Comparing shear bond strength of a composite resin to PEEK and titanium

Dikhabiso Vivian Bwerinofa

Student number: 510877

A Research Report submitted to the Department of Oral Rehabilitation, School of Oral Health Science, Faculty of Health Sciences, University of the Witwatersrand, Johannesburg, South Africa in partial fulfilment of the requirements for the degree of Master of Dentistry in Prosthodontics

Supervisors: **Dr VJ Hoods-Moonsammy**

Dr IE Munshi

Prof JL Shackleton

DEDICATION

This research report is dedicated to my loving husband Sid and precious children, Minana and Anashe, who have been my pillar of strength and source of inspiration when I had reached my lowest point and wanted to give up. Their unwavering emotional and spiritual support is what pulled me through.

A dedication to my beloved parents who have always supported my ventures without question and my siblings for being my biggest cheerleaders. I am grateful for the love and support I have continuously received from my in-laws.

DECLARATION

I, Dikhabiso Vivian Bwerinofa, declare that this research report is my own work. It has been submitted for the degree of Master of Dentistry in Prosthodontics in the Faculty of Health Sciences at the University of the Witwatersrand, Parktown, Johannesburg, South Africa. It has not been submitted before for any other degree or examination at this or any other University.

Dikhabiso Vivian Bwerinofa

This 26th day of February2021

ACKNOWLEDGEMENTS

This research report has been undertaken in partial fulfilment of the degree of Master of Dentistry in Prosthodontics. I wish to acknowledge institutions and individuals for their input towards the formulation of this research report.

Firstly, I would like to express sincere gratitude to my family for their unconditional support. A special thank you to my husband Sid for steering the ship sometimes alone in order for me to pursue my studies.

I would like to wholeheartedly thank my supervisors Dr Vyonne Hoods-Moonsammy, Dr Ismail Munshi and Prof Joy Shackleton for their commitment in assisting me to complete the research within a near impossible time frame. I would also like to thank Prof Dale Howes for helping me formulate the topic and Prof Peter Owen for his contribution in developing the protocol.

I am grateful for all the individuals who assisted me when the going got tough. Prof Phumzile Hlongwa for her mentorship and for throwing me a life line. Dr Ahmed Abdualhafid for his continuous support. Dr Penny Dikgale, Sandile from Sandz laboratory, Senzo and Abigail from Wits laboratory for showing up when I needed a helping hand.

Last but not least a great thank you to Southern Implants (PTY) LTD, Centurion, South Africa, for donating the titanium and PEEK used in the study.

ABSTRACT

Purpose

The aim of this study is to compare the shear bond strength (SBS) of composite resin to PEEK and titanium, and to compare the failure mode (adhesive, cohesive, mixed) from the shear testing.

Materials and methods

Milled PEEK and Titanium blocks (n=51) were grounded with 600-1000 grit silicon carbide paper. Then they were surface treated through sandblasting with 110µm aluminium oxide particles and application of an MDP- containing adhesive (One Coat 7 Universal, Coltene, Switzerland). A composite resin (Gradia® Plus Heavy body paste, GC, Europe) was bonded to the treated PEEK and titanium surfaces. Shear bond testing was done using a universal testing machine (Instron, UK) with a crosshead speed of 1mm/ min. Thereafter, the sheared interface was examined under a stereo microscope (Nikon SMZ 1500) at 16X magnification.

Results

The Shapiro Wilk test for normality showed that the data was normally distributed for all the variables (p-value >0.05). Descriptive statistics by way of the mean and standard deviation were used to summarise the SBS for PEEK and titanium. The average SBS for titanium and PEEK was 25.99±6.12 MPa and 20.76±6.90 MPa respectively. With the test value at 0, a one sample t-test of the mean difference between PEEK and titanium showed that there was a statistically significant difference and therefore shows that the two measurements are significantly different from one another (p-value=0.00). The titanium specimens showed mostly cohesive failure (61%) and PEEK showed predominantly mixed failure (65%)

