Journal of
Composites Science

MDPI

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An Explorative Evaluation on the Influence of Filler Content of Polyetheretherketone (PEEK) on Adhesive Bond to Different Luting Resin Cements

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Abstract: Polyetheretherketone (PEEK) is considered one of the most innovative prosthetic materials of the last few decades. Its chemically inert behavior and high biocompatibility make it a promising material in many areas of dentistry. The aim of this study was to test whether PEEK with different TiO_2 filler contents achieves comparable bond strength values when using different resin cements. N = 70 PEEK samples each with different TiO_2 filler content (20 wt.% TiO_2 vs. 5 wt.% TiO_2 vs. no filler as a control group) were divided into seven groups and cemented with various conventional (ResiCem, RelyX Ultimate, Variolink Esthetic DC) and self-adhesive resin cements (RelyXUnicem 2, Bifix SE, Panavia SA Cement Plus, SpeedCem). The shear strength of the bond was assessed after 24 h and after 25,000 thermal loading cycles. Mann-Whitney U and Wilcoxon tests were used for statistical analysis (significance level: $\alpha = 0.05$). PEEK without filler showed the highest mean shear strength (24.26 MPa using RelyX Ultimate), then high-filled PEEK (22.90 MPa using ResiCem) and low-filled PEEK (21.76 MPa using RelyX Ultimate). Conventional resin cements generally achieved slightly higher adhesive strengths than self-adhesive resin cements. It appears that the filler content does not affects the adhesive bond strengths.

Keywords: biocompatible materials; dental materials; Polyetheretherketone; PEEK; adhesive bond; luting resin cements; shear bond strength; TiO_2 filler content

Citation: Dederichs, M.; Lackner, O.; Kuepper, H.; Decker, M.; Viebranz, S.; Hennig, C.-L.; Guentsch, A.; Kuepper, C. An Explorative Evaluation on the Influence of Filler Content of Polyetheretherketone (PEEK) on Adhesive Bond to Different Luting Resin Cements. *J. Compos. Sci.* **2023**, *7*, 456. https://doi.org/10.3390/jcs7110456

Academic Editors: Rodolfo Reda and Dario Di Nardo

Received: 19 September 2023
Revised: 13 October 2023
Accepted: 31 October 2023
Published: 2 November 2023

1. Introduction

Due to its outstanding mechanical as well as biocompatible properties polyetheretherketone (PEEK) appears to be an interesting material for use in the oral cavity not only because of the growing desire of patients for metal-free dental restorations but also as an alternative material for patients suffering from metal allergies [1,2]. Thus, the areas of application in dentistry quickly expanded beyond the use of temporary restorations. PEEK is increasingly under investigation for all areas of prosthodontics, from removable denture bases [2,3], bar and telescope technology [4–7], to fixed dental prosthesis such as temporaries [8], crown or bridge restorations [9,10]. In orthodontics it could be considered as an alternative to NiTi archwires [11] or retainers, especially in cases where the retainer is also used to replace missing teeth [12]. Furthermore, PEEK is of interest as an alternative material to be used in implant dentistry for healing abutments [13–15], temporaries [16], abutments for fixed dental prosthesis, and attachments [17]. The constantly growing number of potential indications makes PEEK one of the most innovative polymers in the field of dentistry.

The processing methods in dental laboratories are currently based on thermoplastic forming processes, in which frameworks are pressed from PEEK pellets or granules, or on subtractive CAD/CAM manufacturing, in which the frameworks are milled out of blocks or blanks [9,14]. PEEK-based materials for 3D printing of frameworks have also been introduced recently [7,18,19]. The stability of the PEEK framework depends not only on the design of the framework but also on the filler content. Titanium oxide (TiO_2) is the filler of choice for dental applications and has been shown to increase modulus of elasticity, hardness, and flexural strength [20–22]. It is reported that TiO_2, on the one hand, positively influences the crystallization of the PEEK network and, on the other hand, enables a secure incorporation into the PEEK matrix due to its active surface [20]. Confirming this findings, an in vitro study reported that 4-unit fixed PEEK restorations with 30% TiO_2 filler content achieved higher fracture resistance than restorations with 20% TiO_2 filler content [23]. In addition, TiO_2 reveal an antibacterial effect, which supports oral tolerance [21,24].

The favorable biomechanical properties are largely a result of the structure within the PEEK network, which is composed of crystalline and semi-crystalline structural regions, resulting in high temperature resistance and low solubility. However, as a disadvantage of the semi-crystalline structure, PEEK has a grayish opaque appearance. Due to the complete lack of translucency, fully anatomically fabricated PEEK frameworks are unsuitable for the use in aesthetically demanding areas. Modifications to the material via the addition of fillers and colorants lead to a tooth- or gingiva-like coloration but still lack translucency [7,25]. Thus, in order to provide favorable mechanical properties in aesthetically demanding areas, the veneering technique can be applied [26]. By using aesthetic composites or even PMMA veneers, the indications for using PEEK materials could be further extended [25]. In addition, the veneering of PEEK frameworks can improve the fracture load and thereby its longevity [23].

To create long-lasting dental restorations, a sufficient adhesive bond between PEEK and veneering or luting composite is mandatory. Therefore, various methods for surface conditioning of PEEK are well documented and described. However, it is unclear whether the addition of TiO_2 to PEEK materials may have an impact on the bond strength as described for other fillers like SiO_2 in an experimental PEEK composite [27]. The aim of the present explorative study was a qualitative evaluation of the adhesive bond strength between different PEEK materials and conventional and self-adhesive luting cements, whereby PEEK without filler content was considered as control group. The null hypotheses were that (1) regardless of the used luting resin cement, the choice of PEEK framework material with different TiO_2 filler content has no influence on the achievable adhesive bond strength compared to PEEK without TiO_2 filler content, and (2) there is no difference in achievable adhesive bond strength when using conventional or self-adhesive luting resin cements.

2. Materials and Methods

Specification of the included PEEK test specimens, primer and luting resin cements are shown in Tables 1 and 2. A high filled PEEK, with 20% Titanium oxide (TiO_2) filler content (BioSolution A2/B2, Merz Dental GmbH, Luetjenburg, Germany), a low filled PEEK with 5% TiO_2 filler content (BioSolution GUM, Merz Dental GmbH, Luetjenburg, Germany), and a non-filled PEEK (BioSolution Nature, Merz Dental GmbH, Luetjenburg, Germany) were used. The specimen size (length × width × height) was 20 × 10 × 5 mm. First, the luting surfaces of all specimens were activated according to manufacturer's recommendation by air-abrasion with 110 μm alumina particles (Al_2O_3) for 15 s at 0.4 MPa (4 bar) and a sand blasting angle of 45°. After air-abrasion, specimens were cleaned with compressed air for 3 s at 0.2 MPa (2 bar). Then, SunCera Metal Primer (Merz Dental GmbH, Luetjenburg, Germany) was applied for 20 s on each PEEK test specimen and let rest for 60 s. Composite discs were made from SunCera light curing veneering composite (Merz Dental GmbH, Luetjenburg, Germany). The composite was filled in copper ring molds (5 mm diameter and

2 mm height), followed by 180 s light curing in a Dentacolor XS curing unit (HeraeusKulzer GmbH, Wehrheim, Germany).

