Influence of SiO$_2$ content of polyetheretherketone (PEEK) on flexural properties and tensile bond strength to resin cement

Shiro RIKITOKU$^1$, Shiho OTAKE$^1$, Kosuke NOZAKI$^2$, Keiichi YOSHIDA$^1$ and Hiroyuki MIURA$^1$

$^1$ Department of Fixed Prosthodontics, Division of Oral Health Sciences, Graduate School of Medical and Dental Sciences, Tokyo Medical and Dental University (TMDU), 1-5-45 Yushima, Bunkyo-ku, Tokyo 113-8549, Japan

$^2$ Department of Material Biofunctions, Institute of Biomaterials and Bioengineering, Tokyo Medical and Dental University (TMDU), 2-3-10 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-0062, Japan

Corresponding author, Shiho OTAKE; E-mail: s.otake.fpro@tmd.ac.jp

In the present study, the influence of the SiO$_2$ content of polyetheretherketone (PEEK) on the bonding between PEEK and resin cement, and the corresponding mechanical properties, were evaluated. Three experimental PEEK samples with varying amounts of SiO$_2$, and PEEK containing 20 wt% of TiO$_2$ (DK), were investigated. The tensile bond strength (TBS) was evaluated before and after 10,000 thermal cycles, upon polishing, sandblasting, and conditioning of the specimens with BONDMER lightless containing a silane coupling agent, and bonded with ESTECEM II. The crystallinity, flexural modulus, and flexural strength were determined after 10,000 thermal cycles. TBS values were analyzed by two-way ANOVA and a $t$-test with Bonferroni correction ($\alpha<0.05$), while the crystallinity, flexural modulus, and flexural strength were analyzed with one-way ANOVA followed by a $t$-test with Bonferroni correction ($\alpha<0.05$). The TBS improved with increasing SiO$_2$ content in PEEK; moreover, DK and the sample with 40 wt% SiO$_2$ exhibited the highest flexural strength.

**Keywords:** PEEK, Polyetheretherketone, SiO$_2$, Tensile bond strength, Mechanical properties

INTRODUCTION

Polyetheretherketone (PEEK) is one of the main groups of polyaryletherketones. It is a semicrystalline high-performance thermoplastic polymer$^1$. PEEK has attracted attention as a medical implant because it has excellent mechanical properties, chemical stability, dimensional stability, and biocompatibility, and exhibits a low modulus similar to that of human bone$^2$-6.

In the field of dentistry, PEEK materials have been explored for use as removable partial denture frameworks$^7$-9 or fixed dental prostheses$^{10}$-13. Although PEEK is a low-modulus polymer, its mechanical properties can be adjusted by incorporating inorganic fillers and changing the filler content$^{12}$-$15$. Currently, most dental PEEK materials are reinforced by approximately 20 wt% of inorganic filler to increase their rigidity. However, it is necessary to achieve adequate and durable bonding between PEEK and other dental materials to enable their application to dental prostheses; this has proven difficult due to its low surface energy and chemically inert surface texture$^{16}$.

Various studies have investigated whether different surface pretreatments can improve the bond strength between PEEK and dental materials$^{16}$-$38$. In those studies, the PEEK surface was pretreated by sandblasting with piranha solution$^{17}$-$18$, $21$, $23$, $24$, $31$, sulfurous acid$^{17}$-$18$, $21$, $23$, $24$, $30$, or with different types of plasma$^{20}$-$26$, $29$. In addition, the application of various adhesive systems after pretreatment have been investigated$^{17}$-$24$, $26$, $31$, $32$. Those studies reported that the use of adhesive systems based on methyl methacrylate monomer as the main component yields a higher bond strength between the PEEK and dental materials. Moreover, those studies that focused on the TiO$_2$ content of PEEK and also compared the bond strength between PEEK and the resin materials found that the PEEK composition affects the bond strength$^{28}$-$29$.

