The Effect of Surface Pre-Treatments and Dental Adhesives on Shear Bond Strength in Polyetheretherketone (PEEK)

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Abstract

To determine the effects of various surface pre-treatment and dental adhesives on the shear bond strength of PEEK to veneering resin composite.

240 PEEK specimens 5x5x2 mm3 were divided into six groups and subjected to the following treatments (n=40): no treatment, air abrasion, sulfuric acid etching, etching + sodium hydroxide (NaOH), air abrasion + etching, and air abrasion + etching + NaOH. Surface roughness and topography were assessed. Each group of the specimens was classified into 3 subgroups (n=12) according to the adhesive systems: no conditioning, Clearfil™ SE Bond, and HC Primer. Flowable composites were veneered using the metal mold and then deposited in distilled water at 37oC for 24 hours before the shear bond strength test (SBS). The following tests were used to analyze: One-way ANOVA and Dunnett's T3 pos-hoc tests were used to analyze the surface roughness; two-way ANOVA and Dunnett's T3 pos-hoc tests were used to evaluate the SBS data at the confidence interval of 95% ($p<0.05$).

Surface pre-treatment with sandblasting showed the highest roughness ($p<0.05$). Surface pre-treatment and dental adhesive significantly affected the SBS value ($p<0.05$). Surface pre-treatment with air abrasion + etching + NaOH provided significant high SBS value. Conditioning with HC primer demonstrated significant higher SBS value than Clearfil™ SE Bond compared to the same pre-treatment ($p<0.05$).

Among other pre-treatment applications, air abrasion + etching + NaOH pre-treatment exhibited the highest SBS performance, particularly when conditioned with HC primer. Mechanical surface pre-treatment can be used in clinical when combined with HC primer.

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Introduction

Polyetheretherketone (PEEK) is a member of the polyaryletherketone (PEAK) class of semi-crystalline thermoplastics.[1] In the dental field, PEEK with inorganic filler is presently used in dental applications as temporary abutments, removable prosthetic frameworks, and dental implants due to its properties as a biomaterial which made it attractive in the dental field with chemical stability, high melting point, mechanical properties, dimensional stability, and machinability.[2-6] However, PEEK is a chemically inert material and cannot produce the natural color of the tooth or gingiva, leading to the difficulty in surface veneering or cementation bonding. Therefore, several studies have been conducted examining various bonding techniques to improve the adhesion of PEEK to resin composite.[7-12]

According to the previous studies, air abrasion appeared to improve the bond strength by forming an abraded surface while achieving a micro-mechanical anchorage. As a result, this may be used as an initial pre-treatment in clinical applications.[8,13,14] On the other hand, previous studies have indicated that chemical pre-

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treatment, such as sulfuric acid, can improve the bond strength by dissolving surfaces, which creates porosity, and some suggested that this may increase the number of functional groups overlying the PEEK surface.[7,13,15-17] Wang et al. introduced a fast ambient-temperature method to produce sulfonation in PEEK substrate by using a high concentration sulfuric acid in combination with sodium hydroxide solution.[18] This application has not yet been investigated as a bonding property. In addition, previous studies also reported the improvement of the bond strength from the combination of air abrasion and acid etching.[13,15]

Moreover, the dental adhesive systems can enhance the bond strength. Most studies found that methyl methacrylate (MMA)-containing adhesives increased the bond strength when coupled with various surface modifications.[2,13,14,19,20]

However, there is no consensus in the literature on bonding PEEK to resin composite. Furthermore, general knowledge about the potentials and limitations of PEEK is inadequate, and the exact mechanism of adhesion is still unknown. Therefore, this study aimed to evaluate the effect of various surface pre-treatments and dental adhesives on the shear bond strength of PEEK to resin composite. The null hypotheses in this study were that neither surface pre-treatment nor adhesives increased the shear bond strength between PEEK and resin composite.