Table 1. PEEK materials and Primerused.

Polyetheretherketone			
Material	**BioSolution A2/B2 (High Filler Content)**	**BioSolution GUM (Low Filler Content)**	**BioSolution Nature (Without Filler Content)**
Manufacturer	Merz Dental	Merz Dental	Merz Dental
Elastic modulus (MPa) accord. EN ISO 20795-1	5100	4500	4100
Flexural strength (MPa) accord. EN ISO 20795-1	170	170	164
Vickers hardness acc. EN ISO 6507-1	32 HV 0.2	27 HV 0.2	23 HV 0.2
Filler content	20 wt%	5 wt%	<1 wt%
Filler material	TiO_2, <1% TiO_2 based pigments	TiO_2, <1% iron oxide	–
Batch No.	DC4450R	58635979	44617
Primer			
Material	**SunCera Metal Primer**		
Manufacturer	Merz Dental		
Functional components	phosphonic acid monomer, thiocticacid monomer, acetone		
Polymerization	not required		
Batch No.	041812		
Veneering Composite			
Material	**SunCera light curing crown and bridge composite (A1B)**		
Manufacturer	Merz Dental		
Functional components	Urethane dimethacrylate (UDMA), 2-dimethylaminoethyl methacrylate, organic filler, silicate powder, pigments		
Polymerization	Final light curing 180 s		
Batch No.	091604		

Table 2. Luting resin cements used.

Material	Organic Matrix	Filler	Application	Batch No.
Dual-curing conventional luting resin cements				
ResiCem (Shofu, Kyoto, Japan)	UDMA, TEGDMA, carboxylic-acid monomer, initiators, acetone	Fluoro-alumino-silicateglass	etching, sand-blasting, 4 min autopolymerization	101801
RelyX Ultimate (3M ESPE, Bavaria, Germany)	acrylates, methacrylates	43% inorganic fillers (13 µm)	etching, sand-blasting, light curing (10 s), 6 min autopolymerization	4369035
Variolink Esthetic DC (Ivoclar-Vivadent, Shain, Liechtenstein)	UDMA, methacrylate-monomeres	38% ytterbium-trifluorides (0.1 µm)	etching, sand-blasting, light curing (20 s)	X32304
Dual-curing self-adhesive luting resin cements				
RelyXUnicem 2 (3M ESPE)	acrylates, methacrylates	43% inorganic fillers (12.5 µm)	sand-blasting, light curing (20 s), 6 min autopolymerization	670864
Bifix SE (VOCO, Cuxhaven, Germany)	methacrylate-monomers	70% inorganic fillers	sand-blasting, light curing (10 s), 4 min autopolymerization	1831198
Panavia SA Cement Plus (Kuraray, Tokyo, Japan)	MDP, BisGMA, TEGDMA, hydrophobic aromatic dimethacrylates	40% silanized bariumglass-fillers	sand-blasting, light curing (10 s), 5 min autopolymerization	3UO265
SpeedCem (Ivoclar-Vivadent)	dimethacrylates, acid-monomers	40% ytterbium-trifluorides, silicium-disilicate (0.1–7 µm)	sand-blasting, light curing (20 s), 6 min autopolymerization	X32046

UDMA = Urethane dimethacrylate; TEGDMA = Triethylene glycol dimethacrylate; MDP = 10-Methacryloyloxydecyl dihydrogen phosphate; BisGMA = Bisphenol A-diglycidyl-methacrylate.

The prepared composite discs were removed from the copper rings and luted in the center of the conditioned PEEK specimens. Overall, n = 210 PEEK specimens were prepared. For each PEEK modification (high filler content, low filler content, without filler content) n = 70 specimens were used. For each luting resin cement n = 10 PEEK specimens were prepared. These were divided among three conventional luting resin cements (ResiCem, RelyX Ultimate, Variolink Esthetic DC) and four self-adhesive resin cements (RelyXUnicem 2, Bifix SE, Panavia SA Cement Plus, SpeedCem) (Table 2), resulting in preparation of n = 10 specimens per PEEK group and luting resin cement.

The plane bottom side of the SunCera composite discs were loaded with luting cement and fixed in the center of the PEEK specimens. Luting cement excesses were gently removed with a micro brush.

The prepared specimens were light cured for 180 s in a Dentacolor XS curing unit. After a further 5 min of autopolymerization, the specimens were stored in distilled water at 37 °C for 24 h. After 24 h half of the specimens were subjected to shear testing. The remaining specimens went through 25,000 temperature load cycles between 5 °C and 55 °C with a dwell time of 15 s in each bath in a Willytec Thermocycler, followed by shear testing. The sample preparation procedure is presented in Figure 1.

