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

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Abstract

The purpose of this study was to investigate the effect of various surface treatments on the shear bond strength between dental PEEK (PEEK) and adhesive resin cement. 240 specimens were randomly classified into four groups: no treatment, sandblasted, sulfuric-acid-etched, and laser-grooved treatment. Each group was classified into two adhesive resin cement subgroups. Surface roughness, water contact angle, shear bond strength, and failure mode were measured; SEM and XPS results were obtained. The data were statistically analyzed using one-way or two-way analysis of variance and Tukey's honest significant difference test (α=0.05). Laser-grooved PEEK surface showed regular grooves and carbonization by thermal degradation; the surface roughness as well as water contact angle of were the highest in all groups. Shear bond strength values were significantly higher in the laser-groove-treated and sulfuric-acid-etched groups. Laser-groove-treated specimens showed cohesive failure. Laser-grooved treatment can improve shear bond strength between PEEK and adhesive resin cement.

Keywords: dental polyetheretherketone, shear bond strength, adhesive resin cement, adhesive system, Nd:YVO4 laser

INTRODUCTION

Polyetheretherketone is a polymer consisting of aromatic benzene molecules linked by functional ethers or ketone groups[1,2]. Furthermore, polyetheretherketon is a high-performance thermoplastic with excellent mechanical properties, low water absorption, and fracture resistance[3-6]. Dental polyetheretherketon (PEEK) has recently attracted attention in the dental field as a useful material for interim prostheses, removable prosthodontics, splints, implants, and abutment screws[7-13]. 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 cement[14]. Recent research has focused on PEEK surface modification and altered adhesive systems to obtain strong adhesion performance between the PEEK surface and resin cement[15-17]. Several surface treatments, such as conventional sandblasting treatment[12,18,19], acid etching[12,18-22], silicone coating[12,18,23], and plasma treatment[20,24,25] have been studied to improve the bonding strength of the cement. Many researchers have recommended surface treatment with 98% sulfuric acid to improve PEEK bonding[12,18,20-22]; however, this chemical is toxic, and its use in dental clinics presents safety concerns and is not practical[20].

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 lasers 26). 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 adhesion to PEEK17,19). Studies have also shown that chemical pretreatment on PEEK by increasing the number of functional groups to which components of the adhesive system contribute binding can increase shear bond strength24,28). 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.

MATERIAL 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, Ltd., 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 to 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 (YVO4 Laser Marker MD-V9900A, Keyence Co., 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 1064 nm, a laser density of 5.3 mW/cm^2, 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 Co., Tokyo, Japan) 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, Ltd., 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, Inc., Kanagawa, Japan) by the static drop method. In this procedure, 10 μl of H_2O 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 C_{1s} spectra after each PEEK surface treatment was measured using X-ray photoelectron spectroscopy and the accompanying software (XPS, AXIS-HS, Kratos Analytical Ltd, Manchester, UK). Quantitative date was obtained from peak areas of the spectral lines using the supplied software (Vision software, Kratos Analytical Ltd, Manchester, UK) and the peaks at 284.6 eV (CC), 286.0 eV (CO), and 288.4 eV (COO) in the C 1s region were analyzed31). 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 GmbH & Co. KG, Senden, Germany) was applied as an adhesive to the surface on both disc-shaped and cylindrical specimens. The adhesive was cured at 2000 mW/cm^2 (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 Co., Ltd., Moriyama, 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 2000 mW/cm^2 (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 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 Co., Kyoto, Japan) based on the method described by Tsuka et al.30). The following formula was used to calculate shear bond strength: fracture load (N)/bonding surface area (mm^2) = N/mm^2 = 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.27).

(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 θ) compared with untreated PEEK (116.2±4.2 θ), sulfuric-acid-etched PEEK surfaces (114.9±4.9 θ), and laser-grooved PEEK surfaces (126.5±5.7 θ). The laser-grooved PEEK surfaces had also significantly higher water contact angles than sulfuric-acid-etched PEEK. The water contact angles of sulfuric-acid-etched PEEK surfaces were not significantly different from those of untreated PEEK surfaces.

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 C_{1s} 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, Super-Bond 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 ($p=0.0641$). Fig. 6 show 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 24h 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, in order of bond strength, those of the sandblasted and untreated groups ($p<0.05$).

