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Work of adhesion between resin composite cements and PEEK as a function of etching duration with sulfuric acid and its correlation with bond strength values

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ABSTRACT

Objective: This study investigated the impact of sulfuric acid etching duration of PEEK on work of adhesion (WA) with resin composite cements, and compared additionally measured surface parameters to shear bond strength (SBS) results.
Methods: PEEK specimens were fabricated and divided according to different etching times using 98% sulfuric acid ($N=448/n=54$): 0, 5, 15, 30, 60, 90, 120 or 300 s, respectively. The resin composite cements RelyX ARC, Variolink II and Clearfil SA Cement ($N=54/n=18$) were smoothed on a glass plate. The sessile drop method was applied in all contact-angle measurements; distilled water and diiodomethane served as testing liquids. Overall 1350 single contact angle measurements were performed. Thereafter, surface free energy (SFE), WA, interfacial tension (IFT) and spreading coefficient (SC) of all combinations between etched PEEK and resin composite cements were calculated. Data were statistically analysed using Kolmogorov–Smirnov, Shapiro–Wilk tests, descriptive statistics and two-/one-way ANOVA with post-hoc Scheffé test ($p<0.05$). Using Pearson correlation the association between SFE values and SBS results of a previous study was investigated.
Results: Variolink II showed the lowest WA, followed by RelyX ARC and Clearfil SA Cement, respectively. Etching specimens for 60 s showed the lowest WA values while etching times between 0 s and 30 s, and 300 s showed higher results. WA values for groups etched for 90 s and 120 s showed no differences when compared to the 60 s groups. SFE and disperse percentage showed a positive correlation with SBS. A negative correlation was observed between SBS and polar percentage for etched PEEK, WA, IFT and SC.
Conclusions: The WA values do not allow statements about the bond between two materials to be made; other parameters must be taken into account. A waiver of conventional bond test methods is not possible.

1. Introduction

Along with the rise in expectation of the functional and aesthetic aspects of dental restorations in the last years, alternatives to existing polymeric materials have been explored. Among them, the high-performance polymer Polyetheretherketone (PEEK) [1,2] is currently being intensively analysed in the dental field [3].

Although the molecular chain structure is rather rigid, thermoplastic PEEK material is a surprisingly load-bearing material and able to compensate large deformations in both uniaxial tension and compression and can withstand the high compression loads and conditions up to 1383 N (with a plastic deformation starting approximately at 1200 N). It therefore seems suitable to support crowns and even bridges, as, according to Waltimo et al., maximal bite force values of 909 N were recorded in the molar region [4–6]. In contrast to other polymer materials, however, PEEK has a very inert surface. It demonstrates, for example, a low absorption of water and is highly resistent to organic and inorganic chemicals [1,4]. While being advantageous for some medical conditions, it can lead to problems when bonding to dental materials. Attempts

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to activate the surface have involved surface pretreatments with sulfuric acid, which has already been found to be effective [3,5,7]. Accordingly, sulfuric acid also attacks PEEK carbonyl and ether groups, which may lead to more functional groups and even better crosslinking of polymers [8].

Previous studies assessed sulfuric acid etching as a method of PEEK surface pre-treatment, and found that it led to higher bonding capacity than after pre-treatment using air-abrasion, when adhesives in combination with different composite materials were used [3,5]. The self-etching resin composite cements showed lower shear bond strength (SBS) values irrespective of the pretreatment [3]. However, these studies applied a single etching duration of 60 s only, which was effectively shown to be the minimally required etching time according to intrinsic properties of the composite materials used [7].

Usually laboratory test methods such as shear bond and tensile bond strength are used to determine the quality of an interface, i.e. the force per area required to separate the bond between two materials under investigation, as has been done in the previously mentioned studies [9]. In order to screen new materials, a standardized method allowing for the examined surfaces and agents to be evaluated would be desirable, as it could grant an adequate prediction of the bonding abilities of these materials. The present study therefore aimed to predict prospective bonding qualities suggesting a more theoretical approach. Another objective was to determine potentially relevant alternative parameters to evaluate the relationship between the substrate and the adherend. In order to make comparisons between fundamental and practical adhesion, it is necessary to be able to determine values of work of adhesion (WA), which is usually done via contact angle measurements and the determination of other surface characteristics [10]. The interfacial tension (IFT) is a measure of the tension within newly formed bonds and therefore provides information about the long term bonding properties. It defines the load until the debonding of two substrates takes place. The spreading coefficient (SC) describes the regularity of the initial wetting [11].