Conclusion

The SBS of composite resin to titanium was greater than that of composite bonded to PEEK when the surfaces are pre-treated with sandblasting and a universal adhesive containing MDP. PEEK results exceeded the minimum clinically acceptable bond strength. The use of MDP-containing adhesive systems creates the greatest bond between composites and titanium

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION AND LITERATURE REVIEW

1.1. Introduction

Traditionally metal alloys have been the material of choice for substructures or frameworks of dental prostheses veneered with porcelain or composite. However, metal alloys, although strong, have aesthetic shortfalls because of the need to mask their greyish colour. Corrosion degradation, and metal allergy in some patients, are some of the additional disadvantages of metal alloys (Bhola et al., 2011). The need for metal-free dental prostheses prompted the introduction of high strength ceramics such as alumina and zirconia as frameworks. These materials address the aesthetic limitations of the metal alloys, but they are brittle and require very specific veneering techniques to compensate for the different coefficients of thermal expansion and contraction between the veneering and core materials.

Polyether ether ketone (PEEK) has been proposed as an alternative core material. It has diverse applications, and has been used in crowns and bridges, implants and implant abutments, amongst others (Schwitalla and Müller, 2013; Santing et al., 2012). PEEK has displayed very high fracture load values of up to 1383 N with plastic deformation from about 1200N (Stawarczyk et al., 2013a). It has been shown to withstand large deformation in axial and non-axial directions (Kurtz and Devine, 2007). PEEK has demonstrated satisfactory results with many commonly used veneering composite resins available in the market (Stawarczyk et al., 2013a, Lee et al., 2017), and has shown that chipping can be repaired chairside without the need for total replacement (Schwitalla and Müller, 2013). Polymethyl methacrylate (PMMA) resins have also been used as superstructures for removable dental prostheses while PEEK has been used for the framework or substructure (Zoidis et al., 2016; Dawson, et al., 2018). PEEK could act as a core material, veneered with composite resins, as it is suitable for a variety of clinical situations, especially where a more cost-effective solution is required as it is less expensive than its metal counterparts. PEEK's modulus of elasticity is similar to bone, and can therefore reduce stress transferred to the abutment teeth and alveolus (Schwitalla and Müller, 2013). This property is especially relevant for implant-supported prostheses (ISP's).

Titanium, commercially pure titanium (CpTi) and titanium alloys, is commonly used as a substructure for dental prostheses. Due to its biocompatibility, chemical stability and mechanical strength, titanium has many uses in dentistry especially in implantology. It has a high strength-to-weight ratio and a modulus of elasticity similar to bone (Roach, 2007; Prasad et al., 2015). Titanium is a more corrosion resistant metallic biomaterial compared to cobalt and stainless steel based alloys. This is attributed to its alloying elements (noble metals or thermodynamically stable acid-resistant elements) which assist in the formation of a protective oxide film, titanium dioxide (TiO2), on its surface. Titanium is extremely reactive, particularly molten titanium during casting. The chemical reaction with oxygen and the investment materials during casting can adversely affect its mechanical properties. Milling of titanium, using computer-aided design and computer-aided manufacturing (CAD/CAM) systems instead of casting, helps to diminish titanium's reactiveness (Bhola et al., 2011).

PEEK has some similarities to titanium. They are both compatible with milling systems producing prostheses with precision of fit than conventional casting techniques (Jin et al., 2019; Almasri et al., 2011). Titanium and PEEK are lightweight and biocompatible. Their flexural strength allows reduced stress on the alveolar bone and abutment teeth compared to other metals and metal ceramics.

Zirconia has been an alternative for metal-free restorations for fabricating frameworks for crown and bridge restorations, posts, implants and implant abutments (Madfa et al., 2014). Although zirconia shows better aesthetics, high strength and fracture toughness, and is biologically inert, zirconia frameworks for implant-supported prostheses have shown higher strain on the alveolar bone compared to titanium frameworks (Tiossi et al., 2017).