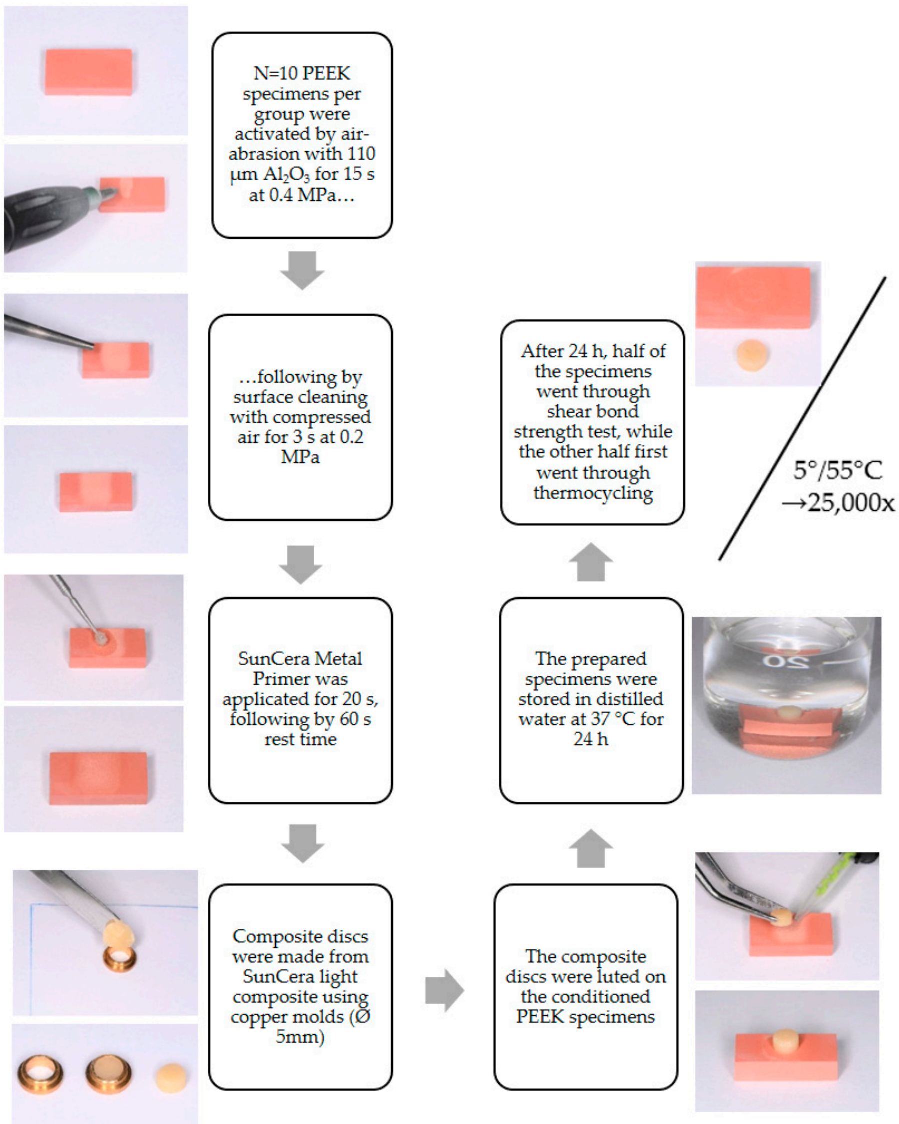

Figure 1. Sample preparation procedure.

Shear bond strength tests were performed by using a Zwick universal testing machine type Z005 (ZwickRoell GmbH & Co. KG, Ulm, Germany) according to ISO EN 10447. The crosshead speed was set to 1 mm/min. Fracture surfaces were evaluated under 20× magnification (Zeiss Axiotech, Zeiss, Jena, Germany) and classified as 'adhesive fracture' if remnants of luting resin cement covered less than 25% of the PEEK specimen's surface, as 'cohesive fracture' if the PEEK specimen's surface was covered more than 75% with luting resin cement remnants after the shear tests, or as 'mixed fracture' if luting resin cement partially remained (covering 25–75%) on the PEEK specimen's surface (Figure 2). To evaluate the surface as well as the morphology of the PEEK specimens, an additional scanning electron micrograph of the air-abraded surface was taken from one material sample of each specimen (Figures 3 and 4).

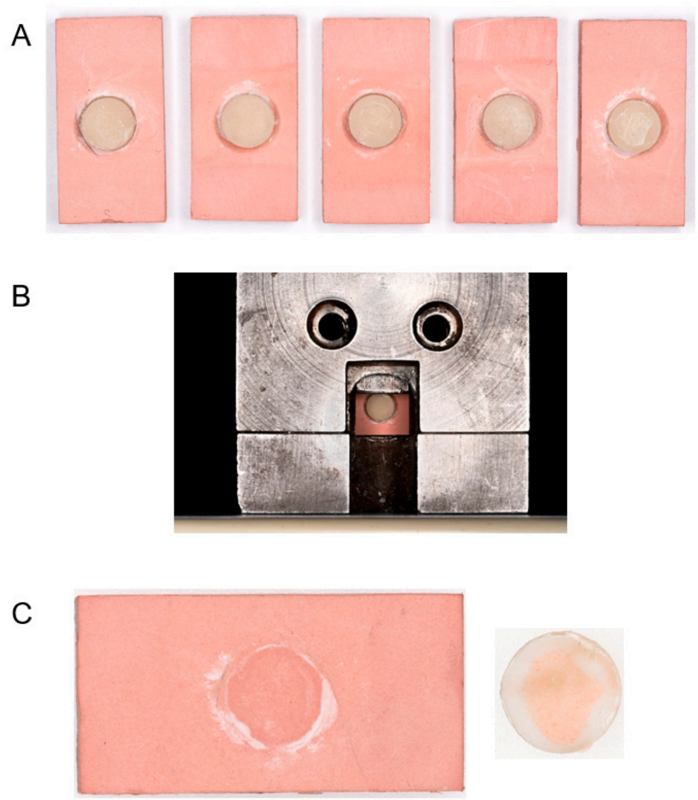

Figure 2. PEEK test-specimens before and after shear-bond-strength test. (**A**) Composite discs were fixed on PEEK specimens according to protocol (Figure 1). (**B**) After 24 h water storage or thermocycling, shear-bond-strength tests were performed. (**C**) Fracture surfaces of PEEK specimens were evaluated under 20× magnification and assessed according to their fracture pattern. (Here: 'adhesive fracture' with less than 25% luting cement remnant on the luting surface of PEEK specimen).

Bond strength values in MPa were collected and statistically analyzed with SPSS Statistics 24.0 (SPSS Inc., Chicago, IL, USA). If prepared specimens did not survive the 24 h water storage or the thermocycling and lost its bond before the shear test, bond strength was set as 0 MPa. The Mann-Whitney-U-test was used to analyze differences between shear bond strength of 24 h values versus values after thermocycling. The Wilcoxon test was used to compare differences between PEEK with different filler contents, as well as to compare differences between each of the luting resin cements. Level of significance was set at $\alpha = 0.05$.

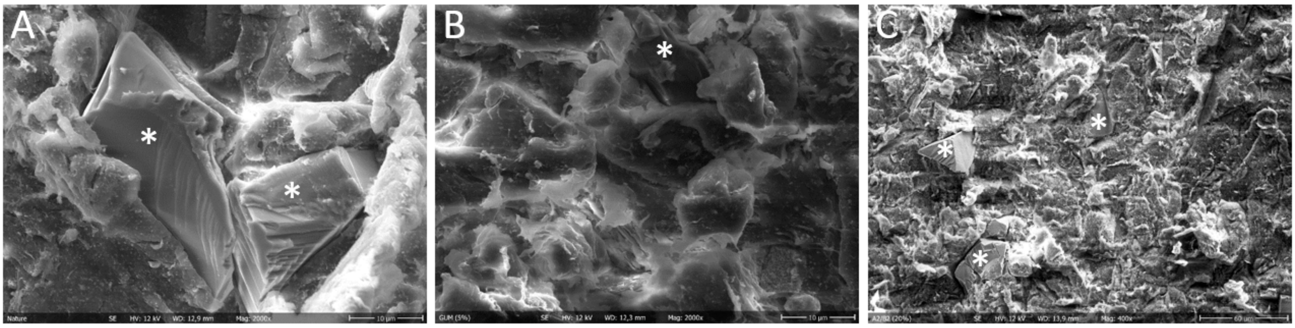

Figure 3. Scanning electron micrographs of the sandblasted PEEK surfaces. Secondary electron projection. (**A**) PEEK without filler content (2000× magnification), (**B**) PEEK with 5% filler content (2000× magnification), and (**C**) PEEK with 20% filler content (400× magnification). Areas marked with an asterisk (*) show residues of the air-abrasion alumina particles (Al_2O_3).

