Effects of different sulfuric acid etching concentrations on PEEK surface bonding to resin composite

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This study evaluated the effects of surface pretreatment with different concentrations of sulfuric acid etching on surface properties and bonding between Polyetheretherketone (PEEK) and a resin composite. Six groups of surface pretreatment (no pretreatment, etched with 70, 80, 85, 90, and 98% sulfuric acid for 60 s) were treated on PEEK. Surface roughness, scanning electron microscopy (SEM) and atomic force microscopy (AFM) analyses were examined. Shear bond strength (SBS) and cross-sectional observations of the interfaces were performed. One-way ANOVA analysis revealed differences in surface roughness and SBS between groups. The 90 and 98% sulfuric acid etching significantly achieved the highest SBS (p<0.05). SEM and AFM demonstrated etched surfaces with wide and deep pores. The 90 and 98% sulfuric acid etching were suggested to be the optimal concentration to improve adhesion between PEEK and the resin composite.

Keywords: PEEK, Roughness, Shear bond strength, Sulfuric acid

INTRODUCTION

Polyetheretherketone (PEEK) is a high-performance semi-crystalline thermoplastic related to the polyaryletherketone (PAEK) group, consisting of three aromatic ring repeating units connected by two ether groups and one carbonyl group. PEEK has excellent mechanical properties, for example, creep resistance, low water absorption and high fracture resistance. It has been proposed as a functional and esthetic metal-free material in various dental applications, such as implants, temporary abutments, orthodontic wires, removable prostheses and fixed prostheses. Veneering resins are recommended to cover the underneath grayish and opaque color of PEEK-based restorations to mimic the natural tooth appearance. However, PEEK has an inert hydrophobic surface and low surface free energy resulting in poor adhesion properties between PEEK and resin composite materials.

Surface pretreatments of PEEK prior to adhesive bonding have been investigated and demonstrated the improvement of bond strength between PEEK and resin composites. It has been reported that sulfuric acid etching when used with resin cements exhibited greater shear bond strength (SBS) than hydrofluoric acid, argon plasma, air abrasion (50–110 µm) and silica coating. Most studies recommended the use of 98% sulfuric acid to modify chemical and physical surface of PEEK to improve bonding. Previous studies revealed that sulfuric acid created sulfonate groups in the polymer chains of PEEK which chemically cross-linked to methylmethacrylate (MMA) dental adhesives. Another study did not found chemical functional groups on PEEK after etching with 98% sulfuric acid for 60 s, but confirmed micromechanical bonding due to penetration of resin tags into pit and porous surface of PEEK.

The use of 98% sulfuric acid has been questioned to be used under clinical condition due to its strong oxidizing property. High porosities and rough surfaces on PEEK with 98% concentration of sulfuric acid etching have been observed which may negatively affect the penetration of adhesives and resulted in weak points of bond interfaces. The use of low concentration of sulfuric acid etching should be considered. To date, the available information on the effects of the optimal concentrations of sulfuric acid etching to achieve ideal surface properties and bond strength of PEEK is very limited. Therefore, the purpose of this investigation was to determine surface roughness, topography characterization and SBS after varying the concentration of sulfuric acid etching. The null hypothesis was that different sulfuric acid etching concentrations exhibited no significant differences in SBS values.

MATERIALS AND METHODS

Specimen preparation and grouping of PEEK specimens

The materials used in this study are listed in Table 1.
Table 1  List of materials used and their characteristics

| Material                        | Manufacturer                  | Composition                                           | Lot. number |
|---------------------------------|-------------------------------|------------------------------------------------------|-------------|
| Dentokeep                       | Nt-trading, Karlsruhe, Germany | Polyetheretherketone (Ceramic-filled 20%)             | 13DK1801    |
| Autopolymerizing acrylic resin  | Lang, Wheeling, IL, USA        | Methyl Methacrylate  99-97-8 N, N-dimethyl-p-toluidine| 1880-13AA   |
| Sulfuric acid                   | RCI Labscan, Samutsakorn, Thailand | 98% Sulfuric acid                                     | 7664-93-9   |
| HelioBond®                      | Ivoclar Vivadent, Schaan, Liechtenstein | Bis-GMA 60%, TEGDMA 40%                              | R23145      |
| Filtek™ Z350XT Flowable restorative* | 3M ESPE, St.Paul, MN, USA   | Methacrylate resin monomers Bis-GMA, TEGDMA and Bis-EMA; dimethacrylate polymer; silica (75 nm) and zirconia (5–10 nm) nanofiller; approximately 65% wt filler load. | N609237     |

Bis-GMA: bisphenylglycidyl dimethacrylate, Bis-EMA: ethoxylated bisphenol-A dimethacrylate, TEGDMA: triethyleneglycol dimethacrylate.

