Nd:YVO₄ laser groove treatment can improve the shear bond strength between dental PEEK and adhesive resin cement with an adhesive system

Hitomi KIMURA¹, Hiroki TSUKA¹, Koji MORITA¹, Isao HIRATA², Fumiko NISHIO¹, Hitoshi ABEKURA¹, Kazuya DOI¹ and Kazuhiro TSUGA¹

¹ Department of Advanced Prosthodontics, Graduate School of Biomedical and Health Sciences, Hiroshima University, 1-2-3 Kasumi, Minami-ku, Hiroshima 734-8553, Japan
² Department of Biomaterials, Graduate School of Biomedical and Health Sciences, Hiroshima University, 1-2-3 Kasumi, Minami-ku, Hiroshima 734-8553, Japan

Corresponding author, Koji MORITA; E-mail: moritak@hiroshima-u.ac.jp

INTRODUCTION

Polyetheretherketone is a polymer consisting of aromatic benzene molecules linked by functional ethers or ketone groups¹⁻². Furthermore, polyetheretherketone is a high-performance thermoplastic with excellent mechanical properties, low water absorption, and fracture resistance³⁻⁶. Dental polyetheretherketone (PEEK) has recently attracted attention in the dental field as a useful material for interim prostheses, removable prosthetics, splints, implants, and abutment screws⁷⁻¹³. PEEK has a high material processability and can be formed by a hot-press method or be fabricated by computer-aided design and manufacturing technology. However, PEEK has a low free energy and an inert hydrophobic surface, resulting in poor adhesion properties between PEEK and adhesive resin cement¹⁴. Recent research has focused on PEEK surface modification and altered adhesive systems to obtain strong adhesion performance between the PEEK surface and resin cement¹⁵⁻¹⁷. Several surface treatments, such as conventional sandblasting treatment¹²⁻¹⁸,¹⁹, acid etching¹²⁻²², silicone coating¹²⁻¹⁸,²³, and plasma treatment²⁰⁻²⁴ have been studied to improve the bonding strength of the cement. Many researchers have recommended surface treatment with 98% sulfuric acid to improve PEEK bonding¹²⁻¹⁸,²⁰⁻²²; however, this chemical is toxic, and its use in dental clinics presents safety concerns and is not practical²⁹.

Nd:YVO₄ lasers, as high-performance lasers, are commonly used in industry. The Nd:YVO₄ laser has excellent mechanical, optical, and physical properties, because it is characterized by power density, a narrow pulse width, and a damage threshold that is hundreds of times higher than those of conventional neodymium-doped yttrium aluminum garnet lasers²⁶. In a previous study, a Nd:YVO₄ laser was used to form an accurate groove on a PEEK surface and measure the shear bond strength without the use of an adhesive system²⁷. We envisioned the possibility of using internally Nd:YVO₄ laser-treated PEEK on molar teeth. Although the result showed it was possible to increase shear bond strength between PEEK and adhesive resin cement, there were concerns about the clinical implications of not using an adhesive system and measuring the shear bond strength immediately after adhesion²⁷. Many studies have reported that an adhesive system containing methyl methacrylate (MMA) can generate adequate bonding⁵⁻⁶. The surface modification of PEEK by laser reported elsewhere is only for chemical surface modification⁷⁻¹³. The surface modification of PEEK by laser reported elsewhere is only for chemical surface modification by irradiating the surface with a laser and not for mechanical surface modification²⁹. Previous studies also noted a need to improve PEEK binding strength more chemically and mechanically to achieve clinically and acceptable long-term adhesion²⁴. However, information on the potential for and limitations of PEEK adherence to adhesive resin cement is still inadequate.

Therefore, the purpose of this study was to investigate the effects on the shear bond strength between laser modified tooth-colored PEEK and adhesive resin cement.
with an adhesive system. The null hypothesis is that PEEK surface pretreatments have no effect on the shear bond strength between laser modified tooth-colored PEEK and adhesive resin cement.

MATERIALS AND METHODS

Specimen preparation and surface treatment
Each of the disk-shaped (diameter: 10 mm, thickness: 3 mm) and cylindrical (diameter: 6 mm, thickness: 4 mm) specimens was cut from PEEK block (VESTAKEEP PEEK, tooth-colored/polyetheretherketone, titanium dioxide pigments, Daicel-Evonik, Tokyo, Japan). All specimens were polished with a 600-grit rotating silicon carbide paper using a polishing machine (MetaServ, Buehler, Tokyo, Japan) under running water for 30 s to make the surface uniform in accordance with the method described by previous paper23,30), after disk-shaped specimens were embedded in autopolymerizing resin (Tray Resin, Shofu, Tokyo, Japan). This polishing is not intended to finish the inner surface in a dental laboratory. Polished specimens were immersed in ethanol and distilled water, ultrasonically cleaned (Ultrasonic cleaning Devices UT-206, Sharp, Tokyo, Japan) for 5 min and then air-dried. Each of specimen (n=240) was randomly divided into four groups for surface treatments by the following four modalities:

