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DOI: https://doi.org/10.1016/j.prosdent.2014.05.014

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Short title: Bonding properties between PEEK and resin composite

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Keywords: tensile bond strength, PEEK, adhesive system, surface treatment, acid etching

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ABSTRACT

Statement of the problem. Polyetheretherketone (PEEK) can be used to support fixed dental prostheses (FDPs). However, information about the durable bond to veneering resins is still scarce.

Purpose. The purpose of this study was to investigate the effect of chemical treatments of PEEK on tensile bond strength (TBS) to veneering resins with special emphasis on surface free energy (SFE) and surface roughness (SR).

Materials and methods. Seven-hundred-fifty PEEK specimens were fabricated and divided into the following 3 pretreatment groups (n=250/group): etching with sulfuric acid for 60 seconds, piranha acid for 30 seconds, and an unetched control. After pretreatment, SFE was determined by using contact angle measurements and SR with a profilometer (n=10/group). The topography of pretreated PEEK surfaces was examined with SEM. Remaining specimens (n=240 per group) were conditioned with visio.link (VL), Signum PEEK Bond (SPB) or were left untreated as control group (CG). Half of each group was veneered with Sinfony, or VITA VM CL (n=40/group), and TBS was measured after storage in distilled water at 37°C for either 24 hours or 60 days. Data were analyzed by 4-way and 1-way ANOVA followed by the Scheffé post hoc test and Chi^2-test (α=.05).

Results. PEEK specimens etched with sulfuric acid resulted in higher SFE and SR than specimens without pretreatment or etching with piranha acid. Etching with sulfuric acid or piranha acid led to no general recommendations with respect to TBS. Conditioning with VL or SPB significantly increased the TBS (P<.001). PEEK veneered with Sinfony showed significantly higher TBS values than those veneered with VITA VM LC (P<.001).

Conclusion. Sufficient TBS for bonding to veneering resin can only be achieved when additional adhesive materials were applied.

CLINICAL IMPLICATIONS

For the veneering of PEEK-based FDPs, additional adhesive systems are necessary. The adhesive systems visio.link and Signum PEEK Bond can be recommended for the conditioning of PEEK surfaces before the veneering process.

INTRODUCTION

Resin-based materials are commonly used for computer-aided design/computer-aided manufacturing (CAD/CAM) in restorative dentistry.[1] Mainly because of their higher fracture resistance, better stress distribution,[2-6] and lower abrasion of the antagonist enamel,[7,8] high-density CAD/CAM polymers can be used as an alternative to glass ceramics. Methacrylate-based materials are still among the most commonly used CAD/CAM polymers. Because of the high conversion rate produced by the industrial polymerization of CAD/CAM blanks, an adequate bond to other methacrylates, including cements or veneering materials, is difficult to achieve. Nevertheless, previous studies have shown that with surface pretreatment by airborne-particle abrasion and adhesive system application, the achievement of adequate bond strength to other methacrylates is possible.[9-12] Polyetheretherketone (PEEK), in contrast, represents a methacrylate-free, high-performance thermoplastic polymer consisting of aromatic benzene molecules, which are connected alternately by functional ether or ketone groups.[13] It shows good dimensional stability[14] and is radiolucent, making it compatible with imaging techniques such as computed tomography, magnetic resonance imaging, and x-ray.[13,15] In order to achieve a higher rigidity of the material for dental application, pure PEEK material has been further optimized by blending, filling, and fiber reinforcement.[16-19] Optimal mechanical properties of the PEEK composite resins were achieved at optimum levels when containing about 7 wt% nano-SiO_2. Reduced wear rates were obtained with a ZrO_2 content of 7.5 wt%.[19] Currently, most dental PEEK materials contain inorganic fillers of about 20 wt%. Because of its attractive mechanical properties[13,20] and its biocompatibility,[13,15] PEEK shows significant advantages for dental applications. However, the grayish or whitish color and the

low translucency of PEEK still limit its use as a monolithic. anatomic contour dental restoration material.[21] Thus, additional veneering is required to obtain satisfactory esthetics. Primarily, however, durable bonding must be achieved to ensure an adequate functional outcome and long-term stability. The latter can be established by chemical adhesion, (micro) mechanical retention, or a combination thereof and depends on the composition and interaction of the materials used.[22]

In general, the mechanical retention of the veneering composite resin depends on its viscosity and therefore on the weight percentage of the filler content.[23] An increase in particle content is associated with an increase in viscosity. The chemical composition and the low surface energy of PEEK may lead to difficulties for bonding to resin-based materials. Previous studies screened the bonding ability between PEEK and composite resins and stated that no, or only insufficient values, can be achieved without any further treatment of the PEEK surface.[16,21,24-27] These studies also showed that additional adhesive systems are essential in establishing a strong bond to composite resins.[21,26,28] Acid treatment leads to emerging carbon-oxygen compounds, thereby providing more functional groups to which the components of adhesive systems can bond.[29] In addition, a hydrolysis of the connecting ether and ketone linkages takes place.[27]

For laboratory investigation of the bonding effectiveness between different materials, microtests or macrotests, depending on the bonding area of the investigated materials, can be used.[30-32] However, these methods show differences such as the type of testing device, the settings of testing machines, and the stress distribution at the bonding interface. Tests were distinguished according to the direction in which a force was applied to the substrate´s surface tensile (TBS) and shear bond strength (SBS). To determine the surface properties of dental restorations, the surface roughness can be measured by a profilometer, while the surface-free energy can be determined by contact angle measurement with appropriate liquids.[33-37]

Etching the PEEK surface with different acids before conditioning with methyl

methacrylate (MMA)-based adhesive systems and before veneering with resins has not been investigated. Therefore, the present study tested the ability of adhesive systems to promote adhesion between MMA-based veneering resins and PEEK after etching by using tensile bond strength evaluation. The null hypotheses investigated were that etched PEEK surfaces and PEEK surfaces after application of adhesive systems show similar bond strength to veneering resins compared to untreated surfaces. In addition, neither the choice of the veneering resin nor the aging level would affect the bond strength.