Materials and methods

Specimen preparation and surface topography

The information of all materials used in this study were shown in Table 1. Two hundred and forty pieces of PEEK 5x5x2 mm^3 were prepared by cutting a PEEK disc with a low-speed diamond saw (Isomet®1000 Precision Saw, Buehler; Illinois, USA). Following that, the specimens were immersed in auto-polymerizing resin. All samples were polished with silicon carbide papers up to 2000-grit with water to standardize the surface, then ultrasonically cleansed for 10 minutes. The specimens were randomly divided into six groups (n=40) based on the types of surface treatment as shown below;

- [C]: No surface pre-treatment as a control group.
- [A]: Air abrasion with 110 µm alumina particles at a distance of 10 mm under 0.4 Mega Pascal (MPa) for 15 seconds, followed by cleaning with a sonicator (Easyclean, Renfert GmbH; Hilzingen, Germany), and a water stream jet cleaner (Streamjet® EV1, Silfradent; Italy).
- [E]: Etching with 90% sulfuric acid (H_2SO_4) for 60 seconds and flushing with de-ionized water for 20 seconds.[16, 17]
- [EN]: After etching with 90% sulfuric acid for 60 seconds and flushing with de-ionized water for 20 seconds, drops of 6%wt Sodium hydroxide (NaOH) solution was covered to the surface for 20 seconds and washed with de-ionized water 20 seconds.
- [AE]: Air abrasion similar to [A] with etching similar to [E].
- [AEN]: As directed by the [AE], flush with a solution of 6%wt NaOH, and washed with de-ionized water 20 seconds.

Surface topography was observed under a scanning electron microscope (SEM; JSM 5910 LV, JEOL; Tokyo, Japan) with gold sputtering on one of each group.

Materials	Manufacturers	Composition	Lot No.
Polyetheretherketone (Dentokeep®)	Nt-trading; Germany	PEEK, 20%	13DK1801
Autopolymerized acrylic resin (Orthojet®)	Lang; Wheeling, Illinois; USA	Methyl methacrylate 99-97-8 N, N-dimethyl-p-toluidine	1880-13AA
98% Sulfuric acid	RCI Labscan Ltd.; Samutsakorn, Thailand	98% Sulfuric acid	7664-93-9
Sodium Hydroxide (Micropearls)	RCI Labscan Ltd.; Samutsakorn, Thailand	>99% Sodium Hydroxide	19080223
Clearfil™ SE Bond	Kuraray; Japan	Primer: Bisphenol A diglycidylmethacrylate, 2-hydroxyethyl methacrylate, 10-methacryloyloxydecyl dihydrogen phosphate, hydrophobic aliphatic dimethacrylate, colloidal silica, dl-camphorquinone, initiators, accelerators Bond: Bisphenol A diglycidylmethacrylate, 2-hydroxyethyl methacrylate, 10-methacryloyloxydecyl dihydrogen phosphate, hydrophobic aliphatic dimethacrylate, colloidal silica, dl-camphorquinone, initiators, accelerators	000051
HC Primer	**SHOFU Dental GmbH;** Ratingen, Germany	UDMA, MMA, Acetone, Polymerization initiator	051808
Flowable resin composite (Filtek Z350XT™ Flowable Restorative®)	3M ESPE, St. Paul, Minnesota, USA	Methacrylate resin monomers, Bis-GMA, TEGDMA, and Bis-EMA; Dimethacylatepolymer; silica and zirconia nanofiller	NA75544

Table 1. Summary of materials in this study.

Surface roughness measurement

Following surface modification, a profilometer (Surftest® SJ-310, Mitutoyo; Kanagawa, Japan) was used to determine the surface roughness (Ra) of three randomized specimens in each sample, and the data was calculated for each of them using three points of single individual measurements (n=9).

Shear bond strength (SBS) measurement and failure analysis

Following surface pre-treatment, each group was classified into three subgroups according to the different adhesive systems (n=12): [-C] No adhesive application, [-P] Clearfil™ SE Bond, and [-M] HC Primer; Fig.1 summarized the groups in this study.

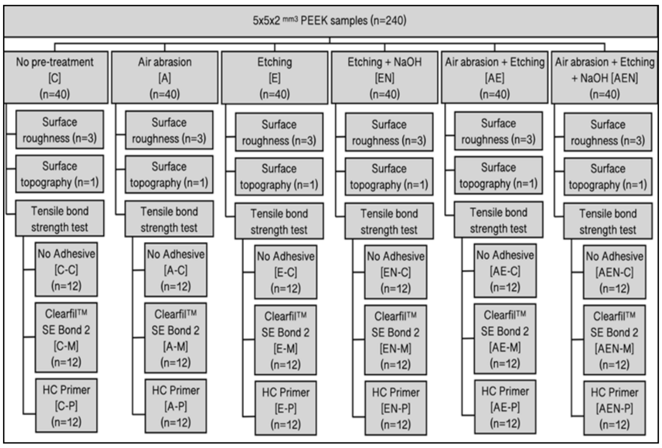


Figure 1. Experimental groups in this study.