Currently, in dental treatment, pretreatment with a silane coupling agent greatly contributes to the attaining of a reliable bond between a dental prosthesis containing inorganic fillers and resin cement$^{30}$. Considering the excellent reactivity between SiO$_2$ and the silane coupling agent, it can be expected that reliable adhesion of the PEEK prosthesis can be more safely and easily achieved by treatment on the chair-side as the SiO$_2$ content increases. However, the mechanical properties of PEEK do not always improve with an increase in the SiO$_2$ content. A study that investigated the effect of filling PEEK with hydroxyapatite on the mechanical properties found that the tensile strength decreases with an increase in the filler content$^{14}$. Considering that the composition of PEEK will affect not only the bond strength but also the mechanical properties, the influence of increasing the SiO$_2$ content of PEEK should be evaluated diversely.

In this study, experimental PEEK with different SiO$_2$ contents, which is more reactive with silane coupling agents, was investigated and compared with PEEK containing 20 wt% TiO$_2$ as a control group. The influence of the SiO$_2$ content of PEEK on the bonding properties between PEEK and the resin cement has not yet been studied.

The first null hypothesis of this study was that the filler content of PEEK has no influence on the tensile bond strength (TBS) between PEEK and resin cement,
and the second null hypothesis was that the filler content of PEEK has no influence on its flexural properties.

**MATERIALS AND METHODS**

*Specimen preparation for tensile bonding test*

In the present study, three types of experimental PEEK with different SiO$_2$ contents (Hybrid PEEK 20 (HP20), Hybrid PEEK 40 (HP40), Hybrid PEEK 50 (HP50), Tokuyama Dental, Ibaraki, Japan) were supplied from Tokuyama Dental, and PEEK containing 20 wt% of TiO$_2$ (Dentokeep PEEK Disc (DK), nt-trading, Karlsruhe, Germany) was used as the control. Each PEEK block was cut into rectangular plates ($n$=128) measuring 14.0×12.0×3.0 mm under running water using a low-speed diamond cutting machine (Isomet, Buehler, Lake Bluff, IL, USA). The specimens were polished, again under running water, using #1500 SiC waterproof abrasive paper (Fuji Star, SANKYO RIKAGAKU, Saitama, Japan) with a polishing machine (Ecomet, Buehler). Subsequently, the specimens were sandblasted with 70-μm alumina powder (HI ALUMINAS, SHOFU, Kyoto, Japan) at 0.2 MPa for 10 s from a distance of 10 mm. Finally, the specimens were ultrasonically cleaned twice in distilled water for 5 min each, and then allowed to dry in air.

**Microstructure observation of the surface**

The surface morphology of each PEEK composition group before and after sandblasting ($n$=8) was examined by scanning electron microscopy (SEM: S-4500, Hitachi High-technologies, Tokyo, Japan) after sputter-coating with platinum.

**Bonding procedure and preparation for TBS measurement**

The specimens were defined with a 03 mm adhesion range by using 100-μm double-sided tape (MAXON® No. 200, HOLBEIN ART MATERIALS, Osaka, Japan). Subsequently, the adhesive system was applied to the surface according to the manufacturer's instructions (Table 1). The rear surfaces of the specimens were reinforced with 2-mm stainless steel plates. The resin cement (ESTECEM II, Tokuyama Dental) was applied to the top surfaces of stainless steel rods (SUS 304 Ø6×20 mm) which were polished under running water with # 600 SiC water-resistant paper (aqua, Sankei, Tokyo, Japan), sandblasted with 70-μm alumina powder (HI ALUMINAS) at 0.4 MPa for 20 s from a distance of 10 mm, ultrasonically cleaned in distilled water for 5 min, twice, and then allowed to air dry. Once dry, they were conditioned with BONDMER lightless (BL). Subsequently, the stainless-steel rods were lightly