MATERIAL AND METHODS

Seven-hundred-fifty PEEK specimens (7×7×2 mm) were sectioned for bond strength measurements (N=720) from 2 blanks (Dentokeep, Lot.No: 11DK14001; nt-trading) with a diamond cutting disk (918PB.104.220; Gebr. Brasseler GmbH & Co KG). Another 30 specimens were fabricated to analyze surface properties (20×20×2 mm). Subsequently, the PEEK substrates were embedded in an autopolymerizing acrylic resin (ScandiQuick; Scan-Dia Hans P. Tempelmann GmbH & Co KG) and polished under abundant water supply for 40 seconds from P500 up to P2400 silicon carbide paper (SiC) (ScanDia Hans P. Tempelmann GmbH & Co KG) with an automatic polishing device with a contact force of 25 N (Tegranim-20; Struers).

After polishing, the specimens were divided into 3 surface pretreatment groups: (n=10 for determination of surface properties and n=240 for tensile bond strength measurements): sulfuric acid etching, piranha acid etching, and no pretreatment. Sulfuric acid was applied for 60 seconds,[25] and piranha acid, a mixture of sulfuric acid and hydrogen peroxide in a ratio of 10:3, was applied for 30 seconds to the PEEK substrate. In general, 100 µL (micro-pipette; Eppendorf) of acid were applied to each surface, followed by careful rinsing with deionized water for 30 seconds. Special care was taken to rinse in a constant motion in a single direction

to avoid any additional directional changes of the delicate new surface topography. Thereafter, specimens were air dried for 10 seconds.

To determine the surface free energy (SFE), a contact angle meter (EasyDrop; Krüss) was used with distilled water or diiodomethane (99%, CAS: 15.842-9; Sigma-Aldrich, Lot.No: S65447-448) at room temperature (23°C). The PEEK substrates were investigated after each pretreatment (n=10 per group) with the static sessile drop technique. Measurements were conducted with 3 drops of each liquid separately. A standardized liquid volume was applied (distilled water: 10µL, diiodomethane: 5µL) and registered with a digital camera (Krüss camera; Krüss) after 5 seconds. From the height and the diameter of each single drop, the contact angles were determined with proprietary software (Easy Drop DSA4; Krüss) based on the Ström database. Depending on the emerging angle of the fluid drops, different computation methods were used. For flat angles of diiodomethane, the circle method was used, while for distilled water, the contact angle was determined by the tangent-1 method. SFE was calculated on the basis of the contact angles.[38,39]

$$SFE_S = cos\theta \cdot SFE_L + IFT_{LS}$$

$$IFT_{LS} = SFE_S + SFE_L - 2 \cdot \left(\sqrt{SFE_S^D \cdot SFE_L^D} + \sqrt{SFE_S^P \cdot SFE_L^P}\right),$$

where SFE_L is the surface energy of the liquid, SFE_S is the surface energy of the solid, SFE_L^P is the surface free energy of the liquid, polar component, SFE_S^P is the surface free energy of the solid, polar component, and SFE_L^D is the surface free energy of the liquid, dispersive component, SFE_S^D: The surface free energy of the solid, dispersive component, IFE_{LS} is the interfacial energy, and θ is the contact angle.

The same specimens were also used to determine the surface roughness (SR) with a profilometer (MarSurf M400+SD26; Mahr) with a 90 degree sensing device and a contact force of 0.7 mN. The diamond probe tip had a diameter of 2 µm, and each specimen was measured 6 times with a measuring track of 6 mm. The distance between the parallel tracks was set at 0.25 mm.

The surface structure topography of each pretreatment group was examined under a scanning electron microscope (SEM: Carl Zeiss Supra 50 VP FESEM; Carl Zeiss). For this purpose, specimens were sputter coated with gold-palladium (Balzers SCD 030; Balzers Union) for 30 seconds in an argon gas atmosphere at a target distance of 50 mm and at a pressure of 5 Pa. The working distance was 5 to 7 mm, and the acceleration voltage accounted for 10 kV.

For the tensile bond strength (TBS) measurements, PEEK substrates (after pretreatment) were further subdivided into 3 groups with respect to the adhesive system used (n=80 per group): visio.link: application and light polymerization (Bre.Lux Power Unit; Bredent GmbH & Co. KG) for 90 seconds; Signum PEEK Bond I+II: application of liquid I and vaporization for 10 seconds, application of liquid II and light polymerization (HiLite Power; Heraeus Kulzer) for 90 seconds; and without the use of an additional adhesive system (control) (Table I).

Consecutively, specimens of each adhesive system group were veneered with either Sinfony (3M ESPE) or VITA VM LC (VITA Zahnfabrik); n=40 per veneering resin. For this purpose, acrylic resin cylinders (DS Mechatronik) with an inner diameter of 2.9 mm and a height of 10 mm were manually filled with one of the veneering resins and polymerized to the PEEK substrate. The polymerization of the veneering resins was performed with Bre.Lux Power Unit for 6 minutes by using the standard program with intensity according to the manufacturer´s information, 190 to 220 mW/cm^2 dependent on wavelength. One half of each group (n=20) was measured after 24 hours storage in distilled water at 37°C (Hera Cell 150; Heraeus Kulzer), whereas the other half was subjected to storage in distilled water for 60 days at 37°C (Fig. 1).

