specifications, chemical compositions, batch number (lot no.) and manufacturers.

<table>
<thead>
<tr>
<th>Product Name</th>
<th>Producer</th>
<th>Constitution</th>
<th>Step of Application according to the manufacturer recommendation</th>
<th>Lot. No</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEEK KETRON</td>
<td>Invisibo PEEK CLASSIC</td>
<td>Polyether-ether-ketone</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Germany.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Visio.link adhesive</td>
<td>Bredent Senden Germany.</td>
<td>MMA, PETIA, Photoinitiators</td>
<td>1. Apply material on the surface by brush 2. Light curing for (90s)</td>
<td>164371</td>
</tr>
<tr>
<td>GC Gradia (Finehybrid)</td>
<td>GC Corporation, Japan.</td>
<td>UDMA, EDMA, 75% by weight filler: ceramic, prepolymer, SiO2</td>
<td>Light cure for 45 s</td>
<td>151124D</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td></td>
<td>H₂SO₄ 98%</td>
<td>Application for 60 s; washing for 60 s with distilled water</td>
<td></td>
</tr>
<tr>
<td>Air-abrasion</td>
<td>KOROX Renfert Germany</td>
<td>50 µm aluminum particles</td>
<td>-</td>
<td>54299</td>
</tr>
</tbody>
</table>

PEEK: Polyether-ether-ketone, MMA: Methylmethacrylate, PETIA: Pentaerythritol triacrylate UDMA: Urethane(meth)acrylate, EDMA: 3,4-Ethlenedioxy-N-methylamphetamine, H₂SO₄: Sulfuric acid
Table 2: Shear bond strength of the different surface treatment groups (±SD)

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th>Shear bond strength (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>5.39±1.36</td>
</tr>
<tr>
<td>Air-abrasion</td>
<td>6.43±1.05</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td>13.43±1.42</td>
</tr>
<tr>
<td>Air-abrasion and acid etching</td>
<td>11.72±1.69</td>
</tr>
</tbody>
</table>

* $P < .05$  SD: Standard deviation
Table 3: Evaluation of Groups in term of Surface Roughness (NM)

<table>
<thead>
<tr>
<th></th>
<th>Surface Roughness (nm)</th>
<th>mean±SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td></td>
<td>293.43±103.14</td>
</tr>
<tr>
<td>Air-abrasion</td>
<td></td>
<td>1378.09±279.43</td>
</tr>
<tr>
<td>Sulfuric Acid</td>
<td></td>
<td>737.2±198.12</td>
</tr>
<tr>
<td>Air-abrasion+ Acid Etching</td>
<td></td>
<td>784.58±263.8</td>
</tr>
<tr>
<td><em>P</em></td>
<td></td>
<td>.000*</td>
</tr>
</tbody>
</table>

_P_ < .05
Figure 1: Illustration of acrylic mold
Figure 2: Illustration of the specimens embedded in the mold with Type 4 stone
Figure 3: AFM images of PEEK surfaces. A: Without pre-treatment (Control). B: Air abrasion C: Sulfuric acid etching D: Air abrasion and acid etching
Figure 4: SEM micrographs of different surface treatment modalities at a magnification of 2000x  A: Without pretreatment (Control)  B: Air abrasion with alumina particles  C: Sulfuric acid etching  D: Air abrasion and acid etching