One hundred and twenty six PEEK specimens (5×5×2 mm³) were sectioned from a PEEK disk with a low-speed diamond saw cutting machine (Isomet® 1000 precision saw, Buehler, Lake Bluff, IL, USA). Subsequently, the PEEK samples were embedded in an auto-polymerizing acrylic resin (Orthojet, Lang Dental Manufacturing, Wheeling, IL, USA) and polished under copious water for 60 s with P400, P800, P1200 and P2000 grit silicon carbide paper (TOA, Samutprakarn, Thailand) in an automatic polishing device (Polishing Machine, MoPao 160E, MEGA Advance, Shandong, China) with vertical force of 25 N to produce a standard surface. All specimens were cleaned in an ultrasonic machine (Transsonic T700, Elma, Singen, Germany) for 10 min and stored in a dry place before surface pretreatment. The specimens were divided into six surface pretreatment groups: control, 70, 80, 85, 90, and 98% sulfuric acid (RCI Labscan, Bangkok, Thailand). Sulfuric acid (100 µL) was applied on 5×5 mm² area of each specimen for 60 s and the specimens were rinsed thoroughly with deionized water for 10 s, then ultrasonically cleaned in distilled water for 10 min and dried at room temperature.

Topographical analysis

Topographical analyses were performed using both a scanning electron microscope (SEM) (JSM-5910LV, JEOL, Peabody, MA, USA) and an atomic force microscope (AFM) (Park XE-70, Park Systems, Suwon, Korea). Three randomly selected specimens (n=3) from each group were gold-sputtered and examined under the SEM. The SEM was operated at 15.0 keV with a working distance of 10.0 mm. Another three specimens were randomly selected from each group and examined using the AFM in contact mode with a diamond tip of 85 nm radius. For each specimen in the etched groups, the AFM scan was carried out in a scanning area of 10×10 µm. Data analysis software (XEI-Image Processing and Analysis, Park XE-70, Park Systems) was used to analyze 3D topographical data.

Surface roughness measurement

The specimens (n=5) were tested with a Profilometer (Surftest-402, Mitutoyo, Kanagawa, Japan) using a stylus gauge, which was set to travel at a speed of 0.1 mm/s with a measuring track of 2 mm. The measurements were performed six times which the distance between parallel tracks was set at 0.5 mm. The mean roughness average (Ra) for each specimen was calculated.

SBS measurement

Unfilled resin material (Heliobond®, Ivoclar Vivadent, Schaan, Liechtenstein) was applied to the remaining specimens (n=10) in each pretreatment group with a single microbrush application. Then, the resin was blown with oil-free air to create a thin layer, and light cured (Elipar® S10 LED curing light, 3M ESPE, St. Paul, MN, USA) (1,000 mW/cm²) for 10 s. Subsequently, a customized split mold cylinder with an inner diameter of 3.0 mm and a height of 2.0 mm was placed on the bonded surfaces. The mold was filled with nanofilled resin composite (Filtek Z350XT® Flowable restorative®, 3M ESPE) and light cured for 40 s. After polymerization, all specimens were stored in distilled water at 37ºC for 24 h before the SBS test. The specimens were positioned in the shearing fixture of a universal testing machine (Instron®5566, Norwood, MA, USA) with the bonded surface parallel to the loading piston. The SBS was tested with a crosshead speed of 1 mm/min until the resin composite cylinder came off. Subsequently, the newton loads at failure were recorded, and SBS values in megapascals (MPa) were calculated following the equation $\sigma = \frac{F}{A}$, where $\sigma$ is the SBS, $F$ is the load at failure (in N) and $A$ is the adhesive area (mm²).
Comparison of the cross-sectional image of the interface layer between PEEK and a composite resin

Three samples of each group after bonding with HelioBond® and Filtek Z350XT™ Flowable restorative® were randomly selected for the cryofracture test. The samples were frozen with liquid nitrogen for 10 min and cleaved to produce a sharp break at the cross-section interfaces. All samples were gold-sputtered and examined under SEM.