After surface pre-treatment, the flowable resin composite was placed in a customized stainless-steel mold with an inner diameter of 3.0 mm and a height of 2.0 mm over the center of the PEEK surface and polymerized per the manufacturer's instructions. All specimens were preserved in distilled water at 37°C for 24 hours prior to the SBS test.

The SBS was measured using a universal testing machine (Instron® 5566, Norwood, Massachusetts, USA) with a crosshead speed of 1.0 mm/min following ISO 29022:2013 and a 500 Newton load cell. Force was applied to the PEEK surface in a parallel direction until debonding occurred. The SBS in Mega-Pascal (MPa) measurement was calculated using the following equation: failure load (N) divided bonding area (mm^2). The failure modes of all detached specimens were investigated using a stereomicroscope (Stereomicroscope; OLYMPUS, Japan) at magnification of 25x.

Composition characterization

In comparison to the control group [C], Fourier-transform infrared spectroscopy (FTIR; Nicolet 6700; Thermo Electron Co., Madison, Wisconsin, USA) was utilized to examine the functional groups in pre-treatment surfaces of [E] and [EN] specimens. Each sample was scanned 32 times in the absorbance modes throughout 4000-400 cm^{-1}.

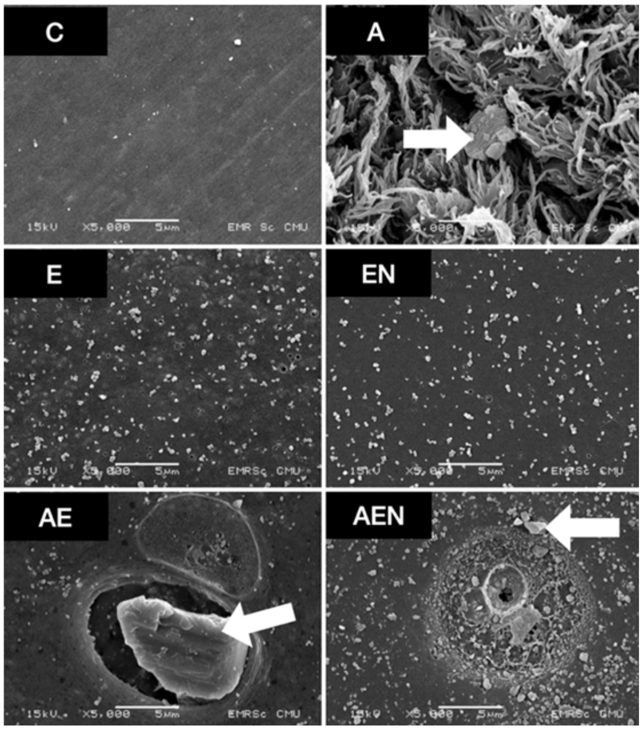


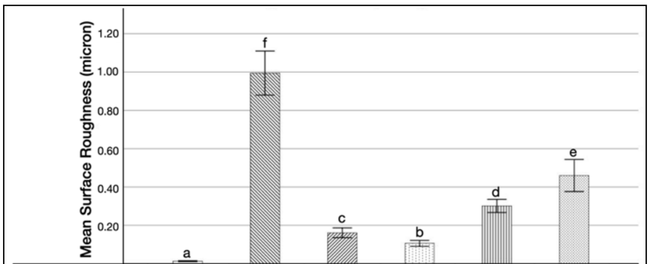
Figure 2. Surface topography of different surface treatment modalities (5000x magnification); [C]: control group, [A]: air-particle abrasion, [E]: Etching, [EN]: Etching + NaOH, [AE]: air-particle abrasion + etching, and [AEN]: air-particle abrasion + etching + NaOH; white arrow represents alumina embedment.

Cross-sectional interfacial analysis via cryofracture technique

Additional eighteen PEEK specimens, size 5x15x2 mm^3, were produced. Before lining up with flowable resin composite, each surface pre-treatment and the dental adhesive system was applied to the PEEK surfaces. The groups were similar to the shear bond strength test. All specimens were subsequently frozen in liquid nitrogen, broken out, and analyzed for sharp interfaces by inspecting through the SEM at a magnification of 3000x.

Statistical analysis

Data is analyzed using descriptive statistics in SPSS version 24.0 (IBM; Armonk, New York, USA). The Kolmogorov-Smirnov test was used to determine the normality of the data distribution. Surface roughness results were analyzed using One-way ANOVA, while two-way ANOVA was used to examine the SBS result. In addition, Dunnett's T3 pos-hoc tests were included (p<0.05). The percentages were used to describe the occurrences of failure modes in each group.