Therefore, the following parameters were assessed in this study: Surface free energy (SFE), interfacial tension (IFT), spreading coefficient (SC) and the work of adhesion (WA). This evaluation was based on the assumption that practically any bond strength between two materials largely depends on the roughness and the wetting abilities of the involved substrates and reactants [12].

When a new surface is created, chemical bonds have to be broken, which is a process that dissipates energy. The SFE is a measure of the amount of energy required for modifying the surface of a solid. It is defined, as the work required to increase the area of a substance by 1 cm^2, and thereby characterizes the intermolecular forces on a surface. Materials with strong intermolecular forces, such as PEEK, display high SFE, and thus also show high melting and boiling points [13]. SFE of a solid is comparable to surface tension (ST) of a liquid, but is not as accessible to direct measurements as the latter. It can be determined by measuring the contact angle (CA) formed by a pair of liquids with recognized surface tensions on a defined surface, for example water and diiodomethane [14]. The wettability of a solid surface by a liquid is also estimated by the dimension of the CA; the lower the CA, the higher is the wettability of the surface [15]. The SFE is the sum of the components considering the polar interactions, dispersive forces, hydrogen bridges, acid-base interactions, metallic bondings, etc. [16]. When CA-measurements are performed, the energy that theoretically would have to be expended to detach the drop from the surface can be classified as the so called WA [17].

The objective of this study was to determine the WA between PEEK and resin composite cements after pre-treatment of the PEEK surfaces with sulfuric acid. The first hypothesis was that an increased etching duration would lead to increased WA. The second hypothesis tested whether the WA parameters correlated with the SBS values measured in a previous study.

2. Material and methods

2.1. Specimen preparation

Four-hundred-and-forty-eight specimens ($6 \times 6 \times 4$ mm) were cut out of round Dentokeep PEEK blanks (nt-trading, Karlsruhe, Germany, Lot. No: 11DK14001). PEEK specimens (Table 1) were embedded in self-curing acrylic resin (SCAN-DIA, Hagen, Germany) in a silicone mould (25 mm diameter, SCAN-DIA). The testing surfaces of all PEEK specimens were polished in a standardized manner with rotating silicon carbide paper (SIC) P1200 for 60 s, followed by P2400 for 40 s under constant water rinsing in a polishing machine (Tegramin 2.0, Struers GmbH, Ballerup, Denmark). Afterwards, the specimens were randomly allocated to eight groups containing 54 specimens each, according to the different etching times of 5, 15, 30, 60, 90, 120 or 300 s, respectively. Twenty μl (micropipette, Eppendorf, Hamburg, Germany) of sulfuric acid (98%, CAS 7664-93-9) were applied covering the entire PEEK surface. After the specified interval had elapsed, careful rinsing with de-ionized water was conducted for 1 min. Rinsing was conducted in a consistent motion in the same direction in order to avoid any potential changes of the delicate new surface topography. The control group was left untreated. All specimens were cleaned for 5 min in distilled water in an ultrasonic bath (Ultrasonic T 14, Kearny, NJ, USA) before further processing. The specimens were only placed next to each other, so as to form a single layer, and were not stacked, in order to protect the surface from any morphologic damage. The PEEK surface was carefully air-dried before drop application, and before SEM pictures were taken.

In addition, three different dual-curing resin composite cements (Table 1) were investigated and 18 specimens of each material were fabricated:: RelyX ARC (3M ESPE, Seefeld, Germany), Variolink II (Ivoclar Vivadent, Schaan, Liechtenstein) and Clearfil SA Cement (Kuraray Dental Co. Ltd., Osaka, Japan). The resin composite cements were mixed in a 1:1 ratio using the mixing carpules provided by the manufacturer, smoothed out (approximately 20×20 mm) with a plastic spatula on a glass plate for maximum time of 10 s and were subsequently analyzed during the non-polymerized state.

2.2. Contact angle measurements

To determine the SFE of both, the solid (PEEK), and the adherend (resin composite cements) the drop shape analysis system Easy Drop (Kruess, Hamburg, Germany) was used. The system consisted of a drop-dispensing unit, a sample stage, a light source and a CCD-camera. Via connection to a computer measurements became visualized and it was possible to do further processing of the results.