Different veneering materials such as composites, porcelains (and other ceramics) and acrylic resins are available in the market; each with its advantages, disadvantages and indications. The choice of veneering material depends on the indications and specific patient factors. Porcelain has traditionally been the veneering material of choice; but it is costly and brittle. Composite resin has increasingly been used as an alternative to porcelain. It is more cost effective, absorbs some of the occlusal stresses preventing them from being transferred to the framework substructure, and its lightweight significantly decreases the weight of the prosthesis. It displays colour stability and is comparatively more aesthetic than acrylic resin (Jin et al., 2019). Any chipping or fracture of the composite can be repaired at the chairside, unlike porcelain. For porcelain fractures, more often construction/the remake of a new prosthesis is required. Poor bonding of composite resins to titanium and PEEK frameworks is a major disadvantage. Many authors have reported significant improvement of the bond strength after mechanical and chemical surface treatment of PEEK and titanium surfaces (Almilhatti et al., 2013; Stawarczyk et al., 2013a; Lee et al., 2015; Lee et al., 2017).

High bond strength between the framework and the veneering materials is a prerequisite for the durability and longevity of dental prostheses. Shear bond strength (SBS) is the magnitude of a compressive force required to break a bonded interface between two dental materials or between a material and a tooth. Shear bond tests are valid methods of determining the bond quality of dental materials because shear forces are dominant during function. They therefore best represent the clinical scenario (Behr et al., 2003). Shear bond strength values greater than or equal to 10 MPa are considered to be adequate (Behr et al., 2011).

Because the success of a hybrid restoration depends primarily on a strong bond between the veneering material and the substructure, it is worthwhile to evaluate the failure mode. This can be adhesive, cohesive or mixed failure. Adhesive failure is defined as "bond failure at an interface between two materials because of tensile or shearing force" while cohesive failure is "bond failure within a dental material as a result of a tensile or shearing force" (Glossary of Prosthodontic Terms, 2017). Mixed failure is a combination of adhesive and cohesive failure.

1.2. Literature Review

1.2.1. Bonding to PEEK

In the 1990s, PEEK was utilised as a metal-free alternative in orthopaedics and trauma units, and it has been used in dentistry for aesthetic abutments and implants, and as a framework and core material (Stawarczyk et al., 2013a).

PEEK is an "aromatic, semi-crystalline linear thermoplastic polymer from the poly aryl ether group (PAEK)", connected by ketone and ether functional groups (Kurtz and Devine, 2007; Stawarczyk et al., 2013a). It is highly resistant to chemical, thermal and radiation damage (Schmidlin et al., 2010). It has high tensile and compressive strength, good wear resistance and fatigue, low coefficient of friction, and its stiffness is comparable to metal alloys (Hunter et al., 1995). Additionally, it is compatible with reinforcing materials such as carbon fibres or glass (Stawarczyk et al., 2014), and has a similar flexural modulus to cortical bone (Hunter et al., 1995).

PEEK prostheses can be milled or constructed through thermo-pressing techniques. Milling of PEEK dental substructures has shown clinically acceptable marginal fit and overall fit of the restoration. This was attributed to the injection-moulded blocks used for milling, and the reduced wear of the burs (Schmidlin et al., 2010).

The greyish colour and low translucency of PEEK makes it unsuitable for monolithic restorations especially for the anterior region, and therefore a veneering material is required, usually composite resin (Stawarczyk et al., 2013a; Stawarczyk et al., 2013b; Stawarczyk et al., 2015). Due to its low surface energy and inert nature, PEEK requires surface modification or surface treatment for bonding to composites to produce adequate bond strength (Schmidlin et al., 2010; Stawarczyk et al., 2014). Without any surface treatment, little or no bonding occurs between PEEK and veneering composite (Schmidlin et al., 2010; Stawarczyk et al., 2014).

Stawarczyk et al., (2013a) evaluated SBS and failure modes between PEEK and two veneering composites [Gradia (GC Europe) and Sinfony (3M ESPE)]. They compared 4 conditioning methods, 98% sulphuric acid, air abrasion with 50 µm and 110µm alumina particles and tribochemical silica coating using the Rocatec® system. Although the 110µm air-abraded and silica-coated groups showed the highest surface roughness values and the lowest contact angles, the acid etch group produced the highest SBS values, 14.30 and 18.56 MPa for the different composite resins. The acid etched group showed cohesive failure of PEEK while the rest of the conditioned surfaces showed adhesive failure.