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 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 adhesiveness27). 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 cement29). 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 cement24,32-34). In addition, it has been reported that the visio.link product is an idealized adhesive system that increases adhesion strength with PEEK surfaces32). On one hand, Scotchbond Unversal Adhesives are effective on dentine, metal and resin materials35), 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 surface36), 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 solution33). Resin cement containing MMA can establish chemical bonds to PEEK without surface functionalization32). As seen in previous studies27,29), 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 al18). 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 y in vivo[24)]. 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[24)]. 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 binding12,18,20-22). Also, previous studies showed that acid etching on a PEEK surface results in a high shear bond strength with resin cement18,20). 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 groups on a PEEK surface and increases its adhesive properties toward resin material38). 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 confirmed22). 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 (Fig. 1). 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 surfaces21,24). 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.

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CONFLICT OF INTEREST

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Figure Captions

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 seconds (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)

Note: Asterisks represent significant difference ($p<0.05$)

Fig. 3 Mean and standard deviation for water contact angle values (n=20)

Note: Asterisks represent significant difference ($p<0.05$)

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 C_{1s} spectra of (A) no treatment, (B) sandblasting treatment, (C) sulfuric acid treatment, and (D) Nd:YVO4 laser groove treatment PEEK surfaces by XPS.

Abbreviated word: 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 24h after specimen preparation and after thermal cycling (10,000 cycles) for no treatment, sandblasting treatment, sulfuric-acid etching, and laser groove treatment

Note: Within the same column, the same superscripted letters indicate no significant differences ($p>0.05$)

Interaction of surface treatment and thermal cycle for RelyX Ultimate Resin Cement: p=0.0402, for Super-Bond C&B: p=0.0641

Fig. 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.

Abbreviated word: a: PEEK, b: Adhesive resin cement

Fig. 8 SEM image of the fractured surfaces of PEEK following shear bond test after the thermal cycle

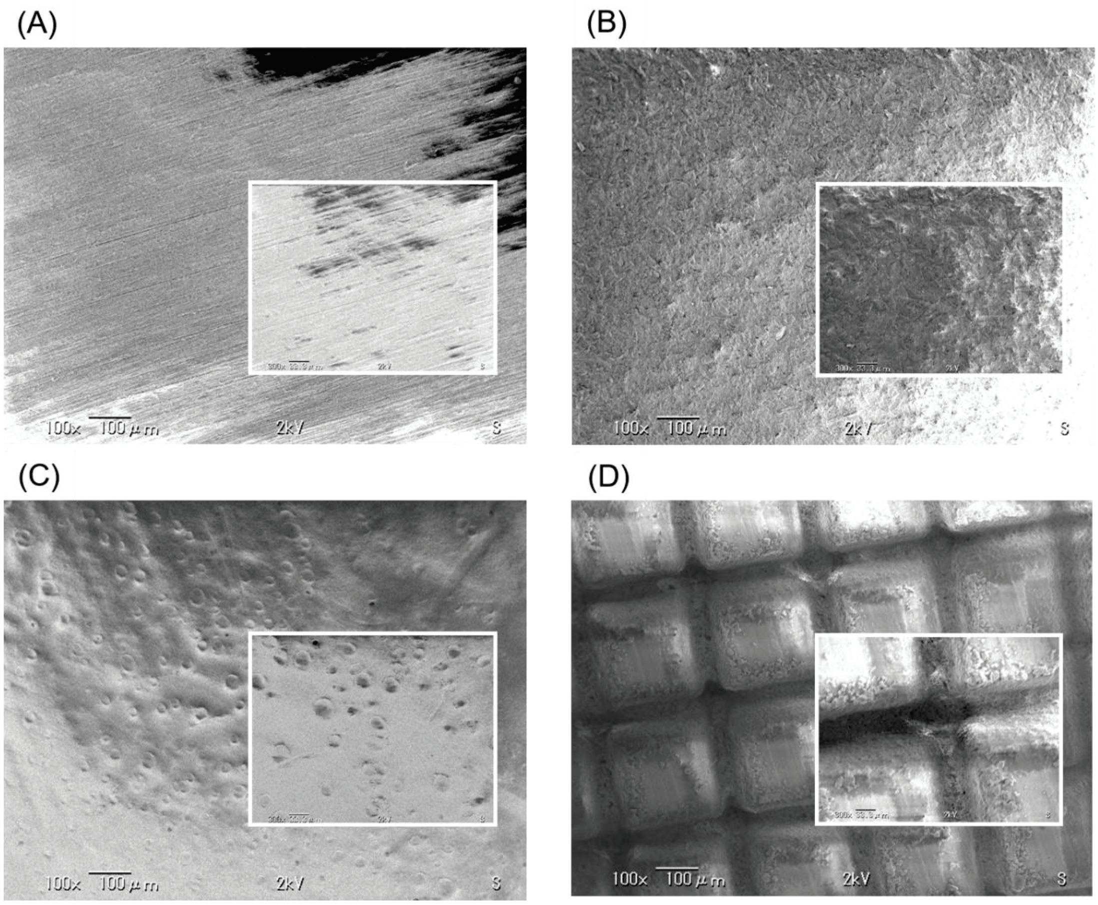
D-1, D-2, D-3: laser groove treatment/Rely X Ultimate Resin Cement