CA-measurements were performed at room temperature, using the sessile drop method. In accordance with standardized procedure, two different techniques were applied, according to the type of liquid used; the circle method, and the Tangent 1 method [18]. The circle method is applied when a drop (such as diiodomethane) exhibits rather flat angles; a circle fitting is performed to evaluate its contour. Mathematically, the drop shape is adjusted to fit the shape of a circular segment, which means that the entire drop shape can be evaluated. The Tangent 1 method is suitable for drops (such as distilled water) which exhibit a larger angle, and are accordingly fitted with a tangent. A function of the drop profile is fitted to the base near the base line according to the adjusted

Table 1
Summary of materials used, such as brands, manufacturers, compositions and Lot. numbers.

Material	Manufacturer	Composition	Lot. no
PEEK	nt-trading, Karlsruhe, Germany	Ceramic filled (20%) polyether ether ketone	11DK14001
RelyX ARC	3M ESPE, Seefeld, Germany	Bis-GMA, MMA,TEGDMA siliziumdioxide, benzoylperoxide,UV-P, silanised ceramic particles	N199496
Variolink II	Ivoclar Vivadent, Schaan, Liechtenstein	Bis-GMA, TEGDMA, UDMA, dibenzoylperoxide,	Base R35481 Catalyst P84939
Clearfil SA cement	Kuraray Dental Co. Ltd., Osaka, Japan	Bifunctional molecules based on self-adhesive MDP-Monomer (acidic methacrylate)	0057BB

Bis-GMA: Bisphenol A diglycidylmethacrylate, MMA: methyl methacrylate, TEGDMA: triethyleneglycol, dimethacrylate, UV-P: ultraviolet-absorbent: 2-benzotriazolyl-4-methylphenol, UDMA: Urethane-dimethacrylate.

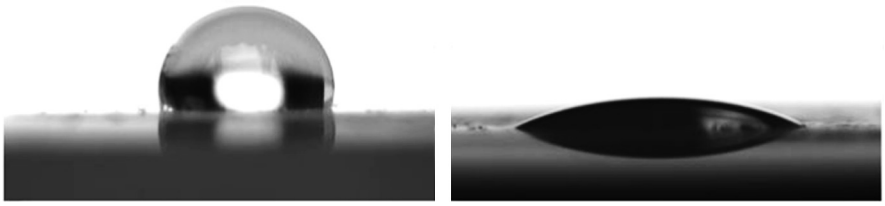

Fig. 1. Different drop topographies of water (left) and diiodomethane (right).

parameters, and to the gradient of the three-phase contact point of the baseline and thereof the contact angle [18].

Each specimen was tested 3 times with distilled water, and 3 times with diiodomethane (CAS 75-11-6, Lot-No. STBC 4546V); this was done separately for each substrate (PEEK and non-polymerized resin composite cements). The specimens were not treated in any way between measurements, as each measurement was performed on a different area of the PEEK and mixed resin composite surface. The mixing process took approximately 10 s. The mixed resin composite cement was kept on the glass plate, and then the process of drop application followed by image capturing began. The image was captured 5 s after drop application. This means that the time between the mixing-start and the capturing of the sixth drop lasted up to one minute. For each specimen and testing liquid, the mean value was calculated. Drop dispensers consisted of a manual double dosing system with 2 glass syringes and were equipped with the needle NE 43 (Kruess) with a diameter of 0.7 mm. Each test drop of water contained 10 μl, while each test drop of diiodomethane contained 5 μl. During the etching process, the 20 μl of sulphuric acid had spread over the entire PEEK surface, due to its low surface tension. In contrast, the 5 μl of diiodomethane and 10 μl of distilled water maintained drop-form maximally changing shape into a hemisphere. In order to standardize the measurements, five seconds after the drop was brought on the specimen surface the image was frozen so as to eliminate possible changes in the drop topography, due to evaporation and blurring. Fig. 1 shows different drop topographies of water and diiodomethane. The CA's of the PEEK surfaces were determined subsequent to the etching, rinsing, and the ultrasonic cleaning process. In order to prevent premature polymerization of the resin composite cements, all measurements were performed in a dark room with a special filter (SCHOTT OG530, Schott, Mainz, Germany) in front of the illuminant.

2.3. Surface properties parameter calculation

The algorithms that were implemented in the DSA4 software allowed determination of SFE (mJ/m^2) with its disperse and polar parts by using the measured CA and the substance characteristics of the testing liquids. Substance characteristics were taken from the system's database, and based on literature values published by the author Ström, Goran [19]. Calculation was performed by means of the Owens–Wendt–Rabel–Kaelble method [20] according to the following equation:

$$\frac{(1+\cos\theta)\,\sigma_L}{(2\sqrt{\sigma_L^D})} = \sqrt{\sigma_S^P}\sqrt{\frac{\sigma_L^P}{\sigma_L^D}} + \sqrt{\sigma_S^D} \quad (1)$$

θ: contact angle, σ_L: ST of liquid, σLD: disperse parts ST of liquid, σLP: polar parts of ST of liquid, σSP: polar parts of SFE of a solid, σSD: disperse parts of SFE of solid.