| Product Name (code) | Manufacturer | Composition | Application steps as recommended by the manufacturer | Lot. No. |
|---------------------|--------------|-------------|------------------------------------------------------|---------|
| HybridPEEK20 (HP20) | Tokuyama Dental, Ibaraki, Japan | 1 μm SiO$_2$ 20 wt% | — | 001M |
| HybridPEEK40 (HP40) | Tokuyama Dental | 1 μm SiO$_2$ 40 wt% | — | 003M |
| HybridPEEK50 (HP50) | Tokuyama Dental | 1 μm SiO$_2$ 50 wt% | — | 001LL |
| Dentokeep (DK) | nt-trading, Karlsruhe, Germany | TiO$_2$ 20 wt% | — | G15DK1401 |
| BONDMER lightless (BL) | Tokuyama Dental | Bond A: Acetone, Phosphoric acid monomer, Bis-GMA, TEGDMA, HEMA, MTU-6; Bond B: Acetone, Isopropyl alcohol, Water, Borate catalyst, γ-MPTES, Peroxide | 1. Mix adhesive A and B for 5 s 2. Apply adhesive on PEEK surface and air-dry for 10 s | 019018 |
| ESTECEM II | Tokuyama Dental | Paste A: Bis-GMA, TEGDMA, Bis-MPEPP, Silica-Zirconia Filler, Camphorquinone, Peroxide Paste B: Bis-GMA, TEGDMA, Bis-MPEPP, Silica-Zirconia Filler, Camphorquinone, Peroxide | 1. Light-cure for 20 s from four sides | 013018 |

Bis-GMA: bisphenol-A-diglycidyl methacrylate, TEGDMA: triethyleneglycol dimethacrylate, HEMA: 2-hydroxyethyl methacrylate, MTU-6: 6-methacryloyloxyhexyl 2-thiouracil-5-carboxylate, γ-MPTES: γ-methacryloyloxy propyltriethoxysilane, Bis-MPEPP: 2,2-bis(4-(methacryloxypolyethoxy)phenyl)propane.
pressed against the PEEK surfaces. The specimens were then light-cured using a light-curing unit (OPTILUX 501, Kerr, Orange, CA, USA) for 20 s each from four directions. Subsequently, the specimens were stored in a thermostatic chamber (Low Temp. Incubator FLT-15W, Tokyo Garasu Kiki, Tokyo, Japan) at 37°C and 100% humidity for 1 h and then stored in distilled water at 37°C for 24 h. Prior to analysis, the specimens were divided into two subgroups according to their aging levels. For one group, the TBS was measured immediately after storage in water for 24 h (TC0), while the other group was exposed to 10,000 thermal cycles 5–55°C with a dwell time of 30 s (Thermalcycler, Seiwa Riken, Tokyo, Japan) before TBS measurements (TC10000).

**TBS measurement and failure analysis**

The TBS was measured using a universal testing machine (Autograph AGS-H, Shimadzu, Kyoto, Japan) at a crosshead speed of 1.0 mm/min (Fig. 1). The TBS value was calculated using software (TRAPEZIUM X, Shimadzu) based on the following formula:

\[ s = \frac{Ft}{A} \]

where \( s \) is the TBS, \( Ft \) is the maximum load at failure, and \( A \) is the adhesive area. The de-bonded area was examined with both a binocular stereomicroscope (SZH 10, Olympus, Tokyo, Japan) at 40× magnification and a SEM (S-4500). The failure types were classified as: 1) adhesive, 2) cohesive within PEEK, 3) cohesive within resin cement, or 4) mixed.

**Specimen preparation for bending test**

The mechanical properties of PEEK with different filler contents were evaluated by a three-point bending test according to ISO 6872: 2015. Each PEEK block was cut into a bar shape \((n=60)\) under running water using a low-speed diamond cutting machine (Isomet). The specimens were wet-ground and polished with #1500 SiC waterproof abrasive paper (FUJI STAR) to dimensions of \((4.0±0.2)\times(14.0±0.2)\times(1.2±0.2)\) mm. To minimize the grinding damage and chipping during the bending test, edge chamfers were prepared with #1500 SiC waterproof abrasive paper (FUJI STAR) lengthwise along the long axis of the specimens. After polishing, the specimens were stored in distilled water at 37°C for 24 h, and the subjected to another 10,000 thermal cycles of 5–55°C with a dwell time of 30 s (Thermalcycler).