Pre-treated surface	C	A	E	EN	AE	AEN
Mean Ra (µm)	0.01	0.99	0.16	0.11	0.30	0.46
SD	0.00	0.15	0.03	0.02	0.05	0.11

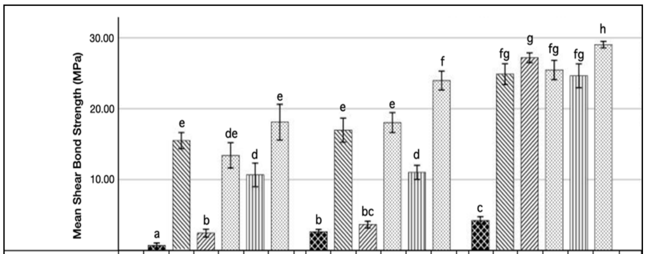
Figure 3. Surface roughness of the different pre-treated surfaces; identical letters indicate statistically significant difference between the experimental groups.

Results

The surface topography was inspected under SEM (Fig.2) at 5000x magnification and demonstrated that surface modifications could alter the surface characteristics; the control group [C] presented a smooth surface, while the etched surfaces [E] revealed circular pits. The spike-like surface was observed when conditioned with alumina air abrasion [A]. In addition, rounded-shaped holed appeared instead of the spike-like character when PEEK was treated with air abrasion combined with etching [AE]. Embedment of alumina particles were found on the surfaces pre-treated with air abrasion. Furthermore, no changes in surface topography were found following NaOH conditioning when comparing [E] to [EN] or [AE] to [AEN].

Surface modification can also increase surface roughness, the values of which are shown in Figure 3. All surface treatments significantly increased surface roughness (p<0.05), with air abrasion alone, providing the highest surface roughness up to 0.99±0.15 µm.

The SBS values are shown in Figure 4. Two-way ANOVA indicated that the surface pre-treatments, dental adhesives, and their interactions significantly affected the SBS value (p<0.05). According to statistical analysis of the SBS value, the pre-treated surface that was combined with air abrasion, etching, and NaOH [AEN] increased the higher adhesion to composite compared to other pre-treated surfaces. In addition, the SBS values were raised in this study when applied HC Primer in pre-treated surfaces.

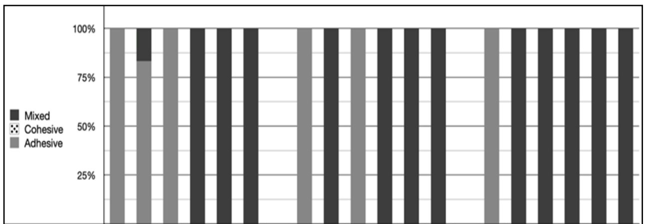


Pre-treated surface	C	A	E	EN	AE	AEN	C	A	E	EN	AE	AEN	C	A	E	EN	AE	AEN
Adhesive	No adhesive [-C]						Clearfil SE [-P]						HC Primer [-M]					
Mean SBS (MPa)	0.70	15.51	2.44	13.42	10.66	18.10	2.65	16.97	3.65	18.05	11.02	23.97	4.22	24.88	27.19	25.47	24.66	29.05
SD	0.56	1.79	0.88	2.81	2.62	3.98	0.53	2.67	0.76	2.22	1.56	2.10	0.84	2.32	1.07	2.13	2.65	0.72

Figure 4. Shear bond strength of the different pre-treated surfaces and adhesive systems to resin composite; identical letters indicate statistically significant difference between the experimental groups.

The highest SBS value observed in [AEN-M] was 29.05±0.72 MPa. Focusing on the pre-treated surfaces in the same adhesive systems, [A] achieved a higher SBS value than either [E] or [AE], and the SBS continued to improve when NaOH was used after etched surfaces [EN, and AEN].

In this study, mixed failures predominated; only six groups were found to have a plurality in adhesive failure, and cohesive failure was not appeared. (Fig.5)



Pre-treated surface	C	A	E	EN	AE	AEN	C	A	E	EN	AE	AEN	C	A	E	EN	AE	AEN
Adhesive	No adhesive [-C]						Clearfil SE [-P]						HC Primer [-M]					

Figure 5. Percentage of each failure modes in the different pre-treated surfaces and adhesive systems to resin composite.