Failure analysis

The de-bonded area was examined with a stereomicroscope at 50× magnification. Four failure types were considered: 1) Adhesive failure mode between PEEK and the resin composite, 2) Cohesive failure mode within PEEK, 3) Cohesive failure mode within the resin composite, 4) Mixed failure mode within PEEK and the resin composite.

Statistical analysis

The Shapiro-Wilk test was used to test the normality of data distribution. The roughness and SBS were analyzed using the One-way ANOVA and Tukey’s post hoc tests (SPSS version 17.0, Chicago, IL, USA). The statistical significance level was set at an alpha level of 0.05.

RESULTS

SEM evaluation

SEM images at 20,000× magnification are shown in Figs. 1 (A.1–F.1). The control group demonstrated a plain, smooth and homogenous surface (Fig. 1 (A.1)). The samples etched with 70 and 80% sulfuric acid etching displayed irregular surfaces of filler particles and small pits (Figs. 1 (B.1) and (C.1)). Those etched with 85 and 90% sulfuric acid displayed large pits and pores (Figs. 1 (D.1) and (E.1)). Sponge-like porous and complex fiber networks were distributed throughout the surfaces etched with 98% sulfuric acid (Fig. 1 (F.1)).

AFM evaluation

AFM images are shown in Figs. 1 (A.2–F.2). In the control group, the PEEK surface was relatively smooth, with irregular striations from the polishing procedure (Fig. 1 (A.2)). PEEK surfaces etched with 70 and 80% sulfuric acid showed uniform pits and pores, revealing rougher surfaces than did the control group (Figs. 1 (B.2) and (C.2)). Etching with 85 and 90% sulfuric acid created large width and depth of craters (Figs. 1 (D.2) and (E.2)), while the 98% sulfuric acid etching did not show complex fiber networks but smooth and highly sub-surface corrosion. This was due to the limitation of the size of the nano-stylus tip (Fig. 1 (F.2)).

Surface roughness

The mean surface roughness values are summarized in Table 2. The control group significantly showed the lowest surface roughness. The 98% sulfuric acid group revealed the highest surface roughness but was not significantly different from the 80, 85 and 90% sulfuric acid groups.

SBS after 24 h water storage

Significant differences in SBS values were observed among the experimental groups (Table 2). The 90 and 98% sulfuric acid group showed higher SBS values than the other groups (p<0.05).

Cross-sectional observations

The interface layers in cross-sectional view were examined using the cryofracture technique and were observed under SEM at 1,000×, 3,000× and 5,000× magnification (Fig. 2). The interfaces could not be detected in the control group because of the failures at the cross-section interfaces during specimen preparation. Resin tags were found in the 80, 85, 90 and 98% sulfuric acid groups (Figs. 2-B.1–3, C.1–3, D.1–3, E.1–3, and F.1–3). Resin tags were not found in the 70% sulfuric acid group (Figs. 2-A.1–3).

DISCUSSION

This study evaluated the influences of different concentrations of sulfuric acid etching on surface properties on adhesion between PEEK and a resin composite. Increased concentrations of sulfuric acid etching showed the increase in SBS with the highest values in the 90 and 98% sulfuric acid groups. Therefore, the null hypothesis was rejected.

Sulfuric acid etching is the method aimed to achieve good surface properties of PEEK for bonding. The application of 98% sulfuric acid etching for 60 s in this study showed almost the same SBS as the previous study19 which employed the same protocol. This SBS exceeded other surface pretreatment such as the piranha solution11,19 and sandblasting18-20. In addition, the 80, 85 and 90% sulfuric acid etching in this study also improved the SBS of etched PEEK to resin composite. The 80% sulfuric acid groups showed significantly increase SBS values which were similar to that of piranha etching in a previous study19. While the 70% sulfuric acid etching did not improve SBS.