(A) No treatment: No surface pretreatment.
(B) Sandblasting treatment: PEEK surfaces were sandblasted with 50-µm alumina oxide particles at a pressure of 0.1 MPa from a distance of 10 mm perpendicular for 10 s.
(C) Sulfuric-acid etching: PEEK surfaces were etched with sulfuric acid (98%) for 1 min and then rinsed with deionized water for 1 min.
(D) Laser groove treatment: PEEK surfaces were irradiated with a Nd:YVO4 laser (YVO 4 Laser Marker MD-V9900A, Keyence, Tokyo, Japan). The design of the laser was to form grooves at an interval of 200 µm in the side and vertically and at a depth of 150 µm based on the method described by Tsuka et al.27). The laser irradiation was also designed to perform in the condition of a perpendicular angle of exposure, a pulse width of 8 ns, an irradiation speed of 500 mm/s, a frequency of 25 kHz, a wavelength of 1,064 nm, a laser density of 5.3 MW/cm2, an exposure time of 33 s, and a distance of 197 mm from the surface.

Scanning electron microscopy (SEM) analysis
Specimen surfaces after surface pretreatment or after fracture after the shear bond strength measurement after the thermal cycling were observed without treatment such as sputtering gold or depositing carbon using a scanning electron microscope (VE-8800, Keyence) operating at 1.7 kV and at a distance of 5.0–6.0 mm.

Surface roughness measurement
The surface roughness of each disk-shaped specimen (diameter: 10 mm, thickness: 3 mm, n=10 each) was measured in triplicate using a surface profilometer (Surfcorder SE700, Kosaka Laboratory, Tokyo, Japan). The cutoff value was set at 0.8 mm, and the measuring length was set to 5 mm. After three points on the specimens were randomly selected, the absolute average surface roughness (Ra) values were calculated as the average of these three measurements.

Water contact angle measurement
The water contact angle of each disk-shaped specimen (diameter: 10 mm, thickness: 3 mm, n=10 each) was measured in triplicate using a contact angle meter (Simage mini, Excimer, Kanagawa, Japan) by the static drop method. In this procedure, 10 µL of H2O was dropped onto a representative spot on the treated surface of each specimen. For angle measurement, a digital microscope (custom contact angle meter) was used. Measurements were performed at room temperature 10 s after the droplet first contacted the surface. After the measurement was performed at three points for each specimen, the average value was calculated.

X-ray photoelectron spectroscopy (XPS)
The elemental composition wide–scan or C1s spectra after each PEEK surface treatment was measured using XPS and the accompanying software (XPS, AXIS-HS, Kratos Analytical, Manchester, UK). Quantitative date was obtained from peak areas of the spectral lines using the supplied software (Vision software, Kratos Analytical) and the peaks at 284.6 eV (CC), 286.0 eV (CO), and 288.4 eV (COO) in the C1s region were analyzed29). Mg Kα X-ray was used with a source power of 72 W (acceleration voltage of 12 kV and filament current of 6 mA).

Bonding procedure
After measurement of the surface roughness and water contact angle, visio.link (Bredent, Senden, Germany) was applied as an adhesive to the surface on both disk-shaped and cylindrical specimens. The adhesive was cured at 2,000 mW/cm2 (G-Light Primal Plus light source, GC, Tokyo, Japan) for 90 s of light following the manufacturer’s recommendations. Each treatment was divided into two subgroups (n=20 each) according to the nature of the cement used: RelyX Ultimate Resin Cement (3M, St. Paul, MN, USA) and Super-Bond C&B (Sun Medical, Shiga, Japan) (Table 1). First, a polyethylene tape with a double-sided adhesive agent and circular hole (diameter: 4.0 mm, thickness: 0.1 mm) was pasted on the surface of the specimen to define the bonding area. Second, a load with hand-finger pressure was applied to the cylindrical specimen to facilitate its adhesion to the adhesive resin cement. Third, in case of RelyX Ultimate Resin Cement, after excess cement was eliminated from the bonding edge and the adhesion, the cylindrical specimen was cured at 2,000 mW/cm2 (G-Light Primal Plus light source) for 10 s in each of the four directions in light and then kept at room temperature for 30 min. In the case of Super-Bond C&B, polymer powder and liquid were mixed, excess cement was removed from the bonded edge, and then kept at room temperature for 30 min. The reason for keeping
Table 1  List of materials used in the present study

| Materials      | Product name          | Main composition                                      | Lot. number | Manufacturer          |
|----------------|-----------------------|-------------------------------------------------------|-------------|-----------------------|
| PEEK           | Vestakeep DC4450      | Polyetheretherketone, 20% Titanium dioxide pigments    | —           | Daical-Evonik         |
| Adhesive system| Visio.link             | MMA, pentaerythritol triacrylate, photo initiators     | 171018      | Bredent               |
| Adhesive resin cements | RelyX Ultimate Resin Cement | Methacrylate monomer, silica, polymerization initiator | 653276      | 3M ESPE               |
| Adhesive resin cements | Super-Bond C&B       | MMA, 4-META, TBB, PMMA                                | SS1         | Sun Medical           |