FTIR spectra of [C], [E], and [EN] specimens were shown in Figure 6. When compared to the control surface, the etched PEEK with or without the addition of NaOH ([E] and [EN]) revealed a new peak of absorption band appearing at 1041 cm^{-1}, assigned to the O=S=O vibration.

The cross-sectional interfacial analysis under SEM at 3000x magnification was shown in Figure 7. This study concentrated on the PEEK-resin and PEEK-adhesive interfaces. Tag-like resin penetrations were seen in the pre-treated PEEK surfaces, while polished PEEK surface [C] could not bond with adhesive nor resin composite, as the detached surfaces. In addition, air space were seen in SEM after cryofracture. The circular pits pattern clearly appeared on etched PEEK surface with air trapped in hole, whereas on abraded surfaces, alumina particles were embedded inward the irregular, and fissured surfaces. PEEK-Adhesive interfaced showed that HC primer was able to penetrate pre-treated PEEK surface deeper when compared with Clearfil™ SE bond.

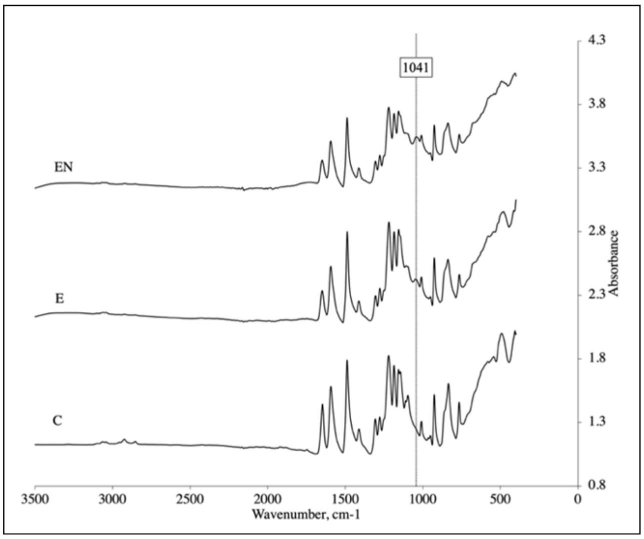


Figure 6. FTIR spectra of [C], etched PEEK [E], and etching + NaOH [EN] PEEK.

Discussion

The results of this study revealed that both surface pre-treatment and adhesive systems could increase the bond strength of PEEK to resin composite. The null hypotheses that neither surface treatments nor adhesive systems affect the SBS between PEEK and resin composite was rejected.

Assessment of the effect of pre-treated surfaces, both mechanical- and chemical-interactions play a vital role in the present study. Alumina air-particle abrasion improved the microroughness on the PEEK surface, while sulfuric etching improved both mechanical interlocking and increasing functional groups overlying on the superficial of PEEK substrate.

Surface roughness was unquestionably regarded as a significant parameter in the dental bonding process.[20,21] Alumina air-particle abrasion is a standard and straightforward procedure used in the dental field for preparing the surface to achieve surface roughness.[(14, 22)]