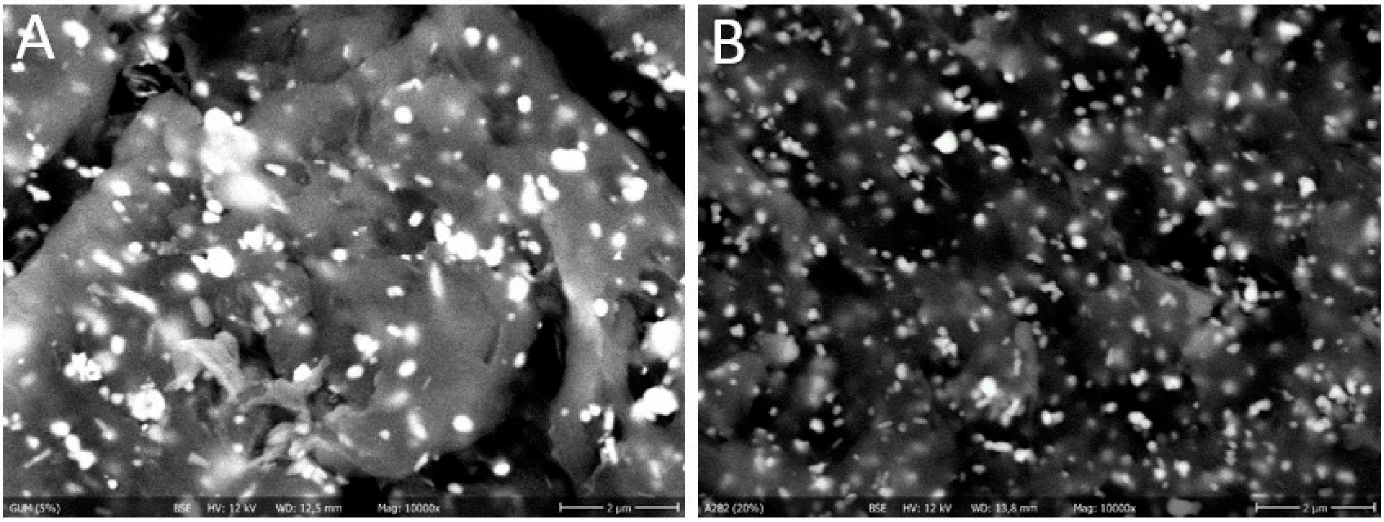

Figure 4. Scanning electron micrographs of the sandblasted PEEK surfaces at 10,000× magnification. Backscattered electron projection. (**A**) PEEK with 5% filler content, (**B**) PEEK with 20% filler content. The TiO_2 filler appears as white spots. A homogeneous distribution of the TiO_2 filler is visible.

3. Results

PEEK specimens with high filler content revealed no significant differences before and after thermocycling. Nevertheless, a slight decrease of mean shear bond strength could be observed after thermocycling. An increase of shear bond strength was only observed with RelyXUnicem 2 (17.02 ± 10.32 MPa to 21.94 ± 4.24 MPa), which could be an effect of n = 1 adhesive failure (0 MPa) in the 24 h-testgroup (Table 3, Figure 5).

Within the low filled PEEK specimens, a significant decrease of shear bond strength after thermocycling was found when using Bifix SE (20.14 ± 2.02 MPa to 15.84 ± 2.59 MPa). Although not significant, most of the other tested luting resin cements slightly lost shear bond strength after thermocycling except the RelyX products, which showed increased bond strengths (but also not significantly different) (Table 4, Figure 5).

Table 3. Shear bond strength values (MPa) of high filled PEEK after 24 h and after thermocycling.

		BioSolution A2/B2 (High Filler Content)				
		Median	**IQR**	**Mean (SD)**	**95%CI**	***p*-Value**
ResiCem	24 h	23.20	6.25	24.58 (3.27)	20.52–28.64	0.548
	thermocyc.	21.50	14.00	22.90 (7.39)	13.73–32.07	
RelyX Ultimate	24 h	22.50	6.40	20.78 (3.64)	16.26–25.30	0.548
	thermocyc.	26.20	20.70	20.56 (12.58) (#1)	4.94–36.18	
Variolink Esthetic DC	24 h	15.70	4.25	16.04 (2.61)	12.79–19.29	0.548
	thermocyc.	14.60	7.35	14.66 (3.92)	9.80–19.52	
RelyXUnicem 2	24 h	19.80	17.25	17.02 (10.32) (#1)	4.20–29.84	0.690
	thermocyc.	21.10	4.24	21.94 (4.24)	16.68–27.20	
Bifix SE	24 h	20.80	3.70	20.44 (2.24)	17.66–23.22	0.222
	thermocyc.	17.40	5.75	17.66 (2.91)	14.05–21.27	
Panavia SA Cement Plus	24 h	17.00	8.65	14.98 (4.55)	9.34–20.62	0.421
	thermocyc.	12.20	10.90	11.12 (6.79) (#1)	2.69–19.55	
SpeedCem	24 h	22.20	3.20	22.48 (1.82)	20.22–24.74	0.151
	thermocyc.	17.50	5.50	19.14 (2.95)	15.48–22.80	

Comparison of shear bond strength after 24 h vs. after thermocycling calculated with Mann-Whitney-U-test. (#[NUMBER]) = Number of specimens that failed before the start of the shear-bond-strength test (MPa = 0). The number after the pound sign indicates the number of adhesive failures within the test series. Adhesive failures were considered in the calculation of mean shear bond strength.

Table 4. Shear bond strength values (MPa) of low filled PEEK after 24 h and after thermocycling.