The bonded specimens were placed in a universal testing machine (Zwick 1445; Zwick) and loaded with a crosshead speed of 5 mm/min.[21] The acrylic resin cylinder was held by a collet, allowing the whole system to self-align. Specimens were positioned in the jig with

the specimen´s surface perpendicular to the loading direction (Fig. 2). The jig was attached to the load cell and pulled apart by an upper chain. The tensile bond strength was calculated.

Failure types were examined under a reflected-light microscope at a 20× magnification (Stemi 2000-C, light source: CL 6000 LED; Zeiss). Failures were classified as cohesive failure in PEEK, cohesive failure in veneering composite resin, adhesive failure, or mixed failure.

Before beginning the study, a power analysis was calculated (nQuery Advisor Version 6.04.10; Statistical Solutions) based on the results of a pilot study with 7 piranha-etched PEEK specimens bonded with Signum PEEK Bond as the adhesive system and veneered with VITA VM LC (mean: 15 ±4.7 MPa). A sample size of 20 in each group was shown to have 98% power to detect a difference of 28% in means caused by aging, assuming that the common standard deviation was 2.6 MPa with a 2-group *t* test with a Bonferroni corrected 2-sided significance level of .005.

For the data analysis, the Kolmogorov-Smirnov and Shapiro-Wilk tests were used to verify the normality of data distribution of all data measured. Descriptive statistics (mean, standard deviation (SD) and 95% confidence intervals (CI)) were computed. Significant differences between the groups were tested with 4-way and 1-way ANOVA, followed by the Scheffé post hoc test. Relative frequencies of failure types, together with the corresponding 95% CI, were computed. Differences between the failure types of tested TBS groups were analyzed with the Chi^2-test. All statistical tests were performed with IBM SPSS (Version 20; IBM Corporation) (α=.05).

RESULTS

The SFE and SR values were normally distributed. PEEK surfaces etched with sulfuric acid showed significantly higher SFE values than groups etched with piranha acid and higher SR values than groups etched with piranha acid or without pretreatment (Table II). However,

the SFE of the unetched control group was not significantly different from that of the groups etched with sulfuric or piranha acid. SEM images after the different pretreatment methods are depicted in Figure 3. Etching with sulfuric acid displayed round cavities on the PEEK surface (Fig. 3A), whereas etching with piranha acid resulted in an irregular structured surface (Fig. 3B). Non- pretreated PEEK showed a plain and homogeneous surface (Fig. 3C).

Only 27.8 % of all TBS groups were not normally distributed (10 groups out of 36, but containing no outliers), which is close to the primary error for a statistical test (Table III). Therefore, for all statistical tests, normal distribution was assumed. Although the 4-way ANOVA interaction (pretreatment × adhesive system × veneering composite resin × aging level) for the TBS data showed no statistical significance (P=.046) when compared to the Bonferroni corrected significance level of α=.003, most of the 3-way and 2-way interactions were significant (P<.001). Therefore, the underlying different analyses were individually computed and divided by these different levels.

With respect to the pretreatment method, the following results were observed: Specimens measured initially showed no effect of pretreatment method in unconditioned groups (P>.084), in conditioned groups using Signum PEEK Bond (P>.054) and in conditioned groups using visio.link and subsequent water storage for 60 days (P>.302), regardless of the veneering composite resin (Table IV). Also, no effect was observed for unconditioned, VITA VM LC veneered specimens after 60 days (P=.317). In the groups conditioned with visio.link and veneered with Sinfony, the specimens etched with piranha acid showed significantly lower initial TBS than specimens which were not pretreated (P=.018). For PEEK surfaces etched with sulfuric acid, no statistically significant differences in initial TBS were found (P>.051) with regard to both other pretreatment methods. When veneering unconditioned, aged PEEK surfaces with Sinfony, etching (with sulfuric or piranha acid) led to significantly higher TBS than when etching was omitted (P<.001). In contrast, when veneering PEEK surfaces with Sinfony after conditioning with Signum PEEK Bond,

etching with sulfuric acid let to significantly lower TBS after aging, than in the group without etching (P=.027). Among this veneering type and aging level, pretreatment using piranha acid showed no different TBS values compared to the other pretreatment methods (P>.098). Within groups conditioned with visio.link and veneered with VITA VM LC, etching with sulfuric acid caused a significantly higher initial TBS than no pretreatment or etching with piranha acid (P<.001). After a water storage time of 60 days, PEEK etched with piranha acid, conditioned with Signum PEEK Bond and veneered with VITA VM LC showed significantly lower TBS than PEEK etched using sulfuric acid or not pretreated (P<.001).

With respect to the adhesive systems used, all groups with additional adhesive systems presented significantly higher TBS than nonconditioned groups, regardless of the pretreatment method, veneering composite resin, and aging level (P<.001) (Table III). In general, in the initial measured groups, no differences between Signum PEEK Bond and visio.link were found (P<.05). After a water storage time of 60 days, groups conditioned with Signum PEEK Bond showed significantly higher TBS then those conditioned using visio.link (P<.001). The exception was the aged piranha acid-etched groups veneered with VITA VM LC; here, no differences between Signum Bond PEEK and visio.link were found (P>.05).

In general, PEEK veneered with Sinfony showed significantly higher TBS values than with VITA VM LC (P<.001). The exceptions were the following groups, which showed no difference in TBS values between the veneering composite resins: non-pretreated and conditioned PEEK substrate after 60 days of water storage (P=.158), sulfuric acid pretreated and unconditioned groups measured initially (P=.073), sulfuric acid pretreated and Signum PEEK Bond conditioned groups measured initially (P=.128), and aged (P=.840).

Unetched specimens and specimens etched with sulfuric acid and combined with Signum PEEK Bond showed a significant increase of TBS values after 60 days of water storage (P<.001), regardless of the type of veneering composite resin used. The same result was obtained after piranha acid etching without conditioning in combination with Sinfony

(*P*=.020) and when applying visio.link in combination with VITA VM LC (*P*=.017). In contrast, sulfuric acid pretreatment with visio.link combined with VITA VM LC (*P*=.004) showed a significant decrease in TBS after 60 days of water storage compared to the initial values. All other groups showed no effect of water storage duration.