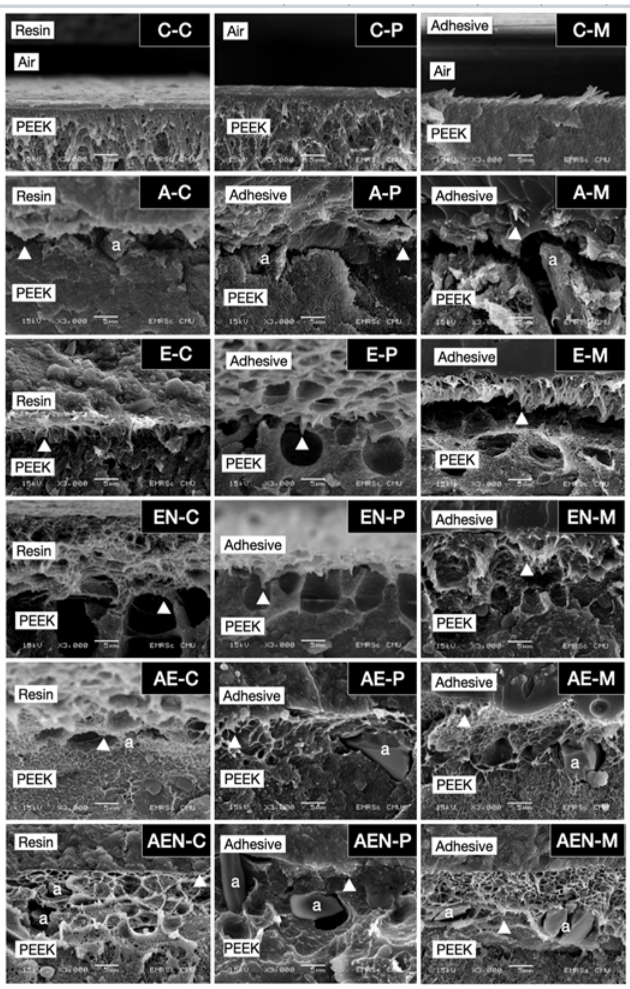


Figure 7. Cross-sectional observation under SEM (3000x) of interfacial layers of each group. (a) identified embedded alumina particles, while arrow heads represented tag-like resin penetrations.

This study found that abraded surfaces using only air abrasion could provide the highest surface roughness. This is in accordance with previous studies, which reported a significant increase in SBS value in abraded surfaces.[5,13,14]

The reason for this improvement was the increasing surface irregularities, which was confirmed by SEM surface topography (Fig.2), facilitating penetration and eventual *in situ* polymerization of the resin along the flaws resulting in micro-mechanical interlocking[1,1315,20].

The observation in this study revealed the penetration of tag-like resin into the PEEK surfaces (Fig.7) in cross-sectional topography.

Prior studies used a high concentration of sulfuric acid to treat the PEEK surface, create porosity by dissolving the amorphous structure, and provide more functional groups through sulfonation.[5,9,11,15,23,24] Wang et al. demonstrated fast-ambient sulfonation, which was validated using FTIR[18], to analyze the chemical structures by determining the relative peak in FTIR spectra correlated with the composition of copolymer.[24]

Following Wang et al., this study found that FTIR analysis of etched-only PEEK [E] and pre-treated PEEK with a combination of sulfuric acid and NaOH [EN] revealed the absorbance peak at 1021 cm^{-1}, which indicated the presence of double bond between sulfur and oxygen. The result indicated the sulfonate functional group (Fig.6) introduced into the polymer backbone, resulting in more functional groups available to bond to the dental adhesive systems. However, in terms of SBS value in this study, the etched-alone PEEK surface had little effect on bond strength even with more significant functional groups capable of bonding overlying the surface, which was similar the previous experiments since the etchant did not produce enough surface roughness.[13,15,25]

When considering surface pre-treatment with a combination of mechanical and chemical processes, the SBS value of surfaces pre-treated with air abrasion and etching appeared higher than when treated with sulfuric alone but lower than when treated with only air abrasion. This result can be explained by the fact that the surface roughness was reduced when the abraded surface was etched.[15] Moreover, this study discovered that when etched-PEEK surfaces were washed with NaOH after being pre-treated with or without air abrasion [EN and AEN], the SBS value increased significantly. The [AEN] surface pre-treatment showed the highest SBS value compared with the other specimen when using the same adhesive application. Previous studies implemented NaOH as a neutralizer for the removal of sulfuric acid residuals.[18,26,27] According to our knowledge, this was the first time the SBS to sodium-salt of sulfonated PEEK was evaluated. Referring to previous arguments, the authors speculate that the SBS value could be affected by the pH of the PEEK surface.

The dental adhesive systems were generally used to facilitate bonding between two substrates. The chemical compositions of the adhesives play an essential role in the effectiveness and long-term stability of the adhesion between PEEK and veneering resins.[2,28] This study examined the various functional monomer components in dental adhesive systems. Clearfil™ SE Bond comprises 10-MDP, while HC Primer contains methyl methacrylate (MMA) and urethane dimethacrylate (UDMA). This study discovered that HC Primer would result in a higher SBS value in all pre-treated PEEK, and that the SBS value was significantly higher than the one that was conditioned with Clearfil™ SE Bond. In addition, the highest SBS value was found in the [AEN-M] group (29.05±0.72 MPa). The MMA-containing adhesive system is the most important factor in increasing the SBS value. Previous studies supported that Visio.link, the MMA-containing adhesive, greatly improved bond strength to veneering composite[5,8,10,13,14,19,20].

This adhesive was also used as a positive control due to its excellent results in many prior studies.[8,13,29] Previous studies described the action of an MMA-containing adhesive in which the MMA monomer swelled the PEEK surface while the dimethacrylate (DMA) monomer contributed the attachment to the veneering resin composite monomer with two carboxyl groups.[13,30,31] However, this study could not compare the SBS value between Visio.link and HC Primer.