		BioSolution GUM (Low Filler Content)				
		Median	**IQR**	**Mean (SD)**	**95%CI**	***p*-Value**
ResiCem	24 h	21.00	5.70	22.84 (3.14)	18.94–26.74	0.548
	thermocyc.	20.50	19.35	16.04 (10.85) (#1)	2.56–29.52	
RelyX Ultimate	24 h	18.40	7.80	18.12 (3.99)	13.17–23.07	0.222
	thermocyc.	19.20	7.00	21.76 (4.24)	16.50–27.02	
Variolink Esthetic DC	24 h	19.40	6.80	20.16 (3.92)	15.29–25.03	0.841
	thermocyc.	18.50	6.85	19.64 (3.56)	15.22–24.06	
RelyXUnicem 2	24 h	18.80	6.70	19.92 (4.34)	14.54–25.30	1.000
	thermocyc.	21.90	8.94	20.32 (4.74)	14.44–26.20	
Bifix SE	24 h	20.50	3.00	20.14 (2.02)	17.64–22.64	**0.032**
	thermocyc.	15.90	4.95	15.84 (2.59)	12.63–19.05	
Panavia SA Cement Plus	24 h	12.30	2.55	12.52 (1.31)	10.90–14.14	0.310
	thermocyc.	10.80	5.65	11.30 (3.60)	6.84–15.76	
SpeedCem	24 h	21.50	8.05	21.36 (4.46)	15.82–26.90	0.095
	thermocyc.	16.40	5.45	16.22 (3.28)	12.14–20.30	

Comparison of shear bond strength after 24 h vs. after thermocycling calculated with Mann-Whitney-U-test. *p*-values of significant differences are highlighted in bold. (#[NUMBER]) = Number of specimens that failed before the start of the shear-bond-strength test (MPa = 0). The number after the pond sign indicates the number of adhesive failures within the test series. Adhesive failures were considered in the calculation of mean shear bond strength.

Within the non-filler PEEK group, the greatest shear bond strength after thermocycling was found with RelyX Ultimate (24.26 ± 5.75 MPa) followed by ResiCem (22.88 ± 8.67 MPa). The lowest shear bond strength was revealed to be with Bifx SE (14.44 ± 8.70 MPa) followed by Panavia SA Cement Plus (17.06 ± 4.46 MPa) and Variolink Esthetic DC (17.70 ± 2.07 MPa). However, all differences before and after thermocycling were not significant (Table 5, Figure 5).

Table 5. Shear bond strength values (MPa) of non filled PEEK after 24 h and after thermocycling.

		BioSolution Nature (without Filler Content)				
		Median	**IQR**	**Mean (SD)**	**95%CI**	***p*-Value**
ResiCem	24 h	22.90	4.15	23.64 (2.92)	20.02–27.26	0.690
	thermocyc.	19.30	16.35	22.88 (8.67)	12.12–33.64	
RelyX Ultimate	24 h	23.20	16.05	23.02 (8.27)	12.75–33.29	0.690
	thermocyc.	23.80	10.15	24.26 (5.75)	17.12–31.40	
Variolink Esthetic DC	24 h	18.80	16.85	13.98 (9.49) (#1)	2.19–25.77	0.841
	thermocyc.	17.50	4.00	17.70 (2.07)	15.13–20.27	
RelyXUnicem 2	24 h	21.40	5.60	20.80 (2.96)	17.12–24.48	0.421
	thermocyc.	18.40	7.40	18.12 (4.28)	12.80–23.44	
Bifix SE	24 h	21.30	5.90	23.06 (3.46)	18.76–27.36	0.056
	thermocyc.	15.80	12.80	14.44 (8.70) (#1)	3.63–25.24	
Panavia SA Cement Plus	24 h	13.40	4.45	12.98 (2.63)	9.72–16.24	0.151
	thermocyc.	17.40	6.95	17.06 (4.46)	11.52–22.60	
SpeedCem	24 h	21.50	2.15	21.60 (1.12)	20.21–22.99	0.548
	thermocyc.	22.80	6.05	21.86 (3.37)	17.68–26.04	

Comparison of shear bond strength after 24 h vs. after thermocycling calculated with Mann-Whitney-U-test. (#[NUMBER]) = Number of specimens that failed before the start of the shear-bond-strength test (MPa = 0). The number after the pound sign indicates the number of adhesive failures within the test series. Adhesive failures were considered in the calculation of mean shear bond strength.

When comparing different luting materials in relation to different PEEK groups, it was found that SpeedCem reached a significantly higher shear bond strength on PEEK without filler compared to PEEK with low filler (21.86 ± 3.37 MPa vs. 16.22 ± 3.28 MPa; $p = 0.043$) (Tables 4–6). All other comparisons between the different PEEK groups were without significance (Table 6, Figure 5).

Table 6. Differences of shear bond strength (p-values) between PEEK with different filler content.

	ResiCem	RelyX Ultimate	Variolink Esthetic DC	RelyXUnicem 2	Bifix SE	Panavia SA Cement Plus	SpeedCem
BS (HF) vs. BS (LF)	0.080	0.893	0.080	0.686	0.225	0.715	0.104
BS (HF) vs. BS (NF)	0.893	0.686	0.225	0.138	0.893	0.225	0.225
BS (LF) vs. BS (NF)	0.138	0.686	0.225	0.500	0.893	0.080	**0.043**

p-values of comparison of differences of shear bond strength after thermocycling between PEEK with different filler content. Comparisons calculated with Wilcoxon-test.

Table 7 compares shear bond strengths of different combinations of luting resin cements within the PEEK groups. Within the group of high filled PEEK, SpeedCem revealed a significantly higher shear bond strength compared to Variolink Esthetic DC (19.14 ± 2.95 MPa vs. 14.66 ± 3.92 MPa; $p = 0.043$). The same trend was observed when comparing RelyX Unicem 2 (21.94 ± 4.24 MPa) to Bifix SE (17.66 ± 2.91 MPa) or Panavia SA Cement Plus (11.12 ± 6.79 MPa) (both $p = 0.043$). Within the group of low filled PEEK, RelyX Ultimate (21.76 ± 4.24 MPa) reached a significantly higher shear bond strength compared to Bifix SE (15.84 ± 2.59 MPa) or Panavia SA Cement Plus (11.30 ± 3.60 MPa) (both $p = 0.043$). Furthermore, Variolink Esthetic DC reached a significantly higher shear bond strength compared to SpeedCem (19.64 ± 3.56 MPa vs. 16.22 ± 3.28 MPa; 0.043). RelyXUnicem 2 showed a significantly higher shear bond strength compared to Panavia SA Cement Plus (18.12 ± 4.28 MPa vs. 17.06 ± 4.46 MPa) ($p = 0.043$). On non-filled PEEK specimens, RelyX Ultimate revealed a significantly higher shear bond strength compared to Bifix SE (24.26 ± 5.75 MPa vs. 14.44 ± 8.70 MPa) ($p = 0.043$). On the other hand, SpeedCem (21.86 ± 3.37 MPa) reached a significantly higher shear bond strength compared to Variolink Esthetic DC (17.70 ± 2.07 MPa) ($p = 0.042$) or Panavia SA Cement Plus (17.06 ± 4.46 MPa) ($p = 0.043$). The evaluation of fracture mode yielded adhesive fractures on the level between PEEK surface and luting resin cement for every tested specimen. Therefore, 100% of all tested specimens revealed adhesive fractures, which show significantly less than 25% luting cement remnants on the sheared PEEK surfaces (compare with Figure 2C).