Surface polarity shows as percentage (%) the proportion of polar parts in relation to the surface free energy in total:

$$\text{Surface Polarity} = \sigma_{\text{polar}}/\sigma_{\text{total}} * 100 \quad (2)$$

Based on the computed SFE of the solid (PEEK-specimens) and the adherent (resin composite cements), the WA (mN/m) between the two possible reactants was calculated using the following formula:

$$\text{WA} = 2\sqrt{\sigma_a^D\ \sigma_b^D} + 2\ \sqrt{\sigma_a^P\ \sigma_b^P} \quad (3)$$

WA=work of adhesion, $\sigma D_{a/b}$=disperse parts of surface energy of reactant a/b, $P_{a/b}$=polar parts of surface energy of a/b.

SC (mN/m) and IFT (mN/m) were calculated as follows:

$$\text{SC} = \text{WA} - 2 * \sigma_S \quad (4)$$

SC=Spreading coefficient, WA=work of adhesion, σ_S=$\text{SFE}_{\text{Solid.}}$

$$\text{IFT} = \text{SFE}_a + \text{SFE}_b - 2 \times \sqrt{\sigma_a^D\ \sigma_b^D} - 2 \times f\sqrt{\sigma_a^P\ \sigma_b^P} \quad (5)$$

IFT=Interfacial tension; SFEa/b=surface free energy of PEEK/composite resin cement, $\sigma_{a/b}^D$=disperse parts of PEEK/composite resin cement, $\sigma_{a/b}^P$=polar parts of PEEK/composite resin cement.

2.4. Surface analysis of etched PEEK specimens

For scanning electron microscopy (SEM) analyses, additional 16 specimens (two of each surface treatment group) were used to determine surface topography. Again, specimens were ultrasonically cleaned, but then gold sputtered (layer thickness: 6 nm). A SEM (Carl Zeiss Supra 50 VP FESEM, Carl Zeiss, Oberkochen, Germany) operating at 10 kV with a working distance of 9 mm was used for the optical evaluation at a magnification of 10,000 ×.

2.5. Statistical analysis

The normality of data distribution was tested using the Kolmogorov–Smirnov and Shapiro–Wilk tests. Descriptive statistics (mean, standard deviation) were computed for the calculated parameters (WA, IFT, SC, SFE). For the determination of significant differences between the tested groups, one- and two-way ANOVA with post-hoc Scheffé test were used. The Pearson correlation coefficient evaluated the effect of the association between pooled mean SBS and SFE, disperse and polar percentage of etched PEEK surfaces and resin composite cements as well as WA, IFT and SC of all tested combinations. P values smaller than 5% were considered to be statistically significant in all tests. The data were analyzed using IBM SPSS (Version 20, IBM Corporation, New York, United States).

3. Results

The Kolmogorov–Smirnov and Shapiro–Wilk tests indicated no violation of the assumption of normality for 87.9% of the tested groups. Only 12.1% were indicated as not normally distributed (14 groups out of 116). As this relative frequency is close to the error of the first kind for a statistical test (probability of incorrectly rejecting the null hypothesis [21]) and none of the groups showed outliers, for all statistical tests, the assumption of normal distribution was used.

Table 2 includes the descriptive statistics of the WA, IFT and SC values for all measured and all calculated material combinations. The table therefore shows values that were both measured physically and some that were calculated.

According to the two-way ANOVA, the etching duration ($p < 0.001$) and the type of resin composite cement ($p < 0.001$) showed a significant impact on the WA, IFT and SC results. Significant interactions between etching time and resin composite cements were also found for all parameters ($p < 0.001$).

In general, WA measured after 60 s of surface etching showed the lowest values. Etching times ranging between 0 s and 30 s as well as 300 s showed significantly higher WA. Calculated WA values for 90 s and 120 s etched groups showed no differences compared to the 60 s groups. For IFT values, PEEK surfaces etched for 300 s showed significantly lower values, followed by the unetched specimens and specimens etched between 5 s and 30 s. The significantly highest IFT was observed for specimens that were etched with sulfuric acid between 60 s and 120 s. Within the SC values, a significant impact of etching time was observed in the following descending order: 90 s and 60 s $<$ 120 s and 15 s $<$ 5 s $<$ 30 s $<$ 0 s $<$ 300 s. Variolink II showed the lowest WA, IFT and SC values, followed by RelyX ARC and Clearfil SA Cement, respectively.