Silthampitag et al. introduced cryofracture technique to examine the interface that retains the morphology of polymerized structures by rapidly splitting the specimens after freezing with liquid nitrogen[7]. The SEM of the interface (fig.7) between pre-treated PEEK and Clearfil™ SE Bond in this study showed the air trapped in the pores of the PEEK surface, implying that the tag-like resin did not deeply penetrate. This could explain why no significant difference in SBS value was observed in pre-treated PEEK conditioned by this adhesive system. Furthermore, in accordance with previous findings, dental adhesives containing 10-MDP did not improve the bond strength.[5,8,13,32] From this study, the quality and quantity of tag-like resins are crucial for bond strength to achieve mechanical interlocking between PEEK and composite.

This study reported that the highest SBS value of PEEK to veneering resin composite was obtained by [AEN-P] group; however, this treatment is not recommended to apply in the dental chair-side due to the hazardous from the high concentration of sulfuric acid. According to ISO 10477, the acceptable SBS value between resin-based material and framework is 5 MPa[33]; hence, this study found that most pre-treated surfaces with adhesive application met the ISO 10477 eligibility criteria, except for the [E-P] group. As a result, chair-side surface modifications using air abrasion with alumina and condition with HC Primer are still suitable for optimizing bonding stability of PEEK to veneering composite. Extra caution should be taken if the surface was pre-treated with air abrasion, as alumina particle would potentially interfere with the bonding if the surface had not been thoroughly cleaned before the procedure.[7,8]

However, based on this study, the use of air streaming after air abrasion would eliminate this problem for the most part.

The study of long-term clinical data for artificial aging should be investigated further. Furthermore, the literal comprehension of the chemical relationship between the interfaces, and the development of suitable protocols of the etchant for chair-side application, should be explored.

Conclusions

Within the limitation of this in vitro study:

1. The highest surface roughness in PEEK pre-treated surface was achieved by air abrasion. ($p<0.05$)
2. The SBS of [AEN-P] group was greater than those of the other groups. ($p<0.05$)
3. PEEK surfaces mechanically pre-treated with air abrasion and conditioned with HC primer were acceptable for bonding stability in clinical applications.

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Declaration of Interest

The authors report no conflict of interest.

References

1. Fuhrmann G, Steiner M, Freitag-Wolf S, Kern M. Resin bonding to three types of polyaryletherketones (PAEKs)-durability and influence of surface conditioning. Dent Mater. 2014;30(3):357-63.
2. 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(5):1278-88.
3. Tekin S, Cangül S, Adıgüzel Ö, Değer Y. Areas for use of PEEK material in dentistry. Int J Dent Res. 2018;8:84-92.
4. Siewert B, Plaza-Castro M, Sereno N, Jarman-Smith M. Chapter 20 - Applications of PEEK in the Dental Field. PEEK Biomaterials Handbook: William Andrew Publishing; 2019:333-42.
5. 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(5):465-72.
6. Kurtz SM. PEEK Biomaterials Handbook. 2nd ed. Elsevier Science; 2019:3-9.
7. Silthampitag P, Chaijareenont P, Tattakorn K, Banjongprasert C, Takahashi H, Arksornnukit M. Effect of surface pretreatments on resin composite bonding to PEEK. Dent Mater J. 2016;35(4):668-74.
8. Lümkemann N, Strickstrock M, Eichberger M, Zylla I-M, Stawarczyk B. Impact of air-abrasion pressure and adhesive systems on bonding parameters for polyetheretherketone dental restorations. Int J Adhes Adhes. 2018;80:30-8.
9. Schmidlin PR, Stawarczyk B, Wieland M, Attin T, Hammerle CH, Fischer J. Effect of different surface pre-treatments and luting materials on shear bond strength to PEEK. Dent Mater. 2010;26(6):553-9.
10. Ates S, Caglar I, Duymus Z. The effect of different surface pretreatments on the bond strength of veneering resin to polyetheretherketone. J Adhes Sci Technol. 2018;32:1-12.
11. Chaijareenont P, Prakhamsai S, Silthampitag P, Takahashi H, Arksornnukit M. Effects of different sulfuric acid etching concentrations on PEEK surface bonding to resin composite. Dent Mater J. 2018;37(3):385-92.
12. Schwitalla AD, Bötel F, Zimmermann T, Sütel M, Müller W-D. The impact of argon/oxygen low-pressure plasma on shear bond strength between a veneering composite and different PEEK materials. Dent Mater. 2017;33(9):990-4.
13. Keul C, Liebermann A, Schmidlin PR, Roos M, Sener B, Stawarczyk B. Influence of PEEK surface modification on surface properties and bond strength to veneering resin composites. J Adhes Dent. 2014;16(4):383-92.
14. Uhrenbacher J, Schmidlin PR, Keul C, Eichberger M, Roos M, Gernet W, Stawarczyk B. The effect of surface modification on the retention strength of polyetheretherketone crowns adhesively bonded to dentin abutments. J Prosthet Dent. 2014;112(6):1489-97.