**Flexural modulus and flexural strength measurement, and fractured surface analysis**

The mechanical properties were measured using a universal testing machine (Autograph AGS-H) at a support span of 12.0 mm and crosshead speed of 1.0 mm/min. The flexural modulus and flexural strength were calculated using software (TRAPEZIUM X). The flexural modulus was calculated using the following formula:

\[ E = \frac{F}{L} \times \frac{4bh^3}{d} \]

where \( E \) is the flexural modulus, \( F \) is the load at a convenient point in the straight-line portion of the load/deflection graph, \( L \) is the span distance, \( b \) is the width of the specimen, \( h \) is the thickness of the specimen, and \( d \) is the deflection at load \( F \). The flexural strength was calculated using the following formula:

\[ \sigma = \frac{3F}{2bh^2} \]

where \( \sigma \) is the flexural strength and \( F \) is the maximum load applied during the bending test. The surface morphology of the fractured surface of PEEK was examined using SEM (S-4500) at a magnification of 5,000×.

**Level of crystallinity**

The level of crystallinity of the PEEK matrix is known to affect its mechanical properties. The crystallinity was calculated for each specimen by Fourier transform infrared spectroscopy (FTIR: Nicolet iS50, Thermo Fisher Scientific, Tokyo, Japan) according to ASTM F2778. The percent crystallinity (XC) was calculated using the following formula:

\[ XC = \frac{(CI - 0.728)}{1.549 \times 100} \]

and CI was divided by the peak height at wavenumbers 1,280 cm\(^{-1}\) and 1,305 cm\(^{-1}\). These peaks are known to be sensitive to the degree of crystallinity, and have previously been correlated to wide-angle X-ray scattering measurements.

**Statistical analysis**

The normality of the data distribution was tested by applying the Shapiro-Wilk test, after which the TBS was analyzed using two-way ANOVA and \( t \)-tests with Bonferroni correction (IBM SPSS statistics V22.0, IBM, Armonk, NY, USA) and the crystallinity, flexural modulus, and flexural strength were analyzed using one-way ANOVA and \( t \)-tests with Bonferroni correction. The statistical significance level was set at \( \alpha = 0.05 \).

**RESULTS**

**Tensile bonding test**

Images of the PEEK surface before and after sandblasting by SEM are shown in Fig. 2. An increase in the amounts of the filler on the polished surface was
confirmed as the SiO$_2$ content increased (Figs. 2(1.B)–(1.D)). Further, sandblasting made the PEEK surfaces rougher (Figs. 2(2.A)–(2.D)). The TBS values and results of the two-way ANOVA and $t$-tests with Bonferroni correction are summarized in Table 2. Two-way ANOVA showed that the filler content of PEEK ($p=0.000$) and aging level ($p=0.002$) significantly affected the TBS between PEEK and the resin cement. At the TC0 aging level, HP40 and HP50 showed significantly higher TBS values than DK, whereas at TC10000, HP40 and HP50 showed significantly higher TBS values than HP20. HP20 significantly lower TBS values after 10,000 thermal cycles. All specimens showed 1) adhesive failure type (Fig. 3).

Three-point bending test

The crystallinity, flexural modulus, and flexural strength, and the results of the one-way ANOVA and $t$-tests with Bonferroni correction are summarized in Table 3. The crystallinity of the PEEK matrix showed no significant difference regardless of the SiO$_2$ content in the experimental PEEK. However, the control group DK showed a PEEK matrix with a significantly higher level of crystallinity compared to HP20. DK and HP20 showed a lower flexural modulus than HP40 and HP50. HP40 showed the highest flexural strength, equivalent to that of DK, while HP50 showed significantly lower values than HP20. SEM images of the fractured surface of PEEK after the bending test are shown in Fig. 4. In the bending test, HP40 and HP50 fractured, whereas DK and HP20 only underwent plastic deformation (Fig. 5); hence, a fractured surface was observed only with HP40 and HP50. For both samples, the fractured surface

Table 2  Mean (SD) values of TBS

| Group   | Tensile bond strength (MPa) |
|---------|-----------------------------|
|         | TC0 | TC10000                   |
| DK      | 11.15 (2.60)$^{Aa}$         | 11.80 (2.36)$^{CdA}$   |
| HP20    | 14.26 (3.64)$^{AB}$         | 9.78 (2.09)$^{C}$      |
| HP40    | 14.31 (2.77)$^{Bb}$         | 13.37 (2.38)$^{Db}$    |
| HP50    | 16.00 (2.85)$^{Bc}$         | 14.41 (3.61)$^{Dc}$    |

Same large superscript letters indicate no significant differences in vertical column at $p<0.05$. Same small superscript letters indicate no significant differences in horizontal column at $p<0.05$. 