Table 7. Differences of shear bond strength (p-values) between different luting resin cements.

	BioSolution A2/B2 (High Filler Content)	BioSolution GUM (Low Filler Content)	BioSolution Nature (without Filler Content)
ResiCem vs. RelyX Ultimate	0.686	0.500	0.892
ResiCem vs. Variolink Esthetic DC	0.080	0.345	0.225
ResiCem vs. RelyXUnicem 2	0.893	0.686	0.686
ResiCem vs. Bifix SE	0.138	0.893	0.138
ResiCem vs. Panavia SA Cement Plus	0.138	0.500	0.138
ResiCem vs. SpeedCem	0.345	0.893	0.686
RelyX Ultimate vs. Variolink Esthetic DC	0.500	0.223	0.138
RelyX Ultimate vs. RelyXUnicem 2	0.893	0.500	0.080
RelyX Ultimate vs. Bifix SE	0.686	**0.043**	**0.043**
RelyX Ultimate vs. Panavia SA Cement Plus	0.225	**0.043**	0.138
RelyX Ultimate vs. SpeedCem	0.686	0.080	0.686
Variolink Esthetic DC vs. RelyXUnicem 2	0.080	0.686	0.893
Variolink Esthetic DC vs. Bifix SE	0.138	0.080	0.500
Variolink Esthetic DC vs. Panavia SA Cement Plus	0.225	0.080	0.345
Variolink Esthetic DC vs. SpeedCem	**0.043**	**0.043**	**0.042**
RelyXUnicem 2 vs. Bifix SE	**0.043**	0.080	0.500
RelyXUnicem 2 vs. Panavia SA Cement Plus	**0.043**	**0.043**	0.500
RelyXUnicem 2 vs. SpeedCem	0.345	0.225	0.225
Bifix SE vs. Panavia SA Cement Plus	0.138	0.080	0.686
Bifix SE vs. SpeedCem	0.345	0.893	0.080
Panavia SA Cement Plus vs. SpeedCem	0.080	0.138	**0.043**

p-values of comparison of differences of shear bond strength after thermocycling when using different luting resin cements. Comparisons calculated with Wilcoxon-test.

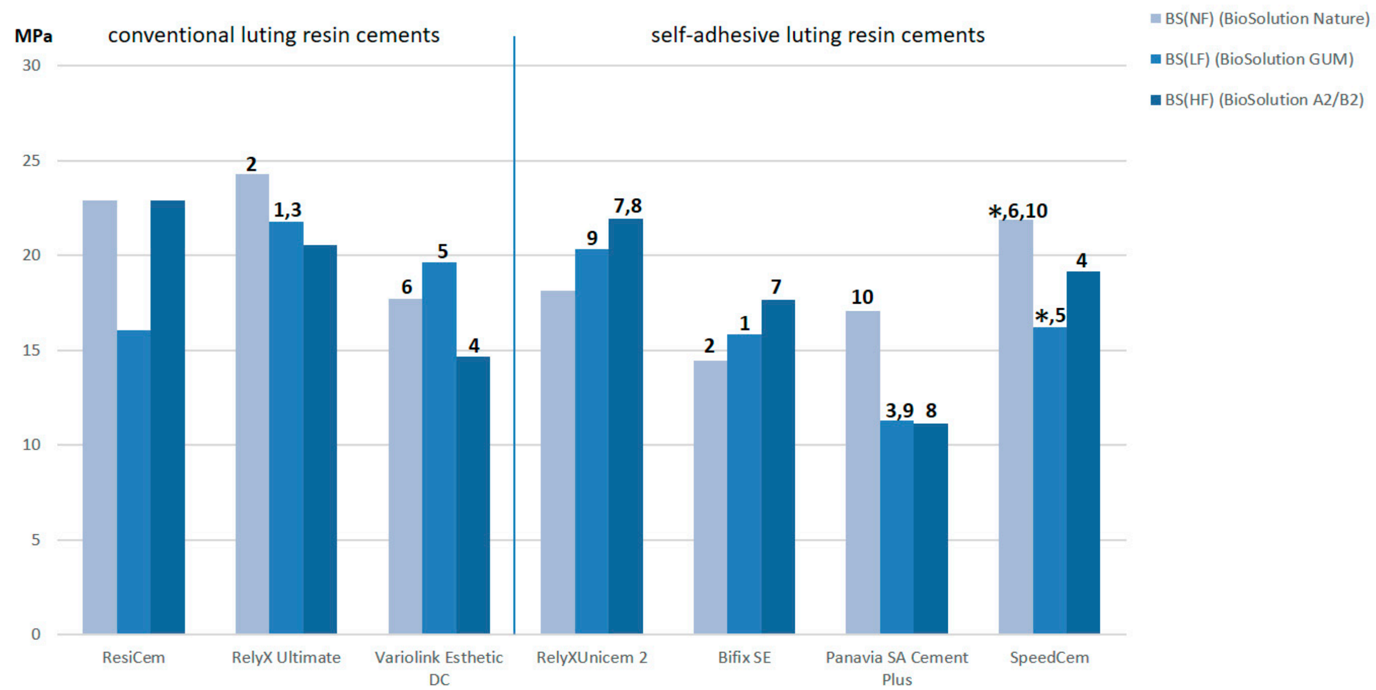

Figure 5. Comparison of shear bond strength values determined for the different PEEK variants using different luting resin cements. Shear bond strenght values are given in megapascals (MPa). Asterisks (*) indicate significant differences in the bond strength between two different PEEK variants using the same luting resin cement (see also Table 6), while the numbers 1–10 represent significant differences within a PEEK variant when using different luting resin cements (see also Table 7).