MMA: methyl methacrylate, 4-META: 4-methacryloxyethyl trimellitate anhydride, TBB: tributylborane, PMMA: polymethyl methacrylate

at room temperature for 30 min, which is our original method, was to allow sufficient curing time for the two adhesive resin cements with different curing times. In addition, we selected this experimental condition in air instead of in distilled water to wait for the cement to cure by keeping it moisture-proof. Fourth, after adhesion, each group was additionally divided into two groups (n=10 each). One group was subjected to shear bond strength test 24 h after adhesion (baseline). The specimens of the baseline group were stored in distilled water at 24°C for 24 h after adhesion. Another group was subjected to alternating thermal cycling at 5°C for 20 s and then 55°C for 20 s in distilled water for 10,000 cycles to investigate the effects of storage and aging 24 h after adhesion. Finally, after thermal cycling, the specimens for shear bond strength were completed.

**Shear bond strength measurement**

The shear bond strength for maximum load before debonding was measured with a universal testing machine (AG-X Plus, Shimadzu, Kyoto, Japan) based on the method described by Tsuka et al. The following formula was used to calculate shear bond strength:

\[ \text{fracture load (N)/bonding surface area (mm}^2) = \frac{N}{\text{mm}^2} = \text{MPa.} \]

**Failure mode analysis**

After the measurements of shear bond strength, the failure mode for each group of specimens was determined by analyzing the fractured surfaces. The failure mode was evaluated by examining the fractured surface after imaging with a digital camera (MR-14EX, Canon Production Printing Systems, Tokyo, Japan). The failure modes were defined as follows according to the method described by Tsuka et al.:

(a) Adhesive failure between the materials and luting agents.
(b) Cohesive failure within luting agents.
(c) Cohesive failure within the materials.
(d) Mixed failure featuring both cohesive and adhesive failures.

**Statistical analysis**

Statistical analyses were conducted with SPSS software (IBM, Armonk, NY, USA). All variables of distribution normality were examined by the Shapiro–Wilk normality test and for homoscedasticity by Bartlett’s test. All data for surface roughness and water contact angle were analyzed for statistical differences by one-way analysis of variance (one-way ANOVA) and Tukey’s honest significant difference (α=0.05). Each data for shear bond strength was analyzed for statistical differences by two-way analysis of variance (two-way ANOVA) and Tukey’s honest significant difference to investigate the effects of the two main factors (surface treatment and thermal cycling) and their interactions with a significant level of 0.05.

**RESULTS**

SEM images of various pretreated PEEK surfaces are shown in Fig. 1. The no treatment PEEK surface showed smooth and homogeneous surface. The sandblasted PEEK surface showed many convex precipitates compared with the untreated PEEK surface. The sulfuric-acid-etched PEEK surface showed large pits and pores. The laser-grooved PEEK surface showed regular grooves in a grid pattern, and undercutting also occurred.

The mean and standard deviation for the surface roughness or water contact angle of specimens subjected to the four surface pretreatments are shown in Figs. 2 and 3. The untreated PEEK surface (0.6±0.2 μm), the sandblasting treated (0.9±0.2 μm), and the sulfuric-acid-etched PEEK surface (0.5±0.2 μm) showed low surface roughness values. However, the surface roughness of the laser-grooved PEEK (18.5±2.6 μm) was significantly higher than that of all the other pretreatments. The water contact angles of the PEEK surfaces were significantly lower for sandblasted PEEK surfaces (61.6±6.6°) compared with untreated PEEK (116.2±4.2°), sulfuric-acid-etched PEEK surfaces (114.9±4.9°), and laser-grooved PEEK surfaces (126.5±5.7°).
Fig. 1 SEM image of the PEEK surface by using a scanning electron microscope operating at 1.7 kV and at a distance of 5.0–6.0 mm after each surface treatment.

A: no surface pretreatment (no treatment), smooth and homogeneous surface, B: air abrasion with 50 µm alumina oxide particles at 0.1 MPa at a 10 mm distance for 10 s (sandblasting treatment), many convex precipitates compared with the untreated PEEK surface, C: acid etched with sulfuric acid (98%) for 1 min and then rinsed with deionized water for 1 min (sulfuric acid etching), large pits and pores surface, D: Nd:YVO4 laser irradiation at an interval of 200 µm in the side and vertically and at a depth of 150 µm (laser groove treatment), regular grooves in a grid pattern and undercutting surface.

