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Effect of different surface pre-treatments and luting materials on shear bond strength to PEEK

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Abstract

Objectives: To assess the bonding potential of a universal composite resin cement and an adhesive/composite system to differently pre-treated PEEK surfaces.

Methods: One-hundred-and-fifty PEEK discs were embedded in epoxy resin, polished (P4000 grit) and treated as follows (n = 30/group): (A) No treatment, (B) Acid-etching with sulfuric acid (98%) for 1 min, (C) sandblasting for 10 s with 50 µm alumina, (D) sandblasting for 10 s with 110 µm alumina, (E) silica coating using the Rocatec system (3M ESPE). Polished and sandblasted (50µm alumina) cp titanium (grade 4) served as a control. Acrylic hollow cylinders were either luted with a universal composite resin cement (RelyX Unicem) or an unfilled resin (Heliobond) and a hybrid composite (Tetric) to the specimens. Bond strength was measured in a shear test and failure modes were assessed. Statistic analysis was performed with one-way ANOVA followed by a post-hoc Scheffé test and unpaired t-tests.

Results: With the universal composite resin cement, no bond could be established on any PEEK surfaces, except specimens etched with sulphuric acid (19.0 ± 3.4 MPa). Shear bond strength to titanium was significantly lower (8.7 ± 2.8 MPa, $p < 0.05$). Applying the adhesive/composite system, shear bond strength values on pre-treated PEEK ranged from 11.5 ± 3.2 MPa (silica coating) to 18.2 ± 5.4 MPa (acid etched) with no statistically significant differences ($p > 0.05$). No bond was obtained on the polished surface.

Significance: Bonding to PEEK is possible when using a bonding system. No adherence can be achieved with the tested universal composite resin cement except on an etched surface. The results strongly encourage further research in PEEK application in dentistry.

Key words: PEEK, composite resin, bonding, shear bond strength, SEM

1. Introduction

PEEK (polyetheretherketone), also referred to as polyketones, is obtained from aromatic dihalides and bisphenolate salts by nucleophilic substitution. The bisphenolate salt is formed in situ from bisphenol and either added sodium or added alkali metal carbonate or hydroxide, by the Williamson ether synthesis. PEEK is a semicrystalline thermoplastic with good mechanical properties [1]. The chemical structure of polyaromatic ketones provides stability at high temperatures (exceeding 300 °C), resistance to chemical and radiation damage, compatibility with many reinforcing agents (such as glass and carbon fibers), and greater strength (on a per mass basis) than many metals, making it highly attractive in industrial applications, such as aircraft and turbine blades, for example [2, 3]. PEEK is also considered an advanced biomaterial used in medical implants, often reinforced by biocompatible fibres such as carbon [1]. In dentistry, this material is mainly used as a plastic temporary abutment for implants in the fabrication of temporary crowns [4]. The material is biocompatible and features a natural tooth-colour appearance. In addition, PEEK can easily be shaped with dental burs. In the field of restorative and prosthetic dentistry, PEEK has not found much attention yet, basically due to difficulties in establishing a strong and durable adhesion to composite resin materials owing to its low surface energy and resistance to surface modification by chemical treatments [5, 6]. Until now, industry bonds elastomers to PEEK typically by conventional abrasive treatments, acid etching, laser treatment or plasma techniques to prepare the engineering plastic's surface followed by the application of epoxy adhesive. Most of these techniques are, however, difficult to apply under clinical settings in dentistry. Information concerning the potential and limitations of this material in bonding to dental materials is scarce if not to say inexistent.

Therefore, it was the aim of the present investigation to assess possible bonding techniques of PEEK to dental composite resin materials. We hypothesized that pre-treatment with either

mechanical and/or chemical measures would result in possible adhesion to PEEK, irrespective whether an adhesive/composite or a universal composite resin cement was used.

2. Materials and methods:

2.1 Specimen preparation

One-hundred-and-fifty PEEK discs (PEEK-CLASSIX, Villmergen, Switzerland) with a diameter of 10 mm and a thickness of 2 mm were embedded in self-curing acrylic resin (ScandiQuick, Scandia, Hagen, Germany) and a standard surface was created by means of a polisher (Reco GMT 5350, Le Leux, Switzerland) with a series of SiC-papers up to P4000 grit. Before initiating the bonding procedure, the specimens were cleaned for 10 min in an ultrasonic water bath (Bransonic Ultrasonic Cleaner 3510 E-DTH, Branson, Danbury, USA) and air-dried.