Table 3 illustrates the CA- parameters such as SFE, disperse and polar parts as well as surface polarity values in percentage for differently etched PEEK surfaces and all three resin composite cements. The etching time for these parameters showed a significant impact on the results ($p < 0.001$). Three-hundred s etching and unetched PEEK specimens showed the lowest SFE values, followed by specimens etched between 5 s and 60 s as well as etched for 120 s. The statistically lowest SFE was observed for 300 s etched PEEK specimens. The highest SFE values were noted for specimens etched for 90 s. Specimens etched between 5 s and 60 s and 120 s showed no statistical differences. PEEK etched for 300 s showed the lowest disperse percentage, followed by unetched PEEK. The highest polar percentages as well as surface polarity was observed for surfaces etched for 300 s, followed by unetched surfaces, and surfaces etched for 15 s.

Table 2
Calculated mean values of the material combinations – etched PEEK surface and resin composite cement – with standard deviation (SD) of WA, IFT and SC values.

	Etching duration (s) of PEEK surface	WA (mN/m) Mean (SD)	IFT (mN/m) Mean (SD)	SC (mN/m) Mean (SD)
RelyX ARC	0	100.0 (2.1)^{a}	2.3(1.2)^{ab}	8.3 (0.8)^{c}
	5	100.0 (3.1)^{a}	3.9(2.2)^{bc}	5.2 (2.0)^{ab}
	15	101.6 (2.2)^{a}	2.8 (1.4)^{abc}	5.9(1.1)^{b}
	30	98.8 (2.6)^{a}	4.4 (2.0)^{bc}	5.4 (1.9)^{ab}
	60	97.8 (2.5)^{a}	5.0 (1.7)^{c}	5.3 (1.8)^{ab}
	90	99.4 (3.1)^{a}	5.3 (2.1)^{c}	2.9 (1.6)^{a}
	120	100.4 (4.2)^{a}	3.6 (2.5)^{bc}	5.4 (1.5)^{ab}
	300	100.7 (2.8)^{a}	0.9 (0.3)^{a}	10.5 (2.4)^{c}
Variolink II	0	97.9 (1.3)^{ab}	0.5 (0.5)^{a}	6.3 (1.0)^{cd}
	5	97.9 (1.6)^{ab}	1.9 (1.3)^{abc}	3.6 (1.5)^{ab}
	15	100.4 (4.1)^{*b}	1.0 (1.2)^{ab}	3.8 (1.0)^{ab}
	30	97.5 (1.5)^{ab}	1.4 (1.0)^{*ab}	5.1 (1.2)^{bc}
	60	96.2 (1.2)^{a}	2.9 (0.7)^{c}	3.4 (1.7)^{ab}
	90	98.0 (1.8)^{ab}	2.5 (0.8)^{bc}	2.4 (1.1)^{a}
	120	97.3 (2.7)^{ab}	2.4 (1.2)^{bc}	3.2 (1.0)^{ab}
	300	95.4 (3.1)^{a}	1.1 (0.6)^{ab}	7.7 (2.7)^{d}
Clearfil SA cement	0	105.3 (5.2)^{bc}	9.7 (3.7)^{*b}	11.8(2.5)^{c}
	5	104.0 (4.8)^{bc}	12.0 (3.5)^{bc}	9.0 (2.6)^{bc}
	15	101.1 (4.2)^{ab}	14.2 (3.7)^{cd}	7.4 (3.3)^{ab}
	30	103.6 (3.7)^{abc}	11.7 (3.0)^{bc}	9.9 (2.5)^{bc}
	60	97.9 (2.7)^{a}	17.5 (1.8)^{d}	3.9 (1.3)^{a}
	90	99.9 (2.6)^{ab}	16.5 (2.2)^{d}	4.0 (2.6)^{a}
	120	100.6 (4.4)^{*ab}	14.8 (3.6)^{cd}	6.7 (2.9)^{ab}
	300	108.0 (5.0)^{*c}	4.6 (1.7)^{a}	19.7 (1.9)^{d}

Different letters indicate statistically significant differences between etching durations within one resin composite cement.

* Not normally distributed.