Fig. 2 Mean and standard deviation for surface roughness values (n=20). Asterisks represent significant difference (p<0.05).

The water contact angles of sulfuric-acid-etched PEEK surfaces were not significantly different from those of untreated PEEK surfaces.

Fig. 3 Mean and standard deviation for water contact angle values (n=20). Asterisks represent significant difference (p<0.05).

The wide scan spectra of four kinds of PEEK surface are shown in Fig. 4. All PEEK surfaces exhibited C, N, and O peaks, an Al peak was observed in sandblasting treatment, and Ti peaks were observed in the laser groove treatment. The C1s spectra of four kinds of PEEK surface are shown in Fig. 5. All PEEK surfaces exhibited CC (C-C bonds), CO (C-O bonds), and COO (O-C=O bonds) peaks. The atomic compositions of C, O, N, Al, and Ti elements and of CC, CO, and COO functional groups with no treatment, sandblasting treatment, sulfuric-acid treatment, and laser groove treatment are shown in Table 2.

Two-way ANOVA in RelyX Ultimate Resin Cement showed significant differences in surface treatment (p<0.001), thermal cycle (p=0.0443), and interaction of the two factors (p=0.0402). On the other hand, SuperBond C&B showed a significant difference in surface treatment (p<0.001) and no significant difference in thermal cycle (p=0.8568) and interaction of the two factors (p=0.0641). Figure 6 shows the variation of the mean value (MPa) and standard deviation of shear bond strength after 24 h of specimen preparation and after thermal cycling (10,000 cycles) for RelyX Ultimate Resin Cement and Super-Bond C&B, respectively. With the exception of the untreated PEEK specimens, all pretreatment and adhesive resin cement combinations showed shear bond strengths of approximately 10 MPa (ranging from 7.9±2.3 to 18. 9±4.3). Among the same surface pretreatment methods and the different thermal cycles, the shear bond strengths of the sulfuric-acid etching and the laser-grooved groups after thermal cycles in RelyX Ultimate Resin Cement were significantly lower than those of each group 24 h after specimen preparation (p<0.05). Among the different surface pretreatment methods and the same thermal cycles, the shear bond strengths of the sulfuric-acid-etched and laser-grooved groups in both cements were significantly higher than,
Fig. 4 Wide-scan spectra of (A) no treatment, (B) sandblasting treatment, (C) sulfuric acid treatment, and (D) Nd:YVO4 laser groove treatment PEEK surfaces by XPS.

Fig. 5 C1s spectra of (A) no treatment, (B) sandblasting treatment, (C) sulfuric acid treatment, and (D) Nd:YVO4 laser groove treatment PEEK surfaces by XPS.
CC: C-C bonds, CO: C-O bonds, COO: O-C=O bonds
Fig. 6 Mean and standard deviation for shear bond strength (MPa) of specimens with different surface treatment of 24 h after specimen preparation and after thermal cycling (10,000 cycles) for no treatment, sandblasting treatment, sulfuric-acid etching, and laser groove treatment.

The distributions of the different failure modes are shown in Table 3. Among untreated and sandblasted specimens, the most frequently observed failure mode was the adhesive presence at the interface between the bonded resin cement and the adhesive surface. Among sulfuric-acid-etched specimens, the adhesive failure and mixed failure modes were observed more frequently. In contrast, cohesive failure was observed in all laser-groove-treated specimens.

The results of SEM analysis after shear bond strength measurement are shown in Figs. 7 and 8. Resin cement was rarely observed on the surfaces of untreated and sandblasted specimens. However, residual resin cement was observed on the surfaces of sulfuric-acid-etched specimens. On the surfaces of laser-groove-treated specimens, large amounts of resin cement and broken PEEK material were observed remaining in the groove.

DISCUSSION

The results of this study demonstrate that laser-groove-treated PEEK with a more physically altered surface showed significantly higher shear bond strength than sandblasted or untreated PEEK. Therefore, the null hypothesis was rejected.

In this study, it is possible that the polymer surface was carbonized because of thermal degradation caused by laser irradiation. In the XPS analysis, the laser-groove-treated PEEK surface contained titanium element. This may indicate that the PEEK material was burned during laser irradiation, and the titanium oxide pigment in PEEK was condensed. Although the titanium element was identified by XPS in this study, we did not investigate the XPS of titanium O1s. Therefore, it is unclear what kind of titanium compounds the titanium elements on the PEEK surface exhibit. On the other hand, titanium