The PEEK surfaces were then treated as follows (n = 30 for each pre-treatment group):

(A) No treatment.

(B) Acid-etching with sulfuric acid (98%) for 1 min. Careful rinsing with de-ionized water for 1 min.

(C) Sandblasting with alumina with a mean particle size of 50 µm (LEMAT NT4, Wassermann, Germany) for 10 s at a pressure of 2 bar and at a distance of 10 mm between the nozzle and the surface

(D) Sandblasting with alumina with a mean particle size of 110 µm as described under point C

(E) Silica coating (Rocatec Delta, 3M ESPE, Seefeld, Germany) with Rocatec Pre (3M ESPE) for 10 s and subsequent Rocatec Plus (3M ESPE) for 12 s. Application of ESPE Sil (3M ESPE) and air-drying for 5 min

Titanium specimens (cp-titanium grade 4) with the same dimensions were prepared as control, following the same procedure as described above under point (C), i.e. polishing and subsequent sandblasting with 50 µm alumina.

Two additional specimens were produced of each surface treatment group and analyzed by means of SEM (CS4, CamScan, Waterbeach, UK) to assess the surface topography after the respective surface pre-treatment. Samples were at a magnification of 2000x.

2.2 Shear bond strength testing

Fifteen samples of each pre-treatment group were randomly allocated to one of the following two bonding procedures/materials (Table 1):

- Application of the universal composite resin cement RelyX Unicem (3M ESPE)
- Application of an unfilled resin material (Heliobond, Ivoclar Vivadent, Schaan, Liechtenstein) and a fine hybrid composite resin material (Tetric, Vivadent).

An acrylic hollow cylinder with an inner diameter of 3.1 mm and an outer diameter of 4.0 mm was pressed onto the different surfaces by means of a special bonding device (Figure 1), the universal cement was filled into the opening of the cylinder and pressed with a force of 100 N and polymerized for 40 seconds (Elipar Freelight 2, 3M ESPE; 1000 mW/cm^2). Thereafter the specimens were carefully removed from the device. When the adhesive composite resin material was used, the bonding agent was applied first, blown to a thin layer with an oil-fee air and after carefully removing all excess material the material was light-cured for 40 seconds. Subsequently, the composite resin material was applied and light cured for additional 40 seconds.

Following bonding procedure the specimens were stored in distilled water at 37 °C for 24 h.

The shear bond strength was tested with a universal testing machine (Z010, Zwick, Ulm, Germany). The specimens were positioned in the sample holder with the treated sample surface parallel to the loading piston in a distance of 200 µm. The loading piston had a chisel

configuration and load was applied with a crosshead speed of 1 mm/min. Load at failure was recorded and shear strength values were calculated according to the equation $\sigma = F/A$, where σ is the shear bond strength, F the load at failure (N) and A represents the adhesive area (mm^2).

For the fracture analysis, the debonded area was examined with a stereomicroscope at 40x magnifications (M3B, Wild, Heerbrugg, Switzerland). Failure was considered: adhesive - if the cement/resin was dislodged from *PEEK/titanium*; cohesive in the cement/resin - if the fracture occurred only in the cement/resin; cohesive in *PEEK/titanium* – if the fracture occured only in the *PEEK/titanium*.

The adhesive interface and adhesive luting material penetration, i.e. possible tag formation was analyzed by SEM (CS4, CamScan, Waterbeach, UK). For this purpose, two notches were prepared at the specimens and the specimens were fractured. The specimens were examined at a magnification of 150 to 2000x.

2.3 Data presentation and analysis

Statistical tests were performed with StatView Version 5 (Abacus Concepts, Berkley, CA). Mean values and standard deviations were calculated and results of the shear bond strength measurements presented as bar charts with standard deviations. One-way ANOVA followed by a post-hoc Scheffé-test and unpaired t-tests were applied to find differences between the experimental treatments. The level of significance was set at 5%..

3. Results

3.1 Surface morphology after pre-treatment

The surfaces after the different pre-treatments are shown in Figures 2 and 3.

Whereas the polishing resulted in a smooth PEEK surface with little surface alterations (Fig. 2A), distinct surface modifications were visible with all other treatments. On PEEK, the

etching with sulfuric acid resulted in a complex fibre network (Fig. 2B and 3A), while sandblasting with a particle size of 50 µm led to an irregular surface (Fig. 2C), which was similar to the likewise treated titanium surface (Fig. 2F), but showed a more accentuated and dispersed surface pattern as compared to the 110 µm pre-treatment (Fig 2D). Concerning the latterly produced and described surfaces, the silica coating resulted in a comparable surface morphology (Fig. 2E).