D-4, D-5, D-6: laser groove treatment/Super-Bond C&B

D-1 (low magnification), D-2 (medium magnification), D-3 (high magnification),

D-4 (low magnification), D-5 (medium magnification), D-6 (high magnification), On the surfaces of laser-groove-treated specimens, large amounts of resin cement and broken PEEK material were observed remaining in the groove.

Abbreviated word: a: PEEK, b: Adhesive resin cement



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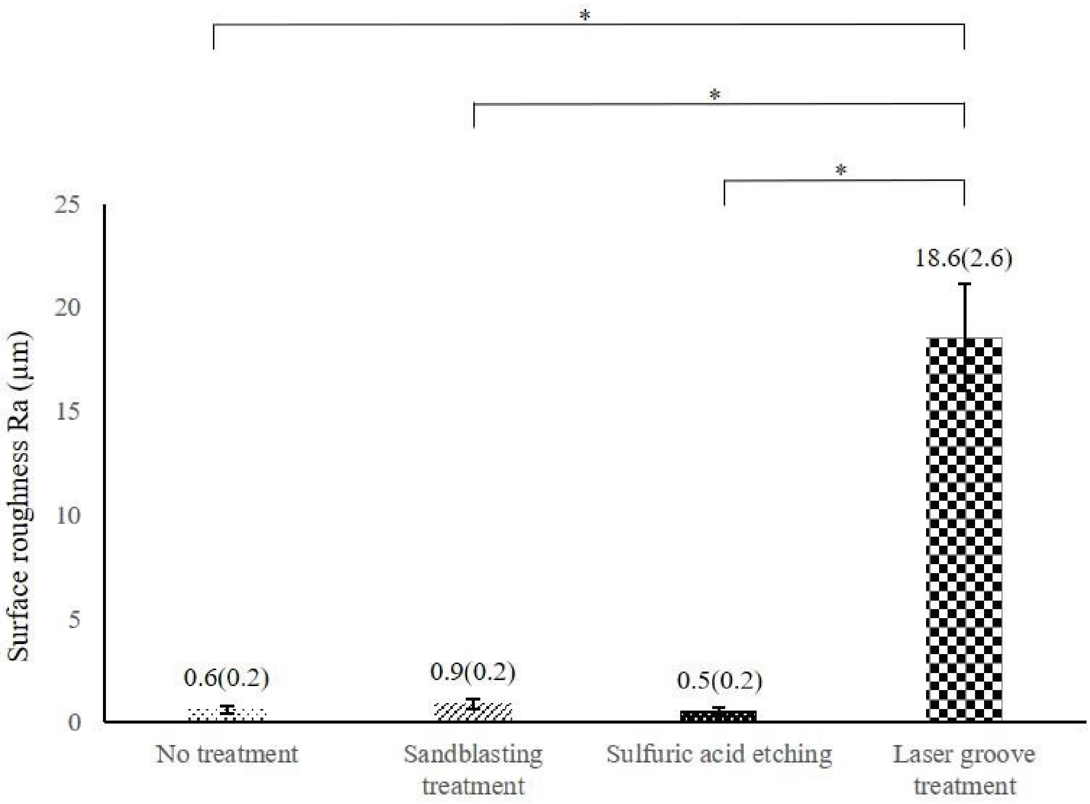


Fig. 2 Mean and standard deviation for surface roughness values (n=20)

Note: Asterisks represent significant difference ($p<0.05$)