Table 2 Atomic compositions of C, O, N, Al, and Ti elements (Upper Table) and of CC, CO, and COO functional groups (Lower Table) in No treatment, Sandblasting treatment, Sulfuric acid treatment, and Laser groove treatment from XPS analysis

| Group                   | %C | %O  | %N | %Al | %Ti |
|-------------------------|----|-----|----|-----|-----|
| No treatment            | 81.9 | 16.0 | 2.1 | 0   | 0   |
| Sandblasting treatment  | 62.9 | 31.7 | 0   | 5.3 | 0.1 |
| Sulfuric acid etching   | 73.5 | 26.2 | 0.3 | 0   | 0   |
| Laser groove treatment  | 72.1 | 23.5 | 1.4 | 0   | 2.9 |

| Group                   | %CC | %CO | %COO |
|-------------------------|-----|-----|------|
| No treatment            | 65.5 | 29.5 | 5.1  |
| Sandblasting treatment  | 63.9 | 20.7 | 15.4 |
| Sulfuric acid etching   | 64.6 | 25.8 | 9.6  |
| Laser groove treatment  | 57.1 | 29.1 | 13.9 |
Table 3  Failure modes

| Group                      | Shear bond strength tested 24 h after specimens preparation | Shear bond strength tested after thermal cycling (10,000 cycles) |
|----------------------------|-------------------------------------------------------------|---------------------------------------------------------------|
|                            | RelyX Ultimate Resin Cement | Super-Bond C&B                                                 | RelyX Ultimate Resin Cement | Super-Bond C&B |
| Failure mode               | a / b / c / d             | a / b / c / d                                                   | a / b / c / d             | a / b / c / d |
| No treatment               | 10 / 0 / 0 / 0            | 9 / 0 / 0 / 1                                                   | 10 / 0 / 0 / 0            | 10 / 0 / 0 / 0 |
| Sandblasting treatment     | 9 / 0 / 0 / 1             | 10 / 0 / 0 / 0                                                  | 10 / 0 / 0 / 0            | 9 / 0 / 0 / 1 |
| Sulfuric acid etching      | 4 / 0 / 0 / 6             | 6 / 0 / 0 / 4                                                   | 5 / 0 / 0 / 5             | 5 / 0 / 0 / 5 |
| Laser groove treatment     | 0 / 0 / 10 / 0            | 0 / 0 / 10 / 0                                                  | 0 / 0 / 10 / 0            | 0 / 0 / 10 / 0 |

Failure modes: a) adhesive failure between materials and luting agents, b) cohesive failure within adhesive luting agents, c) cohesive failure within materials, d) mixed failure with both cohesive and adhesive failures.

Figure 7  SEM image of the fractured surfaces of PEEK following shear bond test after the thermal cycle (A group: no treatment, B group: sandblasting treatment, C group: sulfuric acid etching).

A-1 (low magnification), A-2 (medium magnification), A-3 (high magnification), B-1 (low magnification), B-2 (medium magnification), B-3 (high magnification), C-1 (low magnification), C-2 (medium magnification), C-3 (high magnification). A and B group: No resin cement was observed on both the surface of the no treatment and the sandblasting treated specimens. C group: A resin cement was observed on the surface of the sulfuric-acid-etched specimens. a: PEEK, b: Adhesive resin cement.

Element was not detected in the untreated and sulfuric acid-treated XPS results, even though titanium element is contained in PEEK. It is possible that the titanium contained in the material fell off from the surface or that the titanium was coated by stretching the carbon during polishing, but the details are unknown because the micro-order detection was not performed in this study. In addition, CO- and COO-containing functional groups, such as carbonyl and carboxyl groups, were introduced on the laser-groove-treated surfaces. Metal oxides and
functional groups containing oxygen contribute to increased chemical adhesiveness\(^{27}\). The laser-groove-treated PEEK surfaces showed the highest Ra value. PEEK surfaces with higher surface roughness increase the micro roughness and junction area of the material and increase the mechanical retention with adhesive resin cement\(^{29}\). The surface roughness and water contact angle of the laser-groove-treated PEEK surface are highest, because the contact angle is generally larger by the hydrophobic surface. SEM images after specimens were measured by the shear bond testing and failure mode analysis showed that much resin cement remained, with resin cement fitted in the laser grooves. This showed that the mechanical retention was high. Therefore, from these results of XPS, surface roughness, and water contact angle, laser groove treatment was expected to improve the chemical and physical adhesion on the PEEK surface.