Fig. 2  SEM images of PEEK surface before and after sandblasting at a magnification of 2,000×.
(1) Polished, (2) Sandblasted; (A) DK, (B) HP20, (C) HP40, (D) HP50.

Fig. 3  SEM images of de-bonded area of a representative HP40 surface.
(A) magnification 30×, (B) magnification 2,000×.
Table 3  Mean (SD) values of crystallinity, flexural modulus, and flexural strength

| Group | Crystallinity (%) | Flexural modulus (GPa) | Flexural strength (MPa) |
|-------|-------------------|------------------------|-------------------------|
| DK    | 38.28 (3.24)      | 3.29 (0.21)           | 190.49 (3.24)          |
| HP20  | 34.81 (2.67)      | 3.31 (0.23)           | 180.81 (5.28)          |
| HP40  | 36.00 (2.12)      | 4.61 (0.30)           | 191.99 (3.62)          |
| HP50  | 36.30 (2.04)      | 5.14 (0.53)           | 168.87 (6.11)          |

Same large superscript letters indicate no significant differences in vertical column at p<0.05.

Fig. 4  SEM images of fractured surface of PEEK after bending tests at a magnification of 5,000x. (A) HP40, (B) HP50; Arrow: Filler aggregation.

Fig. 5  Typical load-displacement curves of PEEK samples.

**DISCUSSION**

The excellent mechanical properties and biocompatibility of PEEK make it a very attractive dental material. However, effective and durable bonding between PEEK and the resin cement is a prerequisite for its use as a fixed dental prosthetic material. This study assessed the TBS between experimental PEEK samples with different SiO$_2$ contents and the resin cement. The influence of the PEEK compositions on the mechanical properties was also evaluated.

The results of the tensile bonding test showed that an increase in the filler content led to significantly improved TBS values before and after aging. Therefore, the first null hypothesis, stating that the filler content of PEEK has no influence on the TBS between PEEK and the resin cement, was rejected.

The TBS values increased significantly after aging with an increase in the SiO$_2$ content. The γ-MPTES contained in BL may have improved and facilitated durable bonding between PEEK and the resin cement, owing to its silane coupling effect. With an increase in the SiO$_2$ content, the silane coupling agent was more effective due to the increased exposure of the SiO$_2$ on the PEEK surface. Between DK and HP20, the latter was expected to show higher TBS values, considering the excellent reactivity of SiO$_2$ with the silane coupling agent. However, the TBS values for HP20 and DK did not differ significantly before and after aging. This can be explained by the differences in the morphology, particle size, or coating of the filler particles.

In the present study, to simulate clinical aging, the specimens were aged for 10,000 cycles in a thermal cycling machine. Generally, thermal cycling is used as an artificial aging method to imitate intraoral temperature changes *in vivo*; these temperature changes may induce a decrease in the bond strength. The 10,000 thermal cycles adopted in the present study correspond to about 1 year in an oral environment$^{37}$. Thus, this study achieved clinically relevant results for evaluating the long-term bond strength.

According to the results of the three-point bending test, the flexural modulus increased with an increase in the SiO$_2$ content, and HP40 showed the highest flexural strength. Therefore, the second null hypothesis, stating that the filler content of PEEK has no influence on its mechanical properties, was also rejected.

In a previous study, the flexural properties of PEEK containing 20 wt% TiO$_2$ were investigated using a similar experimental protocol$^{38}$. The range of results was similar to that obtained for the DK group in the present study. Consequently, we can state that the results obtained for the for the experimental PEEK materials in this study are reasonable.