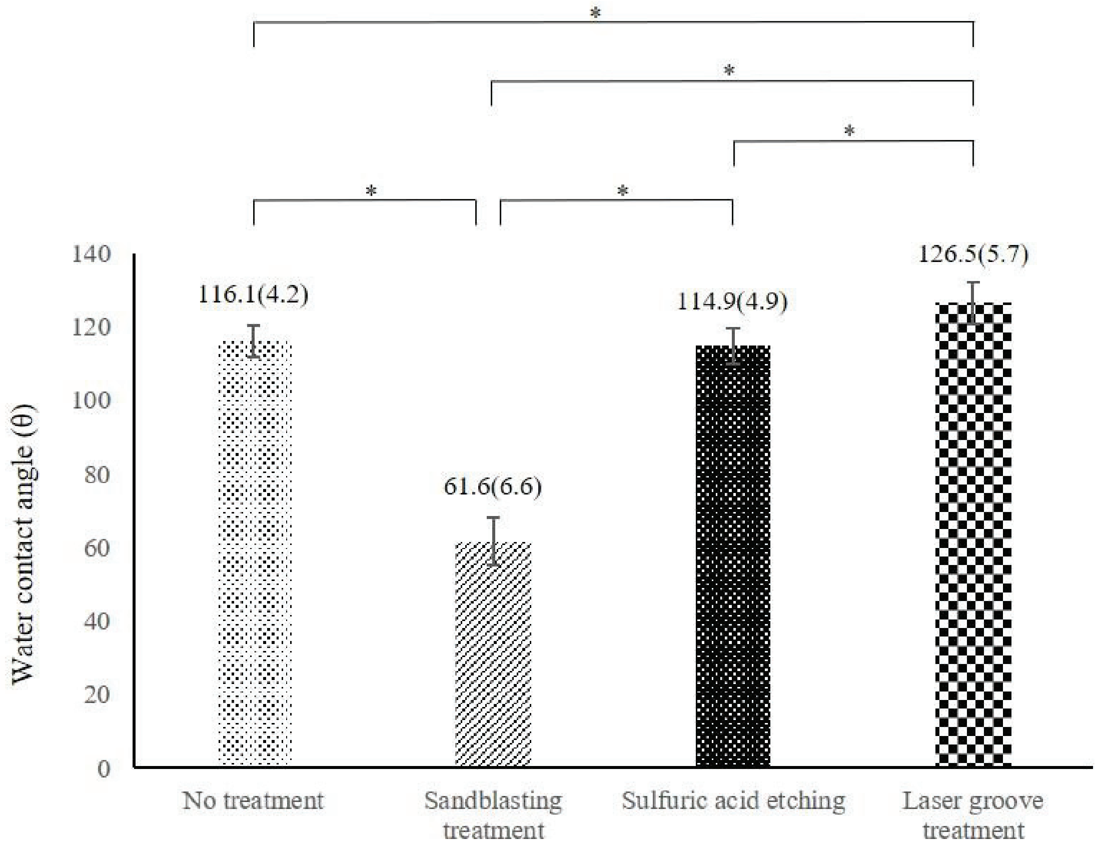
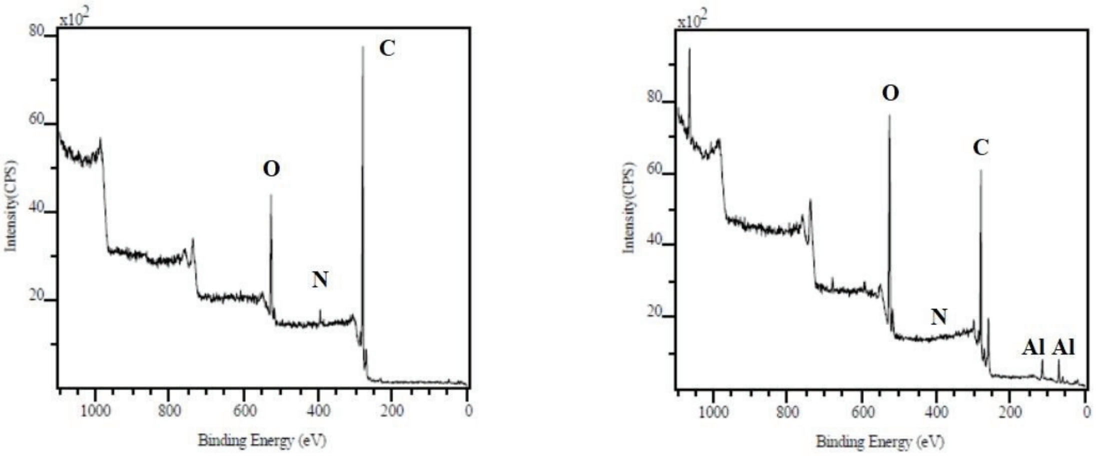