Previous studies have shown that adhesive systems containing MMA monomers have higher shear bond strength between PEEK and resin cement\(^{24,32-34}\). In addition, it has been reported that the visio.link product is an idealized adhesive system that increases adhesion strength with PEEK surfaces\(^{32}\). On one hand, Scotchbond Universal Adhesives are effective on dentine, metal and resin materials\(^{35}\), but have not yet been shown to be effective on PEEK. Therefore, visio.link was selected as the adhesive system in this study. The main component of visio.link consists of MMA and pentaerythritol triacrylate (PETIA). PETIA has a superior capability to change the PEEK surface\(^{36}\), and visio.link provides high adhesive strength values for composite resins based on the RelyX Ultimate Resin Cement. Another study found that the highest shear bond strength between PEEK and resin cement was achieved by an adhesive consisting of PETIA, MMA monomers, and additional dimethacrylates in solution\(^{33}\). Resin cement containing MMA can establish chemical bonds to PEEK without surface functionalization\(^{30}\). As seen in previous studies\(^{27,29}\), the shear bond strength between Super-Bond C&B and PEEK was higher than that between resin-based RelyX Ultimate Resin Cement and PEEK in this study also. On the other hand, since most of the surface of PEEK is coated with visio.link before the adhesive resin, adhesion between PEEK and visio.link may occur instead of adhesion between PEEK and adhesive resin. The CO and COO functional groups of the laser-treated PEEK detected by XPS may react with the visio.link. This chemical reaction has been reported by Schmidlin et al.\(^{18}\). The PEEK surface oxidized by chemical conditioning opens up the aromatic rings, increases the polarity, and adds functional groups that are more reactive with the bonding agent, resulting in increased bond strength. Although the laser grooving process is not a chemical treatment, we were able to confirm the oxidation of the PEEK surface in the same way.

Thermal cycling has also been reported as an alternative to clinical studies to investigate aging\(^{37}\). In this study, specimens were subjected to 10,000 cycles of initial and degradation testing in a thermal cycling device, which is reported to be equivalent to a period of 8–10 years in vivo\(^{30}\). Thermal cycling is the repeated cycling between two temperatures of 5°C and 55°C,
respectively. In this study, thermal cycling also confirmed the aging process and showed high shear bond strength even after thermal cycling. Heat loading may cause mechanical stress and volume changes in the bonded area. In this study, the shear bond strength decreased in all groups except for the no treatment group in RelyX Ultimate Resin Cement, although the difference was not statistically significant. The results of the two-way ANOVA on RelyX Ultimate Resin Cement suggest that shear bond strengths of sulfuric acid-treated and laser-treated groups reduced after thermal cycling and that these treatments may be vulnerable to thermal changes and/or moisture. Comparing the different surface treatments with the same thermal cycle time, the shear bond strengths of sulfuric acid-treated and laser-treated groups was significantly higher than untreated and sandblasted groups. However, there is a significant difference in the interaction between the two factors of surface treatment and thermal cycling. Therefore, the effect of surface treatment and thermal cycling on shear bond strength are not uniform, and this main effect is qualified by a significant interaction. On the other hand, the results of two-way ANOVA on Super-Bond C&B suggest that the shear bond strengths of sandblasted and laser-treated groups are closely associated with the different surface pretreatment methods among the same thermal cycle. No significant difference was found in the interaction between the two factors of surface treatment and thermal cycling. These results indicate that the shear bond strength of laser treated with Super-Bond C&B is greater than that of untreated and sandblasted among the same thermal cycles.

The shear bond strength of sulfuric-acid-etched PEEK was as high as that of laser groove treatment PEEK in this study. Many previous studies reported that 98% sulfuric acid was suitable for modifying the chemical and physical properties of PEEK surfaces for improved binding. Also, previous studies showed that acid etching on a PEEK surface results in a high shear bond strength with resin cement. The findings of high bond strength values with PEEK specimens pretreated with 98% sulfuric acid in this study agree with these reports. Sandblasting and laser irradiation both generate a mechanically increased surface area PEEK surface. It has been reported that sulfuric acid creates functional groups of carbonyl and ether other groups on a PEEK surface and increases its adhesive properties toward resin material. In another study, under the condition of etching for 1 min with 98% sulfuric acid, micromechanical bonding by penetrating resin tag pits into a porous PEEK surface was confirmed. In this study, sulfuric-acid-etched PEEK specimens had low surface roughness values, indicating that observed increases in adhesion strength were not caused by increased surface area. In the SEM image after sulfuric-acid etching, clear pits and porous surfaces were observed on the PEEK surface. Furthermore, 98% sulfuric acid is difficult to use under clinical conditions because of its strong oxidizing properties.

Sandblasting is a common method of surface treatment in clinical dental practice. Sandblasting increases the surface roughness and promotes micromechanical interlocks with dental materials by removing organic contaminants from material surfaces. Consistent with previous studies, the surface roughness and shear bond strength of sandblasted PEEK were not significantly different from untreated PEEK statistically in this study.

The results of this study showed that the shear bond strength between laser groove treatment PEEK and resin cement is comparable to that seen with sulfuric-acid-etched PEEK. Thus, the surfaces with laser groove treatment PEEK can be a viable alternative to acid etching techniques where safety is a concern.

There are some limitations in this study. Firstly, although only one laser parameter was used, the laser groove design is currently experimental, and it would be beneficial to consider other designs. Secondly, since we did not investigate the XPS of O1s, we were able to identify the elements of titanium and Al, but not what kind of compounds they are. Thirdly, no titanium was detected near the untreated and sulfuric acid-treated PEEK surface at the nano-order level. The details of the PEEK surface are unknown because the surface has not been investigated at micro-order level.