4. Discussion

When examining the fracture pattern, it was found that every specimen examined showed an adhesive fracture at the level of the PEEK surface. This impressively demonstrates a stable bond between the methacrylate-based luting resin cement and the urethane dimethacrylate (UDMA)-based SunCera veneering composite. It can be assumed that the test cylinders made of SunCera veneering composite still contained sufficient free non-polymerized carbon-carbon double bonds in the matrix after final light-curing to form a stable covalent bond with the carbon-carbon double bonds of the luting resin cements. Thus, the focus can be placed on the bond between the PEEK surface and the luting resin cement. The highest average mean shear bond strength values after thermocycling were obtained in unfilled PEEK specimens. The lowest average mean values were obtained in PEEK with a low filler content. Furthermore, a significant difference was found between these two PEEK groups when using SpeedCem luting cement. In most cases, however, the differences in bond strength were not significant in relation to the degree of filling of the PEEK framework. In contrast to the present study, Bötel et al. found higher shear bond strength values when using PEEK specimens with 20% filler content compared to PEEK specimens with no filler [28]. Nevertheless, it should be considered that the focus of the investigation by Bötel et al. was the influence of different plasma process parameters and the potential role of filter content was not evaluated in depth. Depending on the kind of plasma used and exposure time, as well as composite used, Bötel et al. found shear bond strengths in unfilled PEEK of 18.3–29.6 MPa and 22.5–34.2 MPa in PEEK with 20% TiO_2 filler content, respectively. In contrast to the present study, Bötel et al. used filled and unfilled PEEK specimens from different manufacturers, and no thermocycling was used. But, regardless of the kind of filler content, they expected that the surface roughness of the PEEK specimens had a high influence on the shear bond strength since they reached higher surface roughness in filled PEEK specimens compared to unfilled specimens [28]. Lümkemann et al. investigated PEEK composites from different manufacturers with 0%, 20% and >30% TiO_2 filler content. They also found higher tensile bond strength when using PEEK with 20% filler content compared to PEEK without filler or even with the higher filler content [29]. Their objective was to determine whether different light curing units could improve tensile bond strength between luting cement and different PEEK composites [29]. They assumed that higher tensile bond strength on PEEK with 20% TiO_2 filler could be affected by an activation of TiO_2 particles due to an intense UV adsorption during irradiation, especially when using a halogen light curing unit [29]. In contrast, they did not observe any further increase in the bond strength at a TiO_2 filler content of >30%. The authors suspected that the particle size and surface properties of the respective TiO_2 filler particles could have an relevant influence on the bond strength [29]. There was no information available on the surface condition of the TiO_2 fillers used for the manufacturing of the PEEK compositions which were used in the present study. However, this information would have been helpful to better assess the bonding mechanism behind the determined bond strength values. For example, it is unclear whether the TiO_2 filler particles have undergone silanization. If a silanized TiO_2 filler content were present, the direct TiO_2 particle surface would already be covered with functional groups and further bonding of the phosphoric acid monomers of the SunCera Metal Primer used would be prevented or significantly reduced. A silanized surface, on the other hand, would offer a chemical bonding link for the methacrylates of the luting resin cements via functionalized groups [30]. This could explain why the predominantly (meth)acrylate-based luting resin cements, such as the RelyX products, generated some of the strongest bonds on the filled PEEK variants in the present study with an average of 20.32 MPa (low filler content) to 21.94 MPa (high filler content). The presence of an already silanized TiO_2 filler would explain why the 10-Methacryloyloxydecyl dihydrogen phosphate (MDP)-based luting resin cement Panavia SA (especially on the PEEK compositions with filler content) showed the lowest bond strength values of the study with an average of 11.12 MPa (high filler content) and 11.30 MPa (low filler content), respectively. An unsilanized TiO_2 surface reveals hydroxyl groups which can be activated by functional monomers [30,31]. The bifunctional phosphoric acid monomers of the SunCera Metal Primer could provide a silanization-like priming of the TiO_2 particle surface. However, the functional phosphoric acid monomers of the SunCera Metal Primer can competitively prevent the linking of the phosphoryl group of the bifunctional MDP-monomers of Panavia SA since SunCera Metal Primer were applied earlier in specimens preparation process. This could explain the reduced adhesion values of Panavia SA in the present study.

However, the assumption of methacrylate affinity of the functionalized surface of the TiO_2 particles was questioned by the finding that the also predominantly methacrylate-based self-adhesive luting cement Bifix SE showed the second lowest bond strengths to filled PEEK at 15.84 MPa (low filled content) and 17.66 MPa (high filled content), respectively. With 70% inorganic fillers, Bifix SE also contains by far the highest amount of fillers of all the luting resin cements. The high filler content of the luting resin cement might influences the bond strength as well. It can only be conjectured why the present study found the highest bond strengths in PEEK without fillers. Two mechanisms can be held responsible for the adhesive bond between PEEK and the luting cements. First, mechanical surface roughening leads to an increased contact area and creates micro retentive areas into which priming agents as well as the low viscosity luting resin cements can penetrate and form a mechanical bond [32,33]. On the other hand, chemical bonding to surface molecules can be created, which requires the priming or adhesive agents [33]. The surface of the PEEK specimens was prepared according to manufacturer's instruction by sandblasting with 110 μm alumina particles (Al_2O_3) at 4 bar air particle pressure. It has been described that particles of the Al_2O_3 persist in the PEEK surface due to the high kinetic energy during sand blasting [33]. The presence of Al_2O_3 residues on the PEEK surfaces was also detected by scanning electron microscopy in the present study. This might potentially happen more often in the unfilled PEEK specimens than in the filled PEEK due to its lower material strength and hardness. It was speculated that the chosen metal primer created an additional adhesive bond to these remaining particles [34,35]. Since the chosen SunCera was a metal primer as well, it can be assumed that the bifunctional phosphoric acid monomers link to the Al_2O_3 surface. That high adhesion values could partly result from interactions between primers like the SunCera Metal Primer with the surface ofAl_2O_3 residues within the PEEK surface, was reported in another study by Silthampitag et al. [34]. Thus, the assumption that the filler content of the PEEK has no influence on the adhesive bond strength cannot be confirmed in general. In the present study evidence was found that non-filled PEEK reveal higher bond strengths than filled PEEK. However, less significant results support these findings. Nevertheless, sufficient surface pretreatment might have a more relevant effect on achievable bond strength.