Fig. 3 Mean and standard deviation for water contact angle values (n=20)

Note: Asterisks represent significant difference ($p<0.05$)



(A) No treatment

(B) Sandblasting treatment

(C) Sufuric acid etching treatment

(D) Nd:YVO4 laser groove treatment

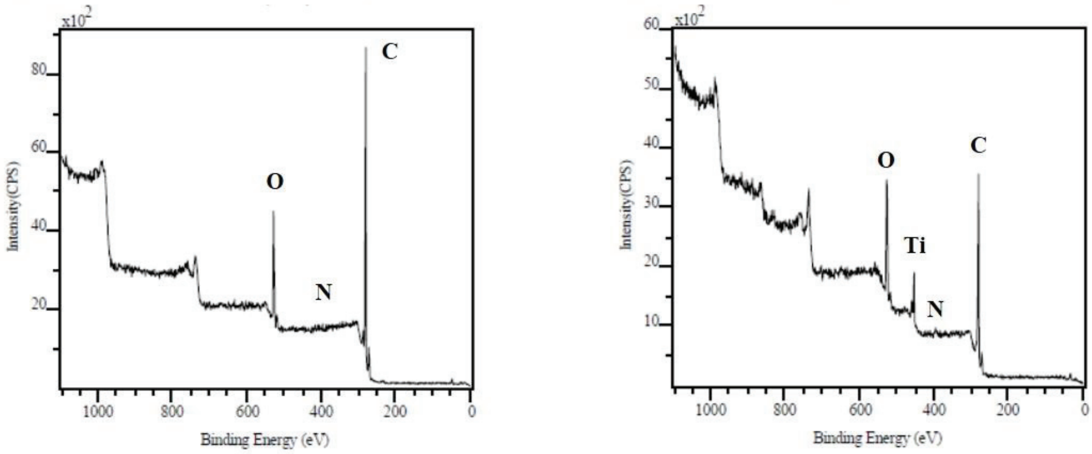


Fig. 4 Wide-scan spectra of (A) no treatment, (B) sandblasting treatment, (C) sulfuric acid treatment, and (D) Nd:YVO4 laser groove treatment PEEK surfaces by XPS.