It seems that micro-topographical changes of PEEK surface after sulfuric acid etching enhanced the penetration of the resin adhesive, resulting in the increased SBS as demonstrated in Fig. 2. The effect
Fig. 1 Representative images of PEEK surface under AFM and SEM.
A: Control group, B: 70% sulfuric acid group, C: 80% sulfuric acid group, D: 85% sulfuric acid group, E: 90% sulfuric acid group, F: 98% sulfuric acid group, 1: SEM magnification 20,000×, 2: AFM
Fig. 2  Cross-sectional SEM images of the treated layer at the interface between PEEK (P) and resin materials (R) in each pretreatment group. A: 70% sulfuric acid group, B: 80% sulfuric acid group, C: 85% sulfuric acid group, D: 90% sulfuric acid group, E: 98% sulfuric acid group, 1: Cryofracture technique 1000×, 2: Cryofracture technique 3000×, 3: Cryofracture technique 5000×, Arrow: Resin tag, R: resin, P: PEEK
Table 2  Mean (SD) of surface roughness and SBS values

| Group               | Surface roughness (µm) | SBS (MPa)   |
|---------------------|------------------------|-------------|
| Control             | 0.04 (0.02)\(^1\)     | 1.75 (0.66)\(^A\)|
| 70% Sulfuric acid   | 0.18 (0.04)\(^2\)     | 1.37 (0.43)\(^A\)|
| 80% Sulfuric acid   | 0.44 (0.12)\(^3\)     | 17.47 (2.15)\(^B\)|
| 85% Sulfuric acid   | 0.57 (0.08)\(^3\)     | 21.53 (5.97)\(^BC\)|
| 90% Sulfuric acid   | 0.62 (0.05)\(^3\)     | 26.68 (4.07)\(^C\)|
| 98% Sulfuric acid   | 0.74 (0.25)\(^3\)     | 27.36 (3.95)\(^C\)|

Different numbers indicate that surface roughness values were significantly different at \( p<0.05 \). Different capital superscript letters indicate that SBS values were significantly different at \( p<0.05 \).

Table 3  Percentages of each failure mode in different concentrations of sulfuric acid etching

| Pretreatment methods | Mode of failure |
|----------------------|-----------------|
|                      | Adhesive between PEEK-resin materials | Cohesive within PEEK | Cohesive within resin materials | Mixed |
| Control              | 100             | 0               | 0                             | 0      |
| 70% Sulfuric acid    | 100             | 0               | 0                             | 0      |
| 80% Sulfuric acid    | 100             | 0               | 0                             | 0      |
| 85% Sulfuric acid    | 70              | 0               | 0                             | 30     |
| 90% Sulfuric acid    | 30              | 0               | 0                             | 70     |
| 98% Sulfuric acid    | 0               | 70              | 0                             | 30     |

Fig. 3  SEM images of the failure modes at the de-bonded PEEK surfaces.
A: adhesive failure mode between PEEK and resin materials, B: mixed failure mode, C: cohesive failure mode within PEEK

of increase concentrations of sulfuric acid etching demonstrated differences in the alteration of PEEK surface. Differences in irregularity of PEEK surfaces after sulfuric acid etching were due to the dissolution of the PEEK matrix by sulfonation reaction\(^{22-25}\). SEM and AFM clearly demonstrated a tendency of increased surface roughness and irregularities of PEEK which correlated to the increased sulfuric acid etching concentrations (Fig. 2). Low sulfuric acid concentration from adding water into 98% sulfuric acid leads to the changes of chemical equilibrium in diluted sulfuric acid and decreasing degree of sulfonation reaction\(^{24}\). Therefore, the lower concentration of sulfuric acid did not create severe surface corrosion of PEEK surface compared to the higher concentration\(^{25}\). The SBS outcomes of the present study were in accordance with the surface topography and cross-sectional analysis. The bonding mechanism at PEEK-resin interface layers
were investigated using the SEM. The cross-sectional specimen preparations were developed by a cryofracture technique in which the specimens were embedded in liquid nitrogen before freeze fracturing. The benefit of this technique was to minimize the stresses on the specimen during fracturing and to preserve the polymer’s structure. The control group and the 70% sulfuric acid showed the lowest SBS when compared to other concentration groups. The bonding interfaces in the control group were not detectable, due to the complete separation of PEEK and resin during freeze fracturing. This low sulfuric acid concentration created some roughness and the diminutive pits and pores of surfaces which could not promote resin tag penetration. The penetration of micro-retentive resin tags into the etched PEEK surface were found at the interfaces of the samples in the 80, 85, 90 and 98% sulfuric acid groups. These resin tag penetrations confirmed the existence of micromechanical interlocking. High concentration of sulfuric acid promoted deeper and more evident pits and porous surface for bonding, consequently, higher resin tag length and the SBS increased. These finding supported the previous study by Silthampitag et al. that surface topography affected the adhesion due to mechanical bonding. The complex fiber network with porosities of etched PEEK surface with 98% sulfuric acid attributed to the higher SBS than the other groups.