3.1. SEM analyses of etched PEEK surfaces

Fig. 2 shows the surface topography at a magnification of 10,000 × after varying the time periods of sulfuric acid etching. Whereas the unprocessed PEEK specimen surface seemed structured and very smooth, etching for 5 s already led to distinct surface modifications, which could be perceived as a loss of shine by the naked eye. At higher magnifications, the surface irregularities became more apparent: Surface area increased and formed pits and pores. At a magnification of 10,000 ×, a fibre-like network could be observed at all stages of the etching duration. Despite increasing etching duration the overall surface topography

Table 3
Mean values with standard deviation (SD) of SFE, disperse and polar values and surface polarity percentage for PEEK surface and resin composite cements separately.

Etching duration/cement	SFE (mJ/m^2) Mean (SD)	Disperse (mJ/m^2) Mean (SD)	Polar (mJ/m^2) Mean (SD)	Surface polarity (%)
0 s	46.3 (1.4)^{b}	43.8 (1.0)^{b}	2.2 (1.0)^{c}	4.8
5 s	47.3 (1.3)^{cd}	46.2 (1.2)^{c}	1.2 (1.1)^{*ab}	2.5
15 s	47.5 (1.0)^{cd}	46.0 (0.9)^{c}	1.4 (1.2)^{*bc}	2.9
30 s	46.6 (1.0)^{bc}	45.4 (1.0)^{c}	1.2 (1.0)^{*ab}	2.6
60 s	46.5 (1.3)^{bc}	46.2 (1.3)^{c}	0.3 (0.4)^{*a}	0.6
90 s	48.0 (1.3)^{d}	47.6 (1.1)^{d}	0.4 (0.6)^{*a}	0.2
120 s	47.2 (1.5)^{*bcd}	46.1 (1.2)^{c}	1.1 (1.6)^{*ab}	0.2
300 s	44.4 (3.0)^{a}	37.5 (2.8)^{a}	6.8 (1.9)^{d}	15.3
RelyX ARC	56.5 (0.8)^{b}	48.8 (0.4)^{*b}	7.7 (0.8)^{b}	13.6
Variolink II	52.7 (0.8)^{a}	48.3 (0.5)^{a}	4.4 (1.1)^{a}	8.3
Clearfil SA cement	68.4 (2.4)^{*c}	48.1 (0.4)^{a}	19.9 (1.0)^{c}	29

^{abcd} Different letters present significant differences between the etching durations.

* Not normal distributed.