Significant differences between the tested groups with respect to the failure types were determined (*P*<.001). Predominantly, adhesive failure types were observed with the exception of groups conditioned with Signum PEEK Bond. Signum PEEK Bond groups primarily showed cohesive failures (Table VI).

DISCUSSION

Based on the mechanical properties, PEEK seems to be a suitable material for dental applications.[20] However, adequate bonding between PEEK and veneering resins remains a key factor in ensuring long-lasting survival and success rates.

The present study assessed the influence of the chemical surface pretreatment of PEEK with different acids in combination with 2 adhesive systems, suggesting a potential adhesion promotion between the PEEK substrate and the veneering composite resins. The results showed that the etching of PEEK increased the SFE and SR; however, it did not clearly improve the bond strength to a veneering resin. Therefore, the first hypothesis, which stated that PEEK after chemical pretreatment achieves similar TBS values to no pretreatment was accepted. Previous studies which investigated the bonding properties of differently pretreated PEEK specimens showed higher bond values after etching compared with untreated specimens.[25-27] While airborne-particle abrasion results in an improvement of the microroughness of the substrate,[20] pretreatment with acids results in an increase of functional carbon-oxygen groups on the superficial layer of PEEK.[27,29] Sulfuric acid attacks the functional ether and carbonyl groups between the benzene rings, while the atomic oxygen (which emerges during the reaction of sulfuric acid and hydrogen peroxide) in piranha acid

reacts directly with the benzene ring.[27] This results in more functional groups available to bond to components of the adhesive system. Thus, the surface polarity increases and an improvement of the diffusion of the adhesive system into the PEEK polymer can occur, resulting in higher bond strengths.[27] However, this theory was not corroborated by the results of the current study, as piranha acid resulted in lower SFE and TBS values. To the authors knowledge, this was the first study which assessed the SFE and TBS of PEEK to resins after pretreatment with sulfuric and piranha acid. According to previous research, a sulfonation of the benzene ring in the PEEK molecule can be theoretically achieved when sulfuric acid is used.[40] The sulfonic acid groups can further react with the methacrylate of the adhesive systems to PEEK. This may explain the higher bond strength values of the PEEK substrate after pretreatment with sulfuric acid in comparison with piranha acid. However the latter study and our investigation did not use the same sulfuric acid concentration and application time. Additional research should therefore analyze the molecular content of substrates after pretreatment by using energy dispersive x-ray spectroscopy (EDX).

The chemical composition of the adhesive systems plays a central role in creating a chemical bond between the different polymers. According to a previous study, without the additional use of an adhesive system after chemical pretreatment, no bond could be established to the veneering composite resin VITA VM CL, whereas somewhat low bond strength values could be observed for Sinfony.[21] Generally, without the additional use of an adhesive system, no bond can be established between PEEK and resin materials.[21,24-26,28] Therefore, the second hypothesis that the use of an additional adhesive system results in similar TBS values when no additional adhesive system is applied was rejected. Kern & Lehmann investigated the TBS of a provisional resin to PEEK with different methods for surface pretreatment and adhesive systems for conditioning.[24] They found the highest values (14.5 ±2.6 MPa) for MMA-containing adhesive systems. Another study, investigating the TBS of veneering composite resins to PEEK after the use of different adhesive systems also

corroborated these findings, namely, that MMA-containing adhesive systems resulted in the highest bond strength values.[21] However, in contrast to the present study, those studies used airborne-particle abrasion[21,24] or tribochemical silica-coating[24] and not acidic pretreatment procedures.

The choice of the veneering composite resin was mainly based on different viscosities. In general, a higher viscosity due to higher filler content may negatively influence mechanical retention.[23] A previous study investigated the TBS of the same veneering composite resin to PEEK, pretreated with airborne-particle abrasion and conditioned with the same adhesive systems.[21] Regardless of the veneering composite resin used, no bonding potential could be found for specimens without an additional adhesive system. In contrast, the present study showed that even when omitting the application of an adhesive system and only etching with piranha acid, TBS values of 7.4 to 9.9 MPa could be reached with Sinfony. Under the same conditions, only very low or no bond values (0 to 0.1 ±0.5MPa for VITA VM CL) could be observed. A possible explanation for this is the lower viscosity of Sinfony compared with VITA VM CL; this characteristic may have enabled the veneering composite resin to more thoroughly penetrate the micropores created by the acid etching. Therefore, the third hypothesis that the option of veneering composite resin had no impact on the TBS values had also to be rejected. The results may therefore lead to the assumption that the veneering composite resin Sinfony can form a more stable bonding pattern by mechanical anchorage than VITA VM CL.

Laboratory tests which determine bond durability use long-term storage and thermal cycling as a means of artificial aging.[24] Therefore, all specimens should be subjected to reproducible standardized stress. However, a generally accepted protocol for performing artificial aging with regard to temperature and dwell time exists.[28] In the current study, an increase, as well as a decrease, of TBS values could be observed after 60 days of water storage at 37°C. Therefore, the fourth hypothesis, that artificial aging has no effect on the

TBS results was also rejected. Prior investigations have stated that because of the process of postpolymerization of the adhesive system and the veneering composite resin, higher bond strength values could be observed after artificial aging.[21,22] However, a decrease in bond strength was also observed in this study, which may be explained by the incorporation of water molecules, resulting in a splitting of the covalent bonds.