15. Hallmann L, Mehl A, Sereno N, Hämmerle CHF. The improvement of adhesive properties of PEEK through different pre-treatments. Appl Surf Sci. 2012;258(18):7213-8.
16. Somdee J, Silthampitag P, Chaijareenont P. Effects of Sulfuric Acid Surface Pretreatment Duration on Microhardness and Microscopic Morphology of Polyetheretherketone. CM Dent J. 2018; 39(3):91-102.
17. Prakhamsai S, Silthampitag P, Chaijareenont P. Effects of Surface Pretreatment on Polyetheretherketone with Sulfuric Acid on Microhardness and Microscopic Morphology. CM Dent J. 2017;38(3):77-88.
18. Wang W, Luo CJ, Huang J, Edirisinghe M. PEEK surface modification by fast ambient-temperature sulfonation for bone implant applications. J R Soc Interface. 2019;16(152):20180955.
19. 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(3):441-8.
20. 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(1):e342-9.
21. Rosentritt M, Preis V, Behr M, Sereno N, Kolbeck C. Shear bond strength between veneering composite and PEEK after different surface modifications. Cli Oral Investig. 2015;19(3):739-44.
22. 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. Dent Mater. 2014;30(8):e209-15.
23. Huang RYM, Shao P, Burns CM, Feng X. Sulfonation of poly(ether ether ketone)(PEEK): Kinetic study and characterization. J Appl Polym Sc. 2001;82(11):2651-60.
24. Araby R, Attia N, Eldiwani G, Khafagi M, Sobhi S, Mostafa T. Characterization and sulfonation degree of sulfonated poly ether ether ketone using Fourier transform infrared spectroscopy. World Appl Sci J. 2014;32:2239-44.
25. Lee KS, Shin MS, Lee JY, Ryu JJ, Shin SW. Shear bond strength of resin composite to high performance polymer PEKK according to surface treatments and bonding materials. J Adv Prosthodont. 2017;9(5):350-7.
26. Ma R, Wang J, Li C, Ma K, Wei J, Yang P, Guo D, et al. Effects of different sulfonation times and post-treatment methods on the characterization and cytocompatibility of sulfonated PEEK. J Biomater Appl. 2020;35(3):342-52.
27. Jeeranun P, Arksornnukit M, Silthampitag P, Chaijareenont P. Sulfonated PEEK Characteristic after Various Surface Cleaning Techniques. J Int Dent Medical Res. 2022;15(1):131-9
28. Van Landuyt KL, Snauwaert J, De Munck J, Peumans M, Yoshida Y, Poitevin A, Cotinho E, et al. Systematic review of the chemical composition of contemporary dental adhesives. Biomaterials. 2007;28(26):3757-85.
29. Stawarczyk B, Taufall S, Roos M, Schmidlin PR, Lümkemann N. Bonding of resin composites to PEEK: the influence of adhesive systems and air-abrasion parameters. Clin Oral Investig. 2018;22(2):763-71.
30. Schmidlin PR, Eichberger M, Stawarczyk B. Glycine: A potential coupling agent to bond to helium plasma treated PEEK? Dent Mater. 2016;32(2):305-10.
31. Stawarczyk B, Silla M, Roos M, Eichberger M, Lümkemann N. Bonding Behaviour of Polyetherketoneketone to Methylmethacrylate- and Dimethacrylate-based Polymers. J Adhes Dent. 2017;19(4):331-8.
32. Stawarczyk B, Beuer F, Wimmer T, Jahn D, Sener B, Roos M, Schmidlin PR. Polyetheretherketone-a suitable material for fixed dental prostheses? J Biomed Mater Res B Appl Biomater. 2013;101(7):1209-16.
33. ISO 10477. Dentistry–Polymer-based crown and bridge materials. International Standards Organization (ISO), Geneva, Switzerland. 2004.