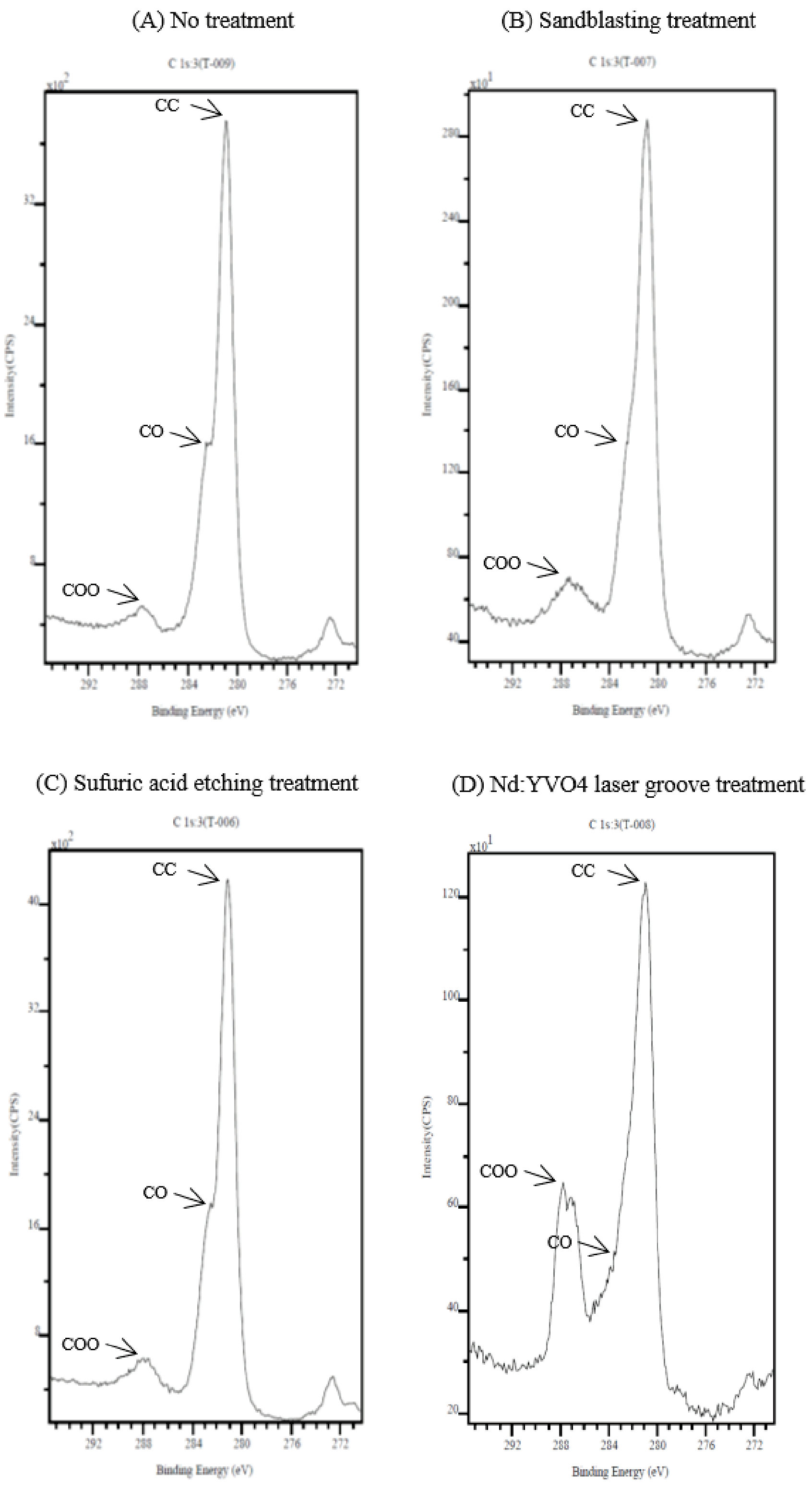


Fig. 5 C_{1s} spectra of (A) no treatment, (B) sandblasting treatment, (C) sulfuric acid treatment, and (D) Nd:YVO4 laser groove treatment PEEK surfaces by XPS.