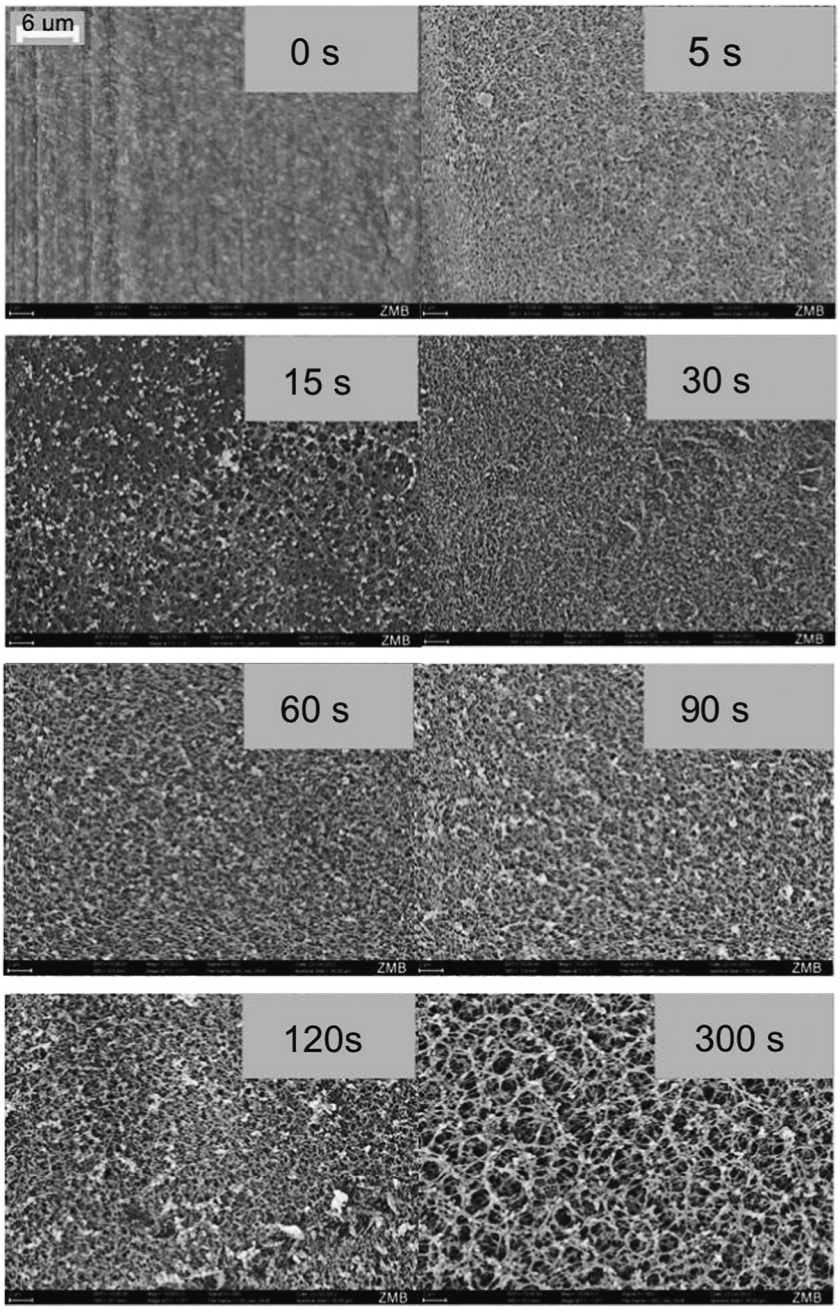

Fig. 2. SEM pictures after different etching durations at a magnification of 10,000 ×.

remained constant, but pits became deeper and wider. Prolonging the etching duration to 90 s and upwards the surface pattern became even more dispersed. An etching period of 300 s led to a distinct dissolution of the PEEK substrate, as a lot of the surface structure was etched away and therefore appeared dissolved.

3.2. Correlation between the theoretical and practical data

In comparison with the results of the SBS-evaluation, [7] only SFE and disperse percentage showed a significant positive Pearson correlation with SBS (SFE: $r^2=0.229$, disperse percentage: $r^2=0.393$, both $p<0.001$). In contrast, a negative correlation was observed between SBS values and polar parts for etched PEEK surfaces ($r=-0.371$, $p<0.001$), WA ($r=-0.203$, $p<0.001$), IFT ($r=-0.11$, $p=0.029$) and SC ($r=-0.411$; $p<0.001$).

4. Discussion

The most frequent reason for loss of a dental restoration is the failure of the bonding between the cement and the restoration, which may lead to secondary caries formation. Therefore an efficient adhesion is a clinical prerequisite, which is tested in general using bond strength models such as shear-bond evaluations [22]. However, these tests also have their limitations and thus, a physical screening of new materials would be desirable. As a model to assess this approach, the present study investigated the impact of different etching durations on the WA between etched PEEK surfaces and resin composite cements. The first hypothesis stated that an increased etching duration would lead to increased WA, which would allow for – at least conceptual – comparisons between fundamental and practical adhesion.

However, this hypothesis had to be rejected, as no straightforward tendencies in WA depending on etching time could be found. As the results showed, prolonged etching duration did not automatically increase WA as expected. Thus – at first sight – the rationale and the results do not seem justified. However, different previous studies have already shown that roughening the PEEK surface leads to higher bond strength values [3,5,7,8], therefore one would also expect an increase in WA. Thus, it remains unclear why 30 and 300 s of etching duration showed higher WA-values than 60 s, 90 s and 120 s.

It must be acknowledged that information on WA-values in dental studies is still scarce. Asmussen and co-workers examined the WA between resin composite cements and differently treated post surfaces and finally also had to admit that their work was based on a number of theoretically sound assumptions, that could be only partly be validated, which corroborates our conflicting results [12]. They found that the bond strength significantly correlated to the disperse parts of WA but not to the polar parts and overall WA. They explained their findings with the fact, that the polymerized surface of the adhesives, on which the surface energy characteristics were determined, might be different from the polymer that forms the interface between adherend and adhesive. Another finding of the study was that there was no straightforward relation of CA, surface energy characteristics and bond strength values [12].

Della Bona and co-workers found that a higher WA was observed when the SFE of the resin cement was higher than the SFE of the substrate [23]. Therefore all surface parameters must be taken into consideration, whereas a focus on individual values indeed may only lead to false assumptions.

The second hypothesis tested whether the WA parameters correlated with the SBS values measured in a previous study. This study was conducted by the same investigators in the same laboratory, using the identical materials and Lot. numbers [7].