Hallmann et al., (2012) showed that bond strength is significantly improved with air abrasion and chemical etching with piranha solution, which consists of sulphuric acid and hydrogen peroxide (H_2SO_4:H_2O_2 = 1:1), as opposed to etching alone. In their study, two different adhesives were compared. The combination of air abrasion with 50 µm alumina particles, etching with piranha solution and the use of Heliobond adhesive produced the highest tensile bond strength. Chemical treatment created a rough surface, which is crucial for adhesion of two polymers. However combining chemical treatment with air abrasion significantly enhanced the bond strength. These authors further concluded that air abrasion created a scaffold for mechanical anchorage of the adhesive. It has been shown that combining air abrasion and an adhesive system containing methyl methacrylate (MMA) groups improved the bond strength of composite veneers to PEEK (Stawarczyk et al., 2013b; Stawarczyk et al., 2014).

1.2.2. Bonding to titanium

It was reported that cast or machined titanium frameworks show poor bonding with veneering agents regardless of the type of veneering material (Yanagida et al., 2002; Egoshi et al., 2013). This is due to insufficient micro- and nano-scale cavities to create a favourable surface roughness for bonding. Egoshi et al., (2013) illustrated that untreated titanium surfaces show poor SBS values. Composite resins are commonly used for veneering metal substructures but chipping and debonding are a common complication. Retention beads are used successfully in cast frameworks to aid with retention of composite veneers. These cannot, however, be incorporated into milled titanium. Therefore, to improve bonding some surface modification is required. Many physical and chemical methods have been investigated in the literature such as sandblasting, acid etching, silica coating, application of adhesive primers and more (Egoshi et al., 2013). Other authors proposed chemical methods with agents containing a silane coupler or a phosphate monomer, which can be found in the conditioning material or the composite resin (Yanagida et al., 2002).

Egoshi et al., (2013) investigated the SBS of composite resin to grade 4 commercially pure titanium with various surface treatments and combinations. The study revealed that combining sandblasting, 45% H_2SO_4 and 15% HCl (SH-etchant), and MDP (methacryloyloxydecyl dihydrogen phosphate) -primer yielded the strongest bond. These authors suggested that the acid etching increased micro- and nanoscale mechanical interlocking thereby increasing the bonding surface area and eliminating contaminants. They also speculated that MDP monomer initiates a chemical reaction on the titanium surface therefore facilitating diffusion of other monomers into the micro- and nanoscale cavities created by sandblasting and acid etching. It has also been suggested that the phosphoric acid group of MDP is effective in improving the adhesion of resin to titanium (Tsuchimoto et al., 2006, Almilhatti et al., 2013).

Almilhatti et al., (2013) evaluated the SBS of a composite resin on commercially pure titanium grade I. Three surface treatments namely polishing, sandblasting with 50µm and 250µm alumina particles, and three metal conditioners or one surface modification system were compared. The study demonstrated that sandblasting together with metal conditioners and surface modification increased the SBS of composite to titanium as opposed to a polished surface.

Table 1: Summary of literature review

Study	Material	Surface treatment	Adhesive system	Veneering material	Results
Stawarczyk et al., 2013a	PEEK	i - 98% sulphuric acid (*N*=45) ii – Air abrasion with 50µm alumina (*N*=45) iii – Air abrasion with 110 µm alumina (*N*=45) iv - Silica coating + 3M ESPE Sil silane coupling agent (*N*=45) v - No surface treatment (*N*=45)		Composites i - Grandia (GC Europe), (*N*=15 per conditioning group) ii - Sinfony (3M ESPE), (*N*=15 per conditioning group)	98% sulphuric acid produced highest SBS* (14.30 and 18.56 MPa with Grandia)
Hallmann et al., 2012	PEEK	i - Etching with piranha* only (*N*=32) ii - Air abrasion with 50µm alumina particles + piranha (*N*=32) iii - Air abrasion with 110µm alumina particles + piranha (*N*=32) iv - Air abrasion with 30µm silica-coated alumina particles + piranha (*N*=32)	i – Heliobond (*N*=16 per conditioning group) ii - Clearfil Ceramic Primer (*N*=16 per conditioning group)	Rely X unicem – resin cement	PEEK; Air abrasion with 50µm alumina + piranha Etching + Heliobond produces highest TBS* (21.4MPa)