Abbreviated word: CC: C-C bonds, CO: C-O bonds, COO: O-C=O bonds

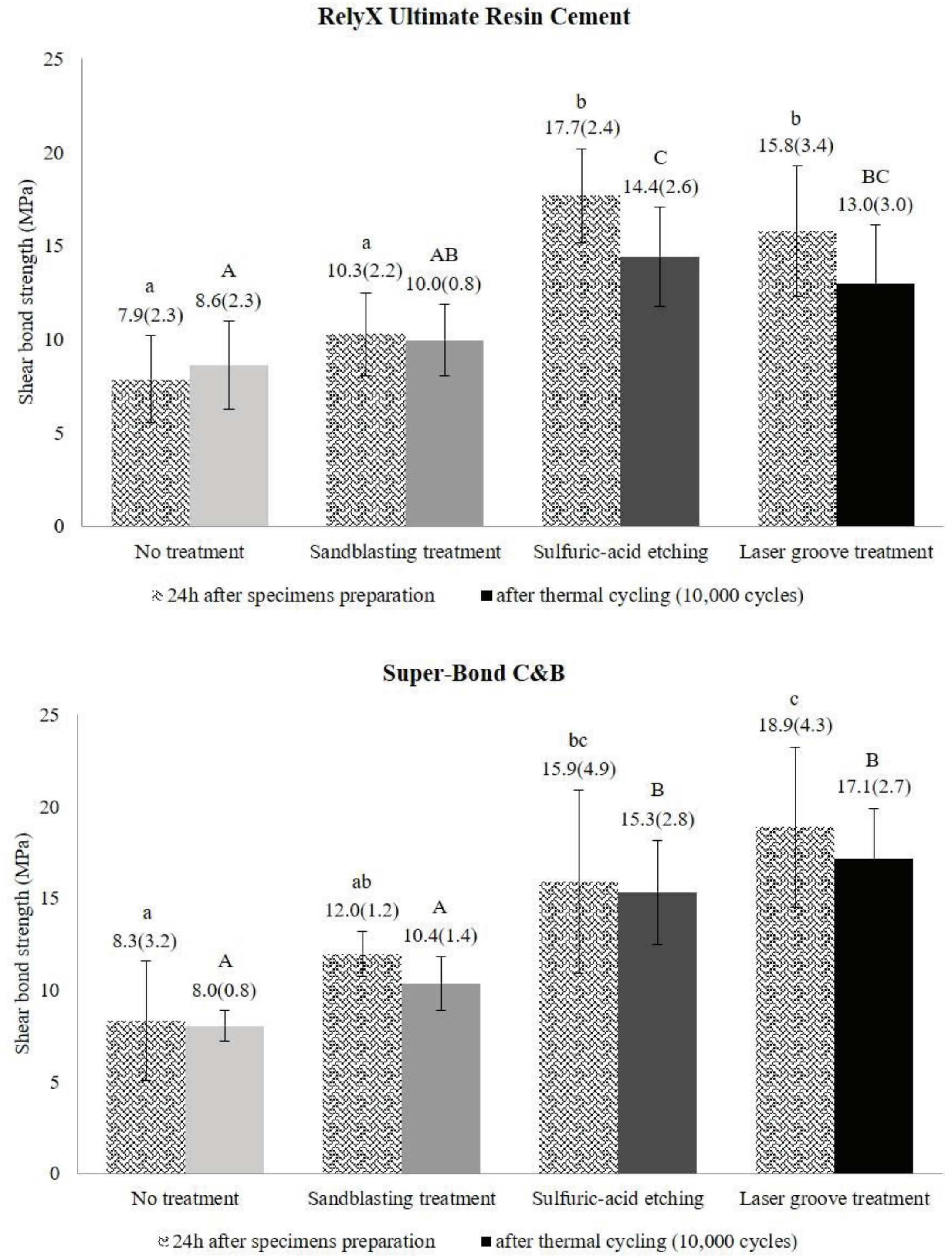


Fig. 6 Mean and standard deviation for shear bond strength (MPa) of specimens with different surface treatment of 24h after specimen preparation and after thermal cycling (10,000 cycles) for no treatment, sandblasting treatment, sulfuric-acid etching, and laser groove treatment

Note: Within the same column, the same superscripted letters indicate no significant differences (*p*>0.05)