CONCLUSION

Based on the findings of this in vitro study, it was concluded that laser groove treatment improves the shear bond strength between laser modified tooth-colored PEEK and adhesive resin cement with an adhesive system.

ACKNOWLEDGMENTS

The authors would like to thank Mr. Katsumi SAWADA (Daical-Evonik, Tokyo, Japan) for providing the PEEK materials, Mr. Sadakazu OYAMA (ULTI-Medical, Osaka, Japan) for fabricating the PEEK specimens, Mr. Kazuhiro KONISHI, Mr. Takayuki MIYASHITA, and Ms. Tomomi KOMURA (Polyplastics, Shizuoka, Japan) for laser-grooving the PEEK surfaces, and Mr. Katsuhiro SUGAWARA (KS Dental, Yokohama, Japan) for technical assistance with manufacturing the specimens. All authors declare no potential conflicts of interest with respect to the authorship and/or publication of this article.

CONFLICT OF INTEREST

No conflict of interest has been declared. This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

REFERENCES

1) Stawarczyk B, Jordan P, Schmidlin PR, Roos M, Eichberger M, Gernet W, et al. PEEK surface treatment effects on tensile bond strength to veneering resins. J Prosthet Dent 2014; 112: 1278-1288.
2) Stawarczyk B, Thrun H, Eichberger M, Roos M, Edelhoff D, Schweiger J, et al. Effect of different surface pretreatments and adhesives on the load-bearing capacity of veneered 3-unit PEEK FDPs. J Prosthodont 2015; 114: 666-673.
3) Katzer A, Marquardt H, Westendorf J, Wening JV, Foerster GV. Polyetherketone — Cytotoxicity and mutagenicity in vitro. Biomaterials 2002; 23: 1749-1759.
4) Kurtz SM, Devine JN. PEEK biomaterials in trauma, orthopedic, and spinal implants. Biomaterials 2007; 28: 4845-4869.
5) Wang H, Xu M, Zhang W, Kwok DT, Jiang J, Wu Z, et al. Mechanical and biological characteristics of diamond-like carbon coated poly aryl-ether-ether-ketone. Biomaterials 2010; 31: 8181-8187.
6) Zhao Y, Wong HM, Wang W, Li P, Xu Z, Chong EYW, et al. Cytocompatibility, osseointegration, and bioactivity of three-dimensional porous and nanostructured network on polyetherketone. Biomaterials 2013; 34: 9264-9277.
7) Meningaud JP, Spahn F, Donsimoni JM. After titanium, PEEK? Rev stomatol Chir Maxillofac 2012; 113: 407-410.
8) Santing HJ, Meijer HJ, Raghoebar GM, Ozcan M. Fracture strength and failure mode of maxillary implant-supported provisional single crowns: A comparison of composite resin crowns fabricated directly over PEEK abutments and solid titanium abutments. Clin Implant Dent Relat Res 2012; 14: 882-889.
9) Wu X, Liu X, Wei J, Ma J, Deng F, Wei S. Nano-TiO2/PEEK bioactive composite as a bone substitute material: in vitro and in vivo studies. Int J Nanomedicine 2012; 7: 1215-1225.
10) Lee WT, Koak JY, Lim YJ, Kim SK, Kwon HB, Kim MJ. Stress shielding and fatigue limits of poly-ether-ether-ketone dental implants. J Biomed Mater Res B Appl Biomater 2012; 100: 1044-1052.
11) Schiwitalla A, Müller WD. PEEK dental implants: a review of the literature. J Oral Implantol 2013; 39: 743-749.
12) Stawarczyk B, Beuer F, Wimmer T, Jahn D, Sener B, Roos M, et al. Polyetheretherketone — A suitable material for fixed dental prostheses? J Biomed Mater Res B Appl Biomater 2013; 101: 1209-1216.
13) Nageeb S, Zafar MS, Khurshid Z, Siddiqui F. Applications of polyetherketone (PEEK) in oral implantology and prosthodontics. J Prosthodont Res 2016; 60: 12-19.
14) Ma R, Tang T. Current strategies to improve the bioactivity of PEEK. Int J Mol Sci 2014; 15: 5426-5445.
15) Olio G. Bond strength testing: What does it mean? Int Dent J 1993; 43: 492-498.
16) Ersu B, Yuzugullu B, Ruya Yazici A, Canay S. Surface roughness and bond strengths of glass-infiltrated alumina-ceramics prepared using various surface treatments. J Dent 2009; 37: 848-856.
17) Marshall SJ, Bayne SC, Baier R, Tom sia AP, Marshall GW. A review of adhesion science. Dent Mater 2010; 26: e1-e16.
18) Schmidlin PR, Stawarczyk B, Wieland M, Attin T, Hämmerle CH, Fischer J. Effect of different surface pre-treatments and luting materials on shear bond strength to PEEK. Dental Mater 2010; 26: 553-559.