At high magnifications, the acid etching with sulfuric acid resulted in a complex fiber network and a porous and blister-like subsurface dissolution of the PEEK material (Figures 3 A and B). This zone, however, could not be penetrated by the different materials, and there was no apparent tag formation. Nevertheless, there was a firm contact between the different materials (Fig 3C-F).

3.2 Shear bond strength measurements

Mean shear bond strength values are shown in Figure 3.

On PEEK surfaces, the following observations were made: On the polished surfaces, no adhesion could be established with both resin systems. Mechanical surface roughening using sandblasting with 50 or 110 µm alumina, or combined mechanical/chemical modification with the Rocatec system did not lead to any adhesion with the universal composite resin cement, whereas the application of an adhesive and the composite resin led to shear bond strength values ranging from 11.5 ± 3.2 MPa (silicate coating) to 13.5 ± 2.4 MPa (sandblasting 50 µm). The latter values were statistically not significantly different ($p > 0.05$). The highest bond strengths as compared to all other treatments could be measured for both resin systems, when the PEEK was chemically pre-treated with 98% sulfuric acid ($p < 0.05$): Shear bond strength values of 18.2 ± 5.4 MPa for the Heliobond/Tetric and 19.0 ± 3.4 MPa for RelyX Unicem could be obtained ($p > 0.05$).

Sandblasting with a mean grit size of 50 μm on the titanium surface was able to establish an adhesion to RelyX Unicem with a bond strength of 8.7 ± 2.8 MPa. This value was, however, significantly lower as compared to the shear bond strength measurements obtained for PEEK in combination with the adhesive system Heliobond/Tetric ($p < 0.05$).

3.3. Failure mode

The results of the fracture analysis are presented in Table 2. The highest percentage of cohesive failures could be observed in PEEK samples pre-treated with acid-etching (47% for Heliobond/Tetric and 33% for RelyX Unicem). In the air-abraded samples, the percentage of cohesive failures was less than 15%. No cohesive failures could be detected when RelyX Unicem was applied on air-abraded titanium.

4. Discussion

In the present study, our hypothesis that pre-treatment with either mechanical and/or chemical measures would result in possible adhesion between PEEK and adhesive/composite was confirmed. An adequate adhesion to PEEK could be established when a hydrophobic dental bonding agent in combination with a composite resin was used. In contrast, the universal composite resin cement failed to bond to sandblasted PEEK. One reason for that finding may be the change from hydrophilic to hydrophobic properties during the setting of the cement, which may negatively interfere during the initial wetting and setting phase [7]. Nevertheless, we employed this material as it is frequently used in daily clinical practice and represents one of the most thoroughly invstigated self-adhesive cements in the literature [8]. Several studies indicated that RelyX Unicem exhibits similar bonding performance as various other prosthodontic resin cement materials and good marginal integrity [9-11]. Retention forces of noble alloy castings cemented on titanium abutments with different cements were investigated

[12]: RelyX Unicem was comparable to the retention achieved using polycarboxylate cement, and significantly higher in comparison to retention following the cementation with zinc oxide, zinc phosphate, and glass-ionomer cements.

To the knowledge of the authors this is the first evaluation of the bonding performance to PEEK in regard to dental applications. Hence, the present results cannot be compared to other available studies. In addition, differences in the methodology and especially the substrata evaluated adequate comparisons and conclusions are significantly impeded.

From a methodological point of view, a shortcoming of this study is the lack of artificial aging by thermocycling or long-term water storage. However, as this was the first study, the main goal was to assess the overall feasibility of establishing bonding to PEEK. Especially the etching process with concentrated sulfuric acid showed very favorable results. Both adhesive materials investigated in this study revealed their highest resistance to shear forces on this surface. It must be noted again that a 98% sulfuric acid cannot be used under clinical conditions, but preliminary tests demonstrated that other acids, like hydrochloric acid or nitric acid did not produce any surface changes even at highest concentrations (data not presented). Sulfuric acid has probably led to a highly porous and permeable surface, providing pronounced undercuts, which could be more easily penetrated by the adhesives, although no tags were observed in the respective SEM images.

In conclusion, this study showed that a hydrophobic adhesive was able to bond to PEEK and a composite resin. The universal composite resin cement, in contrast, seemed not suitable to bond to PEEK. Additional studies, however, are required to investigate leakage of the compounds after thermo-mechanical loading conditions and the mechanical resistance under clinical loading conditions.

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