The crosslinking between functional group of etched PEEK and adhesive systems containing MMA was hypothesized to the improvement of bond strength. Chemical etching from sulfuric acid could improve hydrophilicity of the surface by introducing sulfonic acid group (–SO3) into the polymer chains of PEEK due to sulfonation reaction. The 80, 85, 90 and 98% sulfuric acid etching to PEEK might attribute to the increase in number of functional groups which influence on the increased SBS, while the 70% sulfuric acid etching did not improve SBS. This might be due to the increased in water content which reduced the solubility power of sulfuric acid. PEEK was completely soluble in 94.9% sulfuric acid, nearly completely soluble in 89.9% sulfuric acid, and partially soluble in 84.8% sulfuric acid. The degree of sulfonation reaction depending on the concentration of sulfuric acid etching has been reported. Therefore, the application of high sulfuric acid etching (>90%) on PEEK might have significant effect on sulfonation. In addition, high dissolution of PEEK surface resulted in sponge-like and complex fiber network as demonstrated in SEM and AFM might responsible in high SBS in this study.

It seems that sulfuric acid etching with high concentration is an effective surface pretreatment method to increase SBS between PEEK and resin composite. The surface topography is an important factor which shows mechanical bonding due to the penetration of adhesive bonding into pits and porous which results in resin tags. It has been suggested that the low viscosity adhesive systems should be applied to PEEK before covering its surface with veneering resins. The previous study supported the bonding results that etched PEEK surfaces with adhesive have greater SBS than those without adhesive. The larger surface area of etched PEEK with more sulfonic groups which was penetrated by the adhesive which contained MMA might possibly improve bond strength. However, rather to focus on micromechanical bonding, the present study used Heliobond which is the bonding agent based on Bis-GMA and TEGDMA with no additional functional monomer containing contribute to chemical bonding. Therefore, different type of resin adhesive or cements on adhesion strength and possible chemical interaction should also be investigated.

According to various sulfuric acid concentrations, the 90 and 98% sulfuric acid etching with a minimal etching time of 60 s showed the greatest SBS. However, the cohesive failure mode within PEEK was predominately found in the 98% sulfuric acid group. This result implies that the 98% sulfuric acid etching is able to create fiber-like network surface which resin can penetrate and create micromechanical interlocking. It may also imply the destruction of the etched superficial PEEK surface. This might have a weakening effect on PEEK structure and cause bond degradation at the interfaces. The 98% sulfuric acid is a strong concentration which special care in dental laboratories should be provided. Within the limitations of this study, the 90 and 98% sulfuric acid etching concentrations exhibited significantly high SBS. In order to reduce the risk of subsurface degradation and strong oxidizing effects of sulfuric acid etching, a lower concentration should be used for surface pretreatment. The 90% sulfuric acid concentration seems to be the optimal concentration in etching PEEK surface to improve bonding between PEEK and resin composites. Heliobond is suggested to apply on etched PEEK before covering with veneering composites. In addition, long duration of sulfuric acid etching might increase porosities on PEEK before covering with veneering composites. In long term durability of veneered PEEK restorations, further studies should be conducted on the bond strength provided by specific sulfuric acid concentrations with different etching durations and different types of resin composite materials.

**CONCLUSIONS**

Within the limitations of this *in vitro* study, it can be concluded that:

1. Surface pretreatment with 90 and 98% sulfuric acid achieved higher SBS values than the other groups.
2. Surface topography was the major factor influencing micromechanical bonding between PEEK and resin materials. The cryofracture technique was preferred for the cross-sectional analysis.
ACKNOWLEDGMENTS

This study was supported by the CMU Junior Researcher Fellowship Program. The authors thank Dr. Thanapat Sastraruji, Dental Research Center, Faculty of Dentistry, Chiang Mai University, for his assistance in chemical preparation, Surak Udomsom, Biomedical Engineering center, Chiang Mai University, Thailand, for his assistance in surface topographic analysis, and Dr. M. Kevin O Carroll, Professor Emeritus, University of Mississippi School of Dentistry, USA and Faculty Consultant, Faculty of Dentistry, Chiang Mai University, for his assistance in the preparation of the manuscript. We also are thankful for the support from Research Consultant, Faculty of Dentistry, Chiang Mai University, Thailand.

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