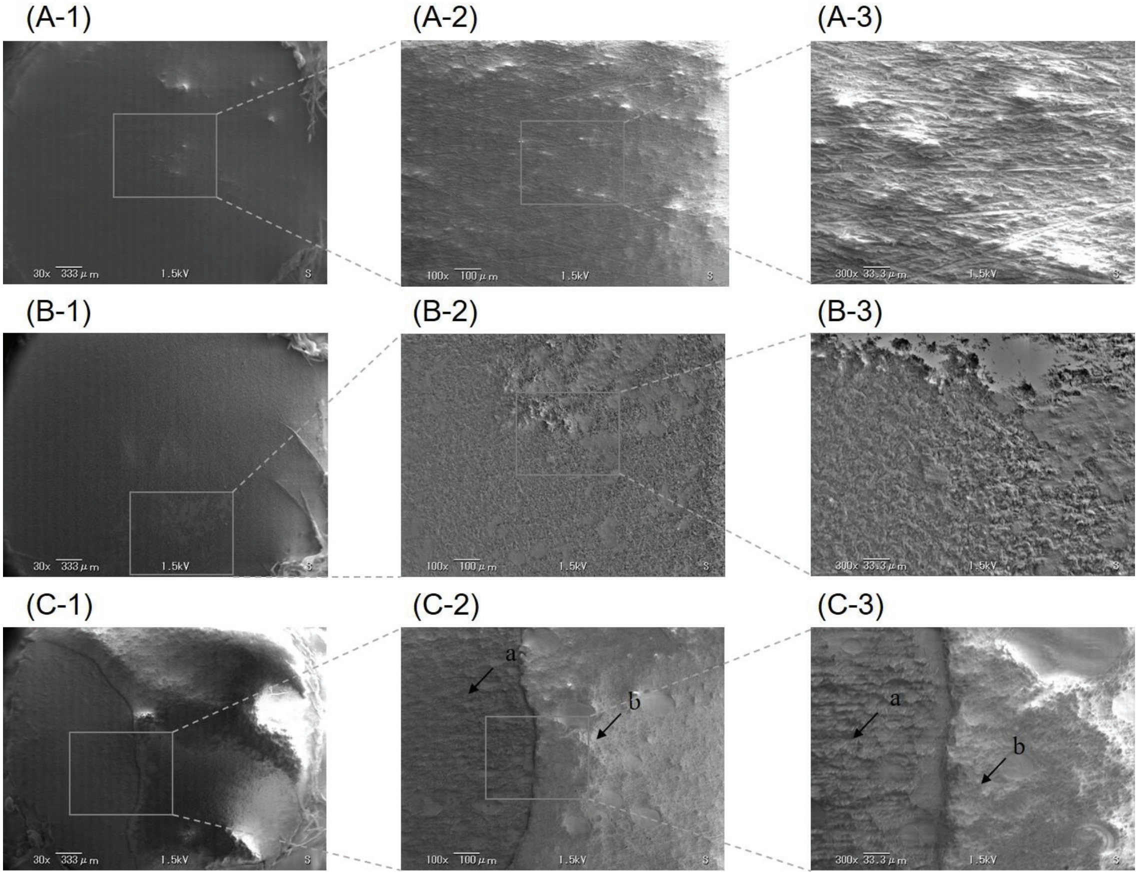


Fig. 7 SEM image of the fractured surfaces of PEEK following shear bond test after the thermal cycle (**A group: no treatment, B group: sandblasting treatment, C group: sulfuric acid etching**).

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)

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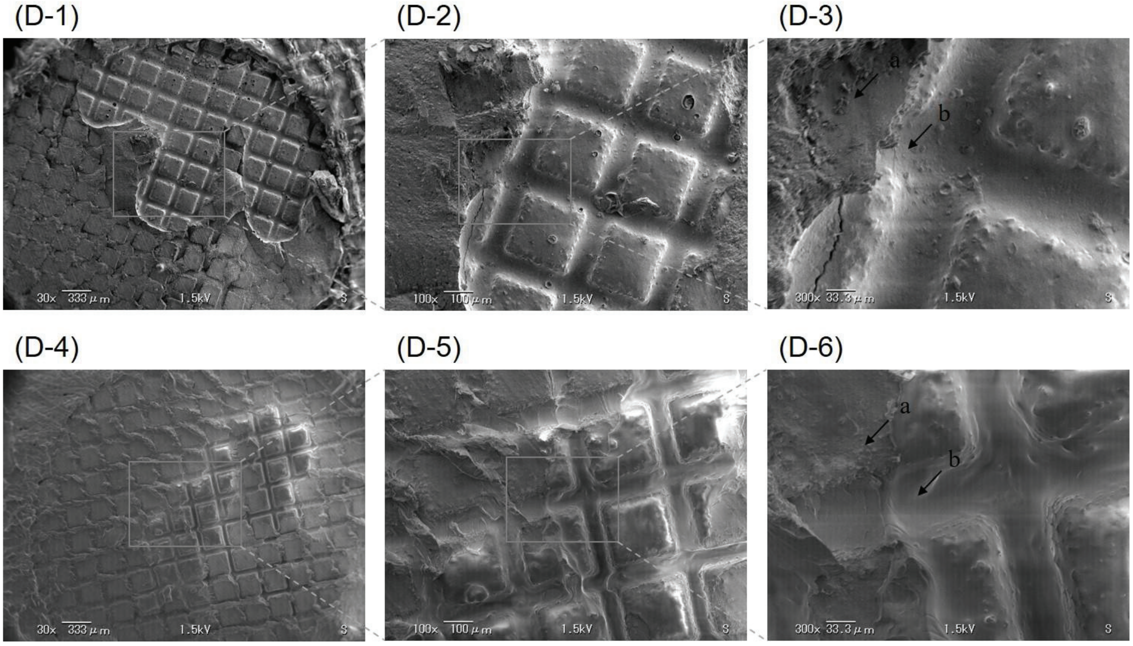

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D-1, D-2, D-3: laser groove treatment/Rely X Ultimate Resin Cement

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D-1 (low magnification), D-2 (medium magnification), D-3 (high magnification),

D-4 (low magnification), D-5 (medium magnification), D-6 (high magnification),

On the surfaces of laser-groove-treated specimens, large amounts of resin cement and broken PEEK material were observed remaining in the groove.

Abbreviated word: a: PEEK, b: Adhesive resin cement

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 GmbH & Co KG
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 Co. Ltd.

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

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 24h 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