Generally, because of the lack of standardization, difficulties arise when comparing bond strength results. A literature review investigating bond strength data for adhesives to dentine showed that different testing variables (for example, specimen geometry, elasticity modulus of involved materials, and loading conditions) had a significant effect on the obtained bond strength values for all test designs under investigation.[32] More specifically, a larger bond size of the macrotests delivers lower bond strength values compared to the microtests.[32] In addition, comparisons between shear and tensile bond strength test designs also exhibit variable stress distributions at the interface because of different loading configurations.[32] However, within a single study, a comparison of the bond quality of the tested materials can at least be made, regardless of the type of test used.

To determine the SFE, the contact angles were determined on the PEEK substrate with the sessile drop technique with static drops. For every measurement, a constant liquid volume was applied to the pretreated PEEK surface. However, the contact angle will not remain constant over a longer period of time, as several factors may influence it.[33] The continuous increase or decrease with time is caused by interactions at the contact zone, for example, chemical reactions between the liquid and the substrate,[34] swelling or dissolving of the substrate by the applied liquid, [35] or the evaporation of the liquid. Therefore, contact angles were measured at a standardized time after application of the liquid drop. In general, the wettability of the substrate and therefore also the SFE is affected by surface modifications such as acid-etching or air abrasion.[36,37]

A general limitation of the present study is the material thickness of the veneering resin and the presence of the acrylic resin mold, which was used for the standardized bonding area to the PEEK substrate. These factors can negatively influence the light intensity and therefore the potential bond strength. With regard to the actual test design, a comparison was only possible to values obtained in earlier studies with the same test design.[11,12,21,26] Based on this laboratory testing, only tendencies of different bond characteristics can be determined, which may provide an indication of the clinical process. To investigate the long-term success of veneering resins in combination with PEEK under actual conditions in human patients, in vivo studies are still required after in vitro testing.

CONCLUSIONS

When veneering PEEK restorations, adhesive systems (such as Signum PEEK bond and visio.link) should be applied so as to ensure a durable bond. Acid pretreatment of the PEEK surface is not required. The veneering resin composites show no impact on the results.

REFERENCES

1. Miyazaki T, Hotta Y, Kunii J, Kuriyama S, Tamaki Y. A review of dental CAD/CAM: current status and future perspectives from 20 years of experience. Dent Mat J 2009;28:44-56.

2. Stawarczyk B, Ender A, Trottmann A, Özcan M, Fischer J, Hämmerle CHF. Load-bearing capacity of CAD/CAM milled polymeric three-unit fixed dental prostheses: Effect of aging regimens. Clin Oral Invest 2012;16:1669-77.

3. Rocca GT, Bonnafous F, Rizcalla N, Krejci I. A technique to improve the esthetic aspects of CAD/CAM composite resin restorations. J Prosthet Dent 2010;104:273-5.

4. Lin CL, Chang YH, Liu PR. Multi-factorial analysis of a cusp-replacing adhesive premolar restoration: a finite element study. J Dent 2008;36:194-203.

5. Schlichting LH, Maia HP, Baratieri LN, Magne P. Novel-design ultra-thin CAD/CAM composite resin and ceramic occlusal veneers for the treatment of severe dental erosion. J Prosthet Dent 2011;105:217-26.

6. Magne P, Stanley K, Schlichting LH. Modeling of ultrathin occlusal veneers. Dent Mater 2012;28:777-82.

7. Krämer N, Kunzelmann K-H, Taschner M, Mehl A, Garcia-Godoy F, Frankenberger R. Antagonist Enamel Wears More Than Ceramic Inlays. J Dent Res 2006;85:1097-100.

8. Kunzelmann KH, Jelen B, Mehl A, Hickel R. Wear evaluation of MZ100 compared to ceramic CAD/CAM materials. Int J Comp Dent 2001;4:171-84.

9. Stawarczyk B, Basler T, Ender A, Roos M, Ozcan M, Hämmerle c. Effect of surface conditioning with airborne-particle abrasion on the tensile strength of polymeric CAD/CAM crowns luted with self-adhesive and conventional resin cements. J Prosthet Dent 2012;107:94-101.

10. Bähr N, Keul C, Edelhoff D, Eichberger M, Roos M, Gernet W, Stawarczyk B. Effect of different adhesives combined with two resin composite cements on shear bond strength to polymeric CAD/CAM materials. Dent Mater J 2013;32:492-501.

11. Keul C, Martin A, Wimmer T, Roos M, Gernet W, Stawarczyk B. Tensile bond strength of PMMA- and composite-based CAD/CAM materials to luting cements after different conditioning methods. Int J Adhesiv Adhes 2013;46:122-7.

12. Stawarczyk B, Trottmann A, Hämmerle CH, Özcan M. Adhesion of veneering resins to polymethylmethacrylate-based CAD/CAM polymers after various surface conditioning methods. Acta Odontol Scand. 2013;71:1142-8.

13. Kurtz SM, Devine JN. PEEK biomaterials in trauma, orthopedic, and spinal implants. Biomaterials 2007;28:4845-69.

14. Skinner HB. Composite technology for total hip arthroplasty. Clin Orthop Relat Res 1988:224-36.

15. Toth JM, Wang M, Estes BT, Scifert JL, Seim HB 3rd, Turner AS. Polyetheretherketone as a biomaterial for spinal applications. Biomaterials 2006;27:324-34.

16. Chu XX, Wu ZX, Huang RJ, Zhou Y, Li LF. Mechanical and thermal expansion properties of glass fibers reinforced PEEK composites at cryogenic temperatures. Cryogenics 2010;50:84-8.

17. Abu Bakar MS, Cheng MH, Tang Sm, Yu SC, Lia K, Tan CT, Khor KA, Cheang P. Tensile properties, tension-tension fatigue and biological response of polyetheretherketone-hydroxyapatite composites for load-bearing orthopaedic implants. Biomater 2003;24:2245-50.