It was tested whether the WA values obtained before bonding and SBS-testing, correlated with the SBS values obtained later on. This hypothesis had to be partially rejected, because – despite positive correlations between SBS and disperse percentage – a negative correlation was detected between SBS and polar percentage, WA, IFT, SC and the resin composite cements. The resin composite cements which showed highest SBS displayed the lowest WA, IFT, and SC.

In this context, some additional explanations should be taken into consideration again: Whereas WA describes the short term binding characteristics of the substrate/cement-system, the IFT is a measure for the tension between the new binding and serves as a factor of long term conduct [11]. The SC additionally determines the regularity of the initial wetting [11]. A previous study found that WA values above 65 mN/m, IFT values below 1-2 mN/M and SC values above 8 mN/m led to durable bonding properties [11]. However, the present study confirmed these statements. The highest SBS values were observed in combination with WAvalues above 65 mN/m.

The IFT between composite resin composite cements and the differently etched PEEK surfaces ranged from 0.5 to 2.9 mN/m for Variolink II, from 0.9 to 5.0 mN/m for RelyX ARC and from 4.6 to 17.5 mN/m for Clearfil SA Cement. This complies with the proposed optimum, as Variolink II displayed the lowest IFT of the three tested substrates, and also showed the highest SBS-values. In general it can be said that the higher the interfacial tension (IFT) is, the lower one would expect the SBS- values to be. In contrast to this correlation, IFT values showed a direct proportionality to SBS values; that is, they were found to increase with increased etching time, and then after reaching a peak, began to decrease again. Differences in surface polarity also have a major impact on the IFT: the two examined substrates (PEEK/resin composite cements) should be approximately equal in their surface polarity; the smaller the difference between the two is, the higher the WA, the higher the SC, and therefore the smaller the IFT is [11]. The trajectory of the IFT may be explained by the change in surface topography during etching; as the etching duration increased, more of the PEEK surface was exposed. This might have raised the surface polarity and thus have increased the interaction with the resin composite cements, and thereby have led to an increase in IFT. After the peak was reached, too much surface substrate was etched away, leaving greater interstices in the surface, causing positive interactions to abate.

Upon inspection of the SC-values, it becomes evident that Clearfil SA Cement, which demonstrated lowest viscosity during processing, spreads best (SC: 4- 20 mN/m), followed by RelyX ARC (SC: 5-10 mN/m). Variolink II was found to be more viscous, and accordingly only reached SC values from 2.4 to 7 mN/m. This corroborates findings from literature that good spreading takes place when SC values above 8 mN/m are reached [11]. The strikingly high SC-values of PEEK etched for 300 s might be explained as follows: after such a long etching duration surface structure is highly dissolved (Fig. 2). This makes it easier for the adherent to penetrate into the pores, but also means that the surfaces are weakened and therefore SBS values are decreased.

However, more factors such as the polymerization process, the oxygen inhibition layer, physical forces, and chemical bindings must be considered. Although measurements were performed in a darkened room with a special filter in front of the illuminant, in order to prevent premature polymerization of the resin composite cements, polymerization may have already begun. This could be of relevance, as on the one hand wetting and compound to the solid (etched PEEK-specimens) also takes place in the non-polymerized state (clinical relevance) and on the other hand the oxygen inhibition layer, which originates during polymerization, might change surface parameters. It also has to be considered that physical forces are not the only interactions that take place in adhesive joints. Rather roughness and mechanical interlocking seem to have a great influence on SBS values [24]. These factors are not recognized in the SFE-parameters. Therefore the results of the present study are in contrast with the common expectations that a roughly etched surface helps to provide more surface energy, [15] and thereby a higher WA. A further limitation of this study was the cleansing process of the PEEK surfaces after etching. Although rinsing of the surface was conducted in a standardized manner, it may still have led to variations in the surface topography. Future studies should consider these points.

Furthermore, it is difficult to reconstruct which chemical bindings, on a molecular level, have been constructed between the resin composite cements and the activated acid etched PEEK surface. Unfortunately, no comparison with other dental materials can be made, as no other studies dealing with SFE values of PEEK were identified. It can be stated that through the large number of specimens per testing group ($n=54$) the results of this study achieved high reliability.

5. Conclusion

Within the limitations of this study, it can be concluded that SBS values cannot be directly compared to SFE-Values. Furthermore, wetting and adhesion processes cannot be characterized by contact angle measurements or WA only. The complexity of interaction and balance between wetting, spreading, WA and IFT as well as SFE with its polar and disperse parts have to be considered. Chemical and mechanical processes must also be taken into account. Therefore, a waiver of conventional bond test methods is not possible, but more research on this topic is needed.

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