19) Uhrenbacher J, Schmidlin PR, Keul C, Eichberger M, Roos M, Gernet W, et al. The effect of surface modification on the retention strength of polyetheretherketone crowns adhesively bonded to dentin abutments. J Prosthodont 2014; 112: 1489-1497.
20) Zhou L, Qian Y, Zhu Y, Liu H, Gan K, Guo J. The effect of different surface treatments on the bond strength of PEEK composite materials. Dental Mater 2014; 30: e209-e215.
21) Sproesser O, Schmidlin PR, Uhrenbacher J, Roos M, Gernet W, Stawarczyk B. Effect of sulfuric acid etching of polyetheretherketone on the shear bond strength to resin cements. J Adhes Dent 2014; 16: 465-472.
22) Silthampitag P, Chaijareenont P, Tattakorn K, Banjongprasert C, Takahashi H, Arksornukit M. Effect of surface pretreatments on resin composite bonding to PEEK. Dental Mater J 2016; 35: 668-674.
23) Kern M, Lehmann F. Influence of surface conditioning on bonding to polyetheretherketone (PEEK). Dental Mater 2012; 28: 1280-1283.
24) Stawarczyk B, Bähr N, Beuer F, Wimmer T, Eichberger M, Gernet W, et al. Influence of plasma pretreatment on shear bond strength of self-adhesive resin cements to polyetheretherketone. Clin Oral Investig 2014: 18: 163-170.
25) Bötel F, Zimmermann T, Sütel M, Müller WD, Schiwitalla AD. Influence of different low-pressure plasma process parameters on shear bond strength between veneering composites and PEEK materials. Dent Mater 2018; 34: e246-e254.
26) Kazama-Koide M, Okhuma K, Ogura H, Miyagawa Y. A new method for fabricating zirconia copings using a Nd:YVO4, nanosecond laser. Dental Mater J 2014; 33: 422-429.
27) Tsuka H, Morita K, Kato K, Kimura H, Abe kura H, Hirata I, et al. Effect of laser groove treatment on shear bond strength of resin-based luting agent to polyetheretherketone (PEEK). J Prosthodont Res 2019; 63: 52-57.
28) Fuhrmann G, Steiner M, Freit ag Wolf S, Kern M. Resin bonding to three types of polyaryletherketones (PAEKs)—durability and influence of surface conditioning. Dent Mater 2014; 30: 357-363.
29) Çulhaoğlu AK, Özkar SE, Sahin V, Yılmaz B, Kılıçarslan MA. Effect of various treatment modalities on surface characteristics and shear bond strengths of polyetheretherketone-based core materials. J Prosthodont 2020; 29: 136-141.
30) Tsuka H, Morita K, Kato K, Kawano H, Abe kura H, Tsuga K. Evaluation of shear bond strength between PEEK and resin-based luting material. J Oral Biosciences 2017; 59: 231-236.
31) Abe Y, Hi asa K, Hirata I, Okazaki Y, Nogami K, Mizumachi W, et al. Detection of synthetic RGDS(PO3H2)PA peptide adsorption using a titanium surface plasmon resonance biosensor. J Mater Sci Mater Med. 2011; 22: 657-661.
32) 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: 441-448.
33) Keul C, Liebermann A, Schmidlin PR, Roos M, Sener B, Stawarczyk B. Influence of PEEK surface modification on the retention of two veneering resin composites. J Adhes Dent 2014; 16: 383-392.
34) Rosentritt M, Preis V, Behr M, Sereno N, Kolbeck C. Shear bond strength between veneering composite and PEEK after different surface modifications. Clin Oral Investig 2015; 19: 739-744.
35) Tsujimoto A, Barkmeier WW, Takamizawa T, Wilwerding TM, Latka MA, Miyazaki M. Interfacial characteristics and bond durability of universal adhesive to various substrates. Oper Dent 2017; 42: E59-E70.
36) Caglar I, Ates SM, Yesil Duymus Z. An in vitro evaluation of the effect of various adhesives and surface treatments on bond strength of resin cement to polyetheretherketone. J Prosthodont 2019; 28: e342-e349.
37) Kern M, Lehmann F. Influence of surface conditioning on bonding to polyetheretherketone (PEEK). Dental Mater 2012; 28: 1280-1283.
38) Stawarczyk B, Bähr N, Beuer F, Wimmer T, Eichberger M, Gernet W, et al. Influence of plasma pretreatment on shear bond strength of self-adhesive resin cements to polyetheretherketone. Clin Oral Investig 2014: 18: 163-170.
39) Bötel F, Zimmermann T, Sütel M, Müller WD, Schiwitalla AD. Influence of different low-pressure plasma process parameters on shear bond strength between veneering composites and PEEK materials. Dent Mater 2018; 34: e246-e254.