18. Vail JR, Krick BA, Marchman KR, Gregory Sawyer W. Polytetrafluoroethylene (PTFE) fiber reinforced polyetheretherketone (PEEK) composites. Wear 2011;270:737-41.

19. Wang Q, Xue Q, Shen W, Zhang J. The friction and wear properties of nanometer ZrO2-filled polyetheretherketone. J Appl Polym Sci 1998;69:135-41.

20. Stawarczyk B, Beuer F, Wimmer T, Jahn D, Sener B, Roos M, Schmidlin PR. PEEK – A suitable material for fixed dental prostheses? J Biomed Mater Res B Appl Biomater 2013;101:1209-16.

21. Stawarczyk B, Keul C, Beuer F, Roos M, Schmidlin PR. Tensile bond strength of veneering resins to PEEK: impact of different adhesives. Dent Mater J 2013;32:441-8.

22. Piwowarczyk A, Lauer HC, Sorensen JA. In vitro shear bond strength of cementing agents to fixed prosthodontic restorative materials. J Prosthet Dent 2004;92:265-73.

23. Han L, Okamoto A, Fukushima M, Okiji T. Evaluation of physical properties and surface degradation of self-adhesive resin cements. Dent Mater J 2007;26:906-14.

24. Kern M, Lehmann F. Influence of surface conditioning on bonding to polyetheretherketon (PEEK). Dent Mater 2012;28:1280-3.

25. Schmidlin PR, Stawarczyk B, Wieland M, Attin T, Hämmerle CH, Fischer J. Effect of different surface pretreatment and luting materials on shear bond strength to PEEK. Dent Mater 2010;26:553-9.

26. Keul C, Liebermann A, Schmidlin PR, Roos M, Sener B, Stawarczyk B. Influence of PEEK surface modification on their properties and bond strength to veneering resin composites. Int J Adhesiv Dent 2014, accepted.
27. Hallmann L, Mehl A, Sereno N, Hämmerle CHF. The improvement of adhesive properties of PEEK through different pretreatments. Appl Surf Sci 2012;258:7213-8.
28. Stawarczyk B, Bähr N, Beuer F, Wimmer T, Eichberger M, Gernet W, Jahn D, Schmidlin PR. Influence of plasma pretreatment on shear bond strength of self-adhesive resin cements to polyetheretherketone. Clin Oral Investig 2013;18:163-70.
29. Ha SW, Hauert R, Ernst KH, Wintermantel E. Surface analysis of chemically-etched and plasma-treated polyetheretherketone (PEEK) for biomedical applications. Surf Coat Technol 1997;96:293-9.
30. Van Meerbeek B, Peumans M, Poitevin A, Mine A, Van Ende A, Neves A, De Munck J. Relationship between bond-strength tests and clinical outcomes. Dent Mater 2010;26:e100-21.
31. Eren D, Bektas ÖÖ and Siso SH. Three different adhesive systems; three different bond strength test methods. Acta Odontol Scan 2013;71:978-83.
32. Scherrer SS, Cesar PF, Swain MV. Direct comparison of the bond strength results of the different test methods: a critical literature review. Dent Mater 2010;26:e78-93.
33. Yekta-Fard M, Ponter AB. Factors affecting the wettability of polymer surfaces. J Adhes Sci Technol 1992;6:253-77.
34. Kwok DY, Lam CNC, Li A, Leung A, Wu R, Mok E, Neumann AW. Measuring and interpreting contact angles: a complex issue. Colloids Surf 1998;142:219-35.
35. Sedev RV, Petrov JG, Neumann AW. Effect of swelling of a polymer surface on advancing and receding contact angles. J Colloid Interface Sci 1996;180:36-42.

36. Phoenix RD, Shen C. Characterization of treated porcelain surfaces via dynamic contact angle analysis. Int J Prosthodont 1995;8:187-94.

37. Jardel V, Degrange M, Picard B, Derrien G. Surface energy of etched ceramic. Int J Prosthodont 1999;12:415-8.

38. Owens DK, Wendt RC. Estimation of the surface free energy of polymers. J Appl Polym Sci 1969;13:1741-7.

39. Kaelble DH. Dispersion-Polar Surface Tension Properties of Organic Solids. J Adhes 1970;2:66-81.

40. Shu S, Kobayashi H, Okubo M, Sabarudin A, Butsugan M, Umemura T. Chemical anchoring of lauryl methacrylate-based reversed phase monolith to 1/16″ o.d. polyetheretherketone tubing. J Chromatogr A 2012;1242:59-66.

LEGENDS

Fig. 1. Study design with pretreatment, adhesive system, veneering resin, and aging level of PEEK specimens for determination of TBS.

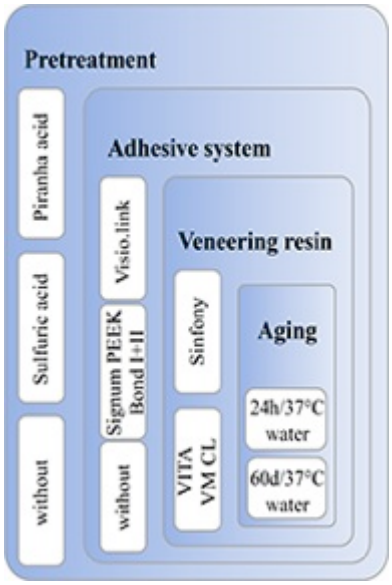


Fig. 2. Test design of TBS measurement with universal testing machine.