With an increase in the SiO$_2$ content, the flexural modulus of experimental PEEK materials increased.
Previous studies reported that the mechanical properties can be influenced by the degree of crystallinity, and increasing the crystallinity can increase the elastic modulus and yield strength, while imparting a lower toughness\textsuperscript{1,2,9-11}. In addition, the degree of crystallinity of the PEEK matrix is also influenced by the filler content\textsuperscript{12}. However, this study shows that increasing the SiO\textsubscript{2} content has no significant influence on the degree of crystallinity of the PEEK matrix; therefore, the changes in the mechanical properties described herein are not derived from the degree of crystallinity of the PEEK matrix.

The experimental PEEK samples showed both ductile and brittle behavior depending on the SiO\textsubscript{2} content. HP20 showed ductility and plastic deformation without breaking, while HP40 and HP50 fractured. This could be attributed to the reduction in the amorphous areas of PEEK, which is a two-phase semicrystalline polymer. The amorphous areas are required in order to impart macromolecular materials a certain degree of elasticity and fracture toughness\textsuperscript{13}. An increase in the SiO\textsubscript{2} content led to a decrease in the volume of the PEEK matrix and a reduction in the amorphous areas of PEEK. Thus, ductility was lost and brittleness was imparted. The increase in the flexural modulus with an increase in the SiO\textsubscript{2} content was also attributed to a similar effect. DK showed a significantly higher degree of crystallinity than HP20; nevertheless, the flexural modulus values showed no significant difference. This could be due to the difference between the densities of SiO\textsubscript{2} and TiO\textsubscript{2}. Even though the filler contents of DK and HP20 were the same (i.e., 20 wt%), the volume of filler in DK was less than that in HP20. Accordingly, DK had more amorphous areas than other PEEK groups in spite of the higher degree of crystallinity of the PEEK matrix.

HP40 showed the highest flexural strength, equivalent to that of DK, while HP50 showed significantly lower values than HP20. Interestingly, the flexural modulus increased with an increase in the SiO\textsubscript{2} content, while the flexural strength decreased remarkably at the boundary between the 40 and 50 wt% SiO\textsubscript{2}. The same phenomenon was reported in previous studies that investigated the tensile strength of PEEK reinforced by nanosized SiO\textsubscript{2}\textsuperscript{14,15}. These studies suggested that the excess addition of filler particles leads to a decrease in the mechanical strength of PEEK due to the local agglomeration of particles. Therefore, the threshold amount of SiO\textsubscript{2} at which the mechanical strength decreases differs depending on the particle sizes of the SiO\textsubscript{2}. The previous study investigated PEEK reinforced by nanosized SiO\textsubscript{2}, whereas the experimental PEEK addressed in the present study contained SiO\textsubscript{2} with a larger particle size. Since the variation in the measured values for the bending test was small, it was assumed that the filler particles were equally distributed; this was subsequently confirmed by SEM images of the PEEK surface (Figs. 2(1.B)–(1.D)). For HP20 and HP40, the homogeneously and individually dispersed nanoparticles could efficiently stop crack propagation, leading to improved impact strength. Conversely, the addition of 50 wt% SiO\textsubscript{2} made PEEK more brittle, probably due to the presence of small particle clusters (Fig. 4B) that may act as stress concentration sites and initiate cracks, causing early failure\textsuperscript{16}.

Although this study could not completely reproduce individual variations in oral environments, it may contribute to enabling the realization of durable and effective bonding between PEEK and resin cement in dentistry applications. In conclusion, this study has demonstrated that increasing the SiO\textsubscript{2} filler content of PEEK enables adequate bonding between PEEK and resin cement by pretreatment with a silane coupling agent, but may have a negative influence on the mechanical properties. As discussed above, experimental PEEK samples containing 40 wt% SiO\textsubscript{2} offers several clinical advantages. Further studies are required to investigate the influence of the type, morphology, particle size, amount, or possible coating of filler particles contained in PEEK, on the long-term durable bonding of PEEK dental restorations.

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