Considering all the luting resin cements used on all of the PEEK specimens, there are n = 63 combinations. Of these, thirty-six are combinations of conventional vs. self-adhesive luting resin cements. Among all possible combinations, ten combinations showed significant differences in the achieved shear bond strength. In four comparisons, conventional luting resin cements performed better than self-adhesive ones, whereas in two comparisons, self-adhesive luting resin cements showed a significantly higher bond strength than conventional luting resin cements. The remaining four significant differences were comparisons within the self-adhesive luting resin cements. In conclusion, in 11% of the comparisons, conventional luting resin cements achieved better bond strength values than self-adhesive luting resin cements, whereas only 5% of the self-adhesive ones achieved higher values than conventional luting resin cements. Sproesser et al. found higher shear bond strength when using conventional luting cements compared to self-adhesive luting cements as well [36]. But they primarily investigated the effect of etching duration on shear bond strength and did not use an additional adhesive in their study [36]. Overall, in the present study both RelyX products reveal highest shear bond strengths and highest percentage of significant results when comparing with the other luting resin cements. These findings are in so far interesting since these luting resin cements belong to two different categories (RelyX Ultimate (conventional) vs. RelyXUnicem2 (self-adhesive)). It can just be speculated, but both materials might be utilizing the same methacrylates. ResiCem and Variolink Esthetic DC are both conventional luting resin cements. While ResiCem showed high overall mean shear bond strengths (16.04–22.90 MPa, overall mean: 20.6 MPa), Variolink Esthetic DC had one of the lowest overall shear bond strengths (14.66–19.64 MPa, overall mean: 17.33 MPa). Both products contain UDMA. Since ResiCem reveal very similar adhesive bond strengths in high filled PEEK (22.90 MPa) as well as in non-filled PEEK (22.88 MPa), a bonding effect to filler content particles appears to be improbable. ResiCem was the only luting resin cement which contains Triethylene glycol dimethacrylate (TEGDMA). Henriques et al. reported that some monomers like TEGDMA might be able to dissolve PEEK superficially, allowing deeper penetration of the monomers and may lead to a stronger adhesive bond [37], which would suggest that the amount of filler content to be irrelevant if special monomers are present. Nevertheless, in approximately 85% of the cases in the present study, no significant differences in bond strength was obtained when using conventional vs. self-adhesive luting resin cements. It is difficult to directly compare the present results with findings from other studies since the combination of surface pretreatment, primer or adhesives and luting cement seems to have a huge effect on achievable shear bond strength [38]. This is impressively demonstrated by a recent review on the mechanical and adhesive properties of PEEK [21]. The average shear bond strength values of the studies investigated by Luo et al. [21] varied between 3.8 MPa [39] and 34.9 MPa [28], both surfaces being pretreated with plasma. Considering only the studies presented in which surface pretreatment was carried out with sandblasting, the average shear bond strength values even varied between 6.4 MPa [40] and 18.3 MPa [39]. To adjust the findings, literature reports a minimum required shear bond strength of 10 MPa for dental materials as acceptable [41–43], and all tested luting resin cements in the present study pass this critical value. But in general, in accordance to literature, it could be assumed that the use of adhesive has a more substantial impact on shear bond strength than the choice between conventional or self-adhesive luting cements [44,45]. The second null hypothesis can, therefore, only be partially confirmed; globally, there is no significant difference in achieved shear bond strength when comparing conventional vs. self-adhesive luting resin cements, but in the present study, conventional luting resin cements appear to be slightly more frequently superior to self-adhesive ones.

The high inert behavior of PEEK holds challenges for the adhesive technique. Aesthetic veneering or adhesive cementation of PEEK-based fixed restorations is more difficult due to the high surface tension and the associated poor wettability. Due to these special properties, the investigation of the adhesive bond to PEEK or the modification of PEEK to achieve higher adhesive bond strengths remains an interest [21]. Numerous studies have shown that the success of adding adhesive bonds to PEEK is significantly influenced by the surface pretreatment [35,46,47]. Surface treatment with 98% sulfuric acid is considered successful [34]. However, due to its high health risk, which outweighs its benefits, this type of pretreatment cannot be recommended for daily use in dental laboratories or dental practices [34,48]. Surface activation by plasma or laser seems to achieve useful effects but requires more technical equipment [49,50]. The most practical way appears to be surface enlargement and activation by way of sandblasting with subsequent application of an adhesive, which can be implemented easily in the dental office as well as in laboratories [47,51]. Sandblasting with 50–110 µm aluminum oxide at 2 to 4 bar has proved to be successful [33,43].

From the large number of possible combinations of PEEK variants and adhesive luting cements, some limitations of the present study must be considered critically. First, considering the large available selection of different PEEK materials for the fabrication of dental restorations and the constantly growing number of luting cements, one limitation is that the present study can only offer an exploratory approach in determining the best material combination due to the immense theoretically possible combinations. The present results should be used to conduct further investigations with a narrower selection of PEEK/luting cement combinations. The adhesive fractures that consistently occurred at the level between the PEEK framework and the luting cement also suggest that the choice of primer could have an influence on the optimization of bond strength, like reported by numerous other studies [45–47,52]. According to manufacturer's specifications, the chosen Metal Primer SunCera is suitable for surface pretreatment of PEEK as well. This is supported by the revealed shear bond strengths, which pass the critical value of 10 MPa, like recommended by Behr et al. [41,42]. In addition, the ISO EN 10447 on which the chosen shear bond strength tests were based, demanded shear bond strength values of at least 5 MPa to consider an adhesive bond as acceptable. This value was achieved as well, so that SunCera Metal Primer could be considered as suitable for the conducted experiments. Nevertheless, some manufacturers recommend special primers and adhesives for their luting cements, while others do not have any specific primers. Therefore, another limitation of the present study was that only one single priming agent was used in order to standardize the testing procedure as far as possible. The relevance of a suitable priming agent is impressively demonstrated in a study by Rikitoku et al. in which an experimental PEEK with SiO_2 filler initially showed a higher tensile bond strength than a PEEK reference product with the same wt% content of TiO_2 [27]. In this study, a silane-containing bonding agent was used. The authors suggest a higher initial tensile strength for PEEK with SiO_2 filler compared to PEEK with TiO_2 due to a stronger coupling of the silane to the SiO_2 filler [27]. These results support the importance of a suitable primer or adhesive. Further research should investigate whether different combinations of primers and luting cements generate an improved adhesive bond strength on PEEKs with different filler content.

5. Conclusions

Overall, non-filled PEEK reached the highest mean shear bond strength while low filled PEEK reached the lowest mean values. However, in detail, less significant differences were found in shear bond strength when comparing non-filled PEEK with low or high filled PEEK, respectively. Therefore, the first null hypothesis, that the choice of PEEK framework material with different TiO_2 filler content has no influence on the achievable adhesive bond strength could not be confirmed in general. In most of the comparisons between conventional luting resin cement vs. self-adhesive luting resin cement, no significant difference could be found. However, within the significant cases, conventional luting resin cements revealed a superior adhesive bond. Therefore, the second null hypothesis, that there is no difference in achievable adhesive bond strength when using conventional or self-adhesive luting resin cement can only be partially confirmed.

Author Contributions: Conceptualization, M.D. (Marco Dederichs), H.K. and A.G.; methodology, H.K. and O.L.; statistical analysis, M.D. (Marco Dederichs) and S.V.; investigation, O.L.; data curation, M.D. (Marco Dederichs), S.V., M.D. (Mike Decker) and C.-L.H.; writing—original draft preparation, M.D. (Marco Dederichs); writing—review and editing, C.K., A.G., S.V., O.L., C.-L.H., H.K., M.D. (Marco Dederichs) and M.D. (Mike Decker); supervision, A.G. and C.K.; project administration, H.K. and C.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors thank Merz Dental GmbH (Luetjenburg, Germany) for providing the PEEK specimens. The company had no influence on collection and analysis of data or on the preparation of the manuscript. We also thank David Berzins (Dental Biomaterials, Marquette University School of Dentistry, WI, USA) for critical manuscript review and Sandor Nietzsche (Center for Electron Microscopy, Jena University Hospital) for preparing the SEM images.

Conflicts of Interest: The authors declare no conflict of interest.

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