		v - Air abrasion with 110µm silica-coated alumina particles + piranha (*N*=32) v – No surface treatment (*N*=32)			
Fuhrmann et al., 2014	PEEK	i – air brasion alumina (*N*=30 for each material) ii – (i) + resin primer (Luxatemp Glaze & Bond) for 20s before LC for 20s (*N*=30 for each material) iii – (ii) but resin primer left for 5 min before LC for 20s (*N*=30 for each material) iv – tribochemical silica-coating (Rocatec Soft) + silane primer (Monobond Plus) left for 5min before LC (*N*=30 for each material) v – (iv) + adhesive primer (Luxatemp Glaze & Bond) (*N*=30 for each material)	Resin primer (containing methacrylate) (Luxatemp Glaze & Bond) Silane primer (Monobond Plus)	Luting resin (Multilink Auomix, Ivoclar Vivadent)	Highest overall TBS was with tribochemical silica-coating + silane primer + adhesive primer PEEK – 21.8±8.8 MPa
Egoshi et al., 2013	Titanium (commercially pure grade 4)	i – sandblasting 50µm alumina + SH-etchant* + MDP-primer (*N*=8) ii - sandblasting 50µm alumina + SH-etchant (*N*=8)	Estenia C&B Opaque Primer (MDP-primer)	Estenia C&B Body Opaque OA3 Estenia C&B Dentin DA3	Highest shear bond strength was with sandblasting 50µm alumina + SH-etchant + MDP-primer 29.9 ±4.1 MPa

		iii - SH-etchant + MDP-primer (*N*=8) iv - sandblasting 50µm alumina + MDP-primer (*N*=8) v - sandblasting 50µm alumina only (*N*=8) vi- SH-etchant only (*N*=8) vii - MDP-primer (*N*=8) viii - no sand/no etch/no primer (*N*=8)			

Almilhatti et al., 2013	Titanium (grade 1 cast)	i - Sandblasting 50µm Al_2O_3 + TL ii - Sandblasting 50µm Al_2O_3 + MPP iii - Sandblasting 50µm Al_2O_3 +OP iv - Sandblasting 50µm Al_2O_3 + S v - Sandblasting 250µm Al_2O_3 + TL vi - Sandblasting 250µm Al_2O_3 + MPP vii - Sandblasting 250µm Al_2O_3 +OP vii - Sandblasting 250µm Al_2O_3 + S	Opaque resin (C & B Opaque)	Composite resin (Artglass)	Highest shear bond strength was with sandblasting 250µm + metal conditioners TL and OP 13.2 ± 2.0MPa

* Piranha = 50%H_2SO_4 50% H_2O_2, SBS = Shear bond strength, TBS = Tensile bond strength, MDP-primer = methacryloyloxydecyl dihydrogen phosphate, MMA= methyl methacrylate, SH-etchant = 45% H_2SO_4 + 15% HCL, LC = light cure, Metal conditioners TL= Targis link, MPP = Metal Photo Primer, OP = Cesead II Opaque Primer, S = Siloc Bonding System

2. AIMS AND OBJECTIVES

2.1. Aim

The aim of this study is to compare the shear bond strength of composite resin to PEEK and to titanium.

2.2. Objectives

1) To measure shear bond strength between composite and PEEK using a universal testing machine.

2) To measure shear bond strength between composite and titanium using a universal testing machine.

3) To compare the shear bond strengths in objectives 1 and 2.

4) To determine and compare failure modes of composite to titanium and PEEK using a stereo microscope