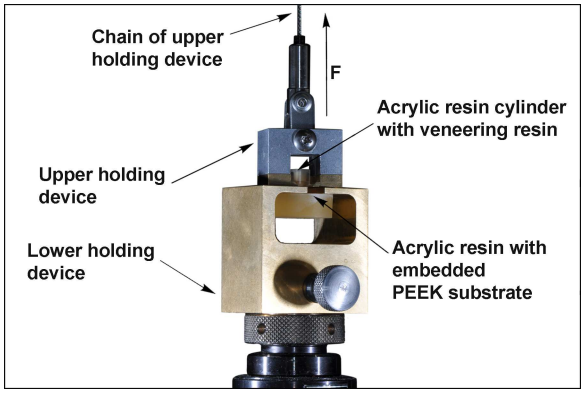
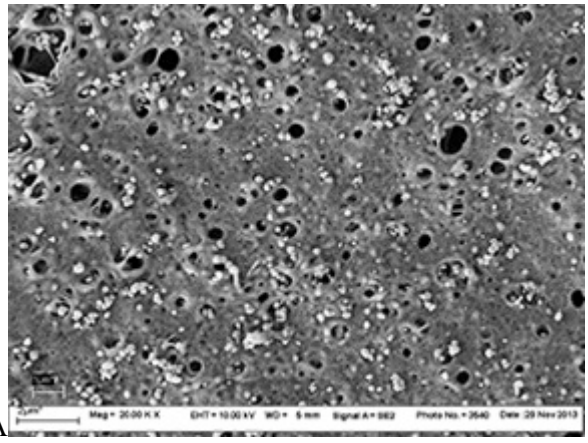
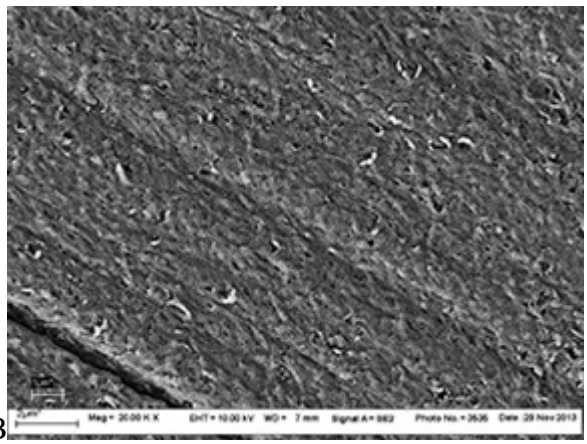


Fig. 3. Surface topography of pretreated PEEK specimens (magnification: 20’000×): A, Sulfuric acid etched. B, Piranha acid etched. C, Without pretreatment.

A 

B 

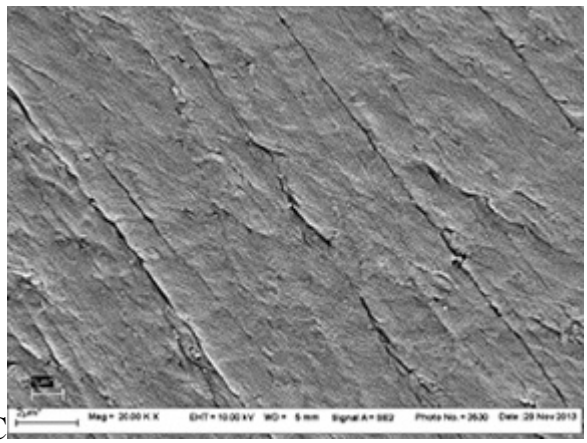
C 

Table I. Product name, manufacturer, batch number and chemical composition of pretreatment, adhesive systems, and veneering resins evaluated.

Materials	Product Name	Manufacturer	Batch No	Composition
Pretreatment	Sulfuric acid	Merk KGaA	K43190280206	98% Sulfuric acid (H_2SO_4)
	Hydrogen peroxide	Hospital pharmacy, Ludwig Maximilian University of Munich		30% Hydrogen peroxide (H_2O_2)
Adhesive system	visio.link	Bredent GmbH & Co. KG	114784	MMA, PETIA, dimethacrylates, photoinitiators
	Signum PEEK Bond I + II (experimental adhesive)	Heraeus Kulzer	010121/010110	*Bond I:* bifunctional molecules based on phosphoric acid esters and thiol compounds *Bond II:* MMA, PMMA, Photoinitiators
Veneering resins	Sinfony	3M ESPE	476735/412492	silane treated glass powder, diurethane dimethacrylate, dicyclopentyldimethylene diacrylate, substituted dimethacrylate, silane treated silica, glass ionomer filler, HEMA
	VITA VM LC	VITA Zahnfabrik H. Rauter GmbH & Co.KG	33941/33621	7,7,9-Trimethyl-4,13-dioxo-3,14-dioxa-5,12-diaza-hexadecan-1,16-dioldimethacrylat (mixture of isomers), TEGDMA, Bis-GMA, 2-dimethylaminoethyl methacrylate

MMA, Methylmethacrylate PETIA, Pentaerythritol triacrylate. Bis-GMA, Bisphenol-A-diglycidylmethacrylate. TEGDMA, triethylene glycol dimethacrylate

Table II. Descriptive statistics for surface energy (SFE) and surface roughness (SR) of pretreated PEEK surfaces.

PEEK pretreatment	SFE [mN/m]		SR [μm]	
	Mean (SD)	95% CI	Mean (SD)	95% CI
Sulfuric acid	50.1 (3.8)[b]	(47.2;52.9)	0.037 (0.004)[b]	(0.032;0.051)
Piranha acid	46.4 (1.2)[a]	(45.3;47.3)	0.032 (0.003)[a]	(0.029;0.035)
Without	48.4 (1.9)[ab]	(46.9;49.8)	0.031 (0.003)[a]	(0.027;0.033)

[abc] different letters presented significant differences among PEEK surface pretreatment on SFE and SR, separately.

Table III. Mean, SD, and 95% confidence interval of TBS (MPa) of different veneering composite resins on PEEK specimens.

Pretreatment	Adhesive system	Veneering resin composite	24 h / 37°C distilled water		60 d / 37°C distilled water	
			Mean (SD)	95%CI	Mean (SD)	95%CI
Sulfuric acid	visio.link	Sinfony	23.2 (4.3)[b]	(21.1;25.3)	21.3 (5.0)[b]	(18.9;23.7)
	Signum PEEK Bond		21.3 (7.0)[b]	(17.9;24.6)	25.3 (3.8)[c]	(23.4;27.2)
	without		7.4 (7.6)[a]	(3.7;11.0)*	9.9 (5.7)[a]	(7.0;12.6)
Piranha acid	visio.link		19.0 (6.9)[b]	(15.6;22.3)	21.6 (5.6)[b]	(18.8;24.3)
	Signum PEEK Bond		24.5 (7.7)[b]	(20.5;27.9)	25.3 (3.8)[c]	(21.5;30.6)
	without		3.2 (7.3)[a]	(0;6.6)*	14.1 (9.9)[a]	(9.3;18.8)
Without	visio.link		23.4 (4.5)	(21.1;25.5)	23.2 (7.2)	(19.7;26.7)
	Signum PEEK Bond		21.1 (6.1)	(18.1;24.0)*	31 (6.4)	(27.8;34.0)
	without		3.7 (4.7)	(1.4;5.9)*	1.3 (3.8)	(0;3.1)*
Sulfuric acid	visio.link	VITA VM LC	19.5 (5.1)[b]	(17.0;22.0)	15.1 (4.0)[b]	(13.1;17.0)
	Signum PEEK Bond		18.0 (6.6)[b]	(14.7;21.1)	25.6 (4.1)[c]	(23.5;27.6)
	without		0.1 (0.2)[a]	(0;0.2)*	0.2 (0.6)[a]	(0;0.5)*
Piranha acid	visio.link		13.6 (4.6)[b]	(11.3;15.8)	17.5 (4.0)[b]	(14.9;20.5)
	Signum PEEK Bond		16.7 (7.1)[b]	(13.2;20.0)	12.6 (9.6)[b]	(8.0;17.2)
	without		0.1 (0.5)[a]	(0;0.4)*	0 (-)[a]	-
Without	visio.link		13.2 (4.9)[b]	(10.8;15.6)	16.2 (6.2)[b]	(13.2;19.1)
	Signum PEEK Bond		13.1 (5.3)[b]	(10.5;15.7)	23.7 (4.6)[b]	(21.4;25.9)
	without		0.7 (1.6)[a]	(0;1.5)*	0 (0.1)[a]	(0;0.1)*

*not normally distributed; [abc] different letters presented significant differences among adhesive system methods used within 1 pretreatment method, 1 veneering composite resin, and 1 aging level.

Table IV. Statistical effect of pretreatment methods within 1 adhesive system, 1 veneering composite resin, and 1 aging level. S: pretreatment with sulfuric acid, P: pretreatment with Piranha acid, W: no pretreatment].

Adhesive system	Sinfony		VITA VM LC	
	24 h / 37°C distilled water	60 d / 37°C distilled water	24 h / 37°C distilled water	60 d / 37°C distilled water
visio.link	no effect	W<S=P; *P*<.001	no effect	no effect
Sinfony PEEK Bond	P=S<S=W; *P*=.018	no effect	W=P<S, *P*<.001	no effect
Without	no effect	S=P<P=W, *P*=.024	no effect	P<W=S, *P*<.001

Table V. Relative frequency (%) of failure types for each group.

Pretreatment	Adhesive system	Veneering resin composite	Initial				After
			adhesive	cohesive PEEK	cohesive veneering resin	mixed	adhes
Sulfuric acid	visio.link	Sinfony	0 (0;17)	0 (0;17)	55 (31;77)	45 (23;69)	0 (0;1
	Signum PEEK Bond		0 (0;17)	5 (0;25)	85 (62;97)	5 (0;25)	0 (0;1
	Without		90 (68;99)	0 (0;17)	0 (0;17)	10 (1;32)	100 (8
Piranha acid	visio.link		100 (83;100)	0 (0;17)	0 (0;17)	0 (0;17)	100 (8
	Signum PEEK Bond		95 (75;100)	0 (0;17)	0 (0;17)	5 (0;25)	95 (75
	Without		100 (83;100)	0 (0;17)	0 (0;17)	0 (0;17)	100 (8
Without	visio.link		100 (83;100)	0 (0;17)	0 (0;17)	0 (0;17)	100 (8
	Signum PEEK Bond		95 (75;100)	0 (0;17)	0 (0;17)	5 (0;25)	100 (8
	Without		100 (83;100)	0 (0;17)	0 (0;17)	0 (0;17)	95 (75
Sulfuric acid	visio.link	VITA VM LC	95 (75;100)	0 (0;17)	0 (0;17)	5 (0;25)	100 (8
	Signum PEEK Bond		0 (0;17)	45 (23;69)	40 (19;64)	15 (3;38)	0 (0;1
	Without		100 (83;100)	0 (0;17)	0 (0;17)	0 (0;17)	100 (8
Piranha acid	visio.link		85 (62;97)	0 (0;17)	15 (3;38)	0 (0;17)	95 (75
	Signum PEEK Bond		65 (40;85)	0 (0;17)	0 (0;17)	35 (15;60)	95 (75
	Without		100 (83;100)	0 (0;17)	0 (0;17)	0 (0;17)	100 (8
Without	visio.link		100 (83;100)	0 (0;17)	0 (0;17)	0 (0;17)	90 (68
	Signum PEEK Bond		90 (68;99)	0 (0;17)	0 (0;17)	10 (1;32)	90 (68
	Without		100 (83;100)	0 (0;17)	0 (0;17)	0 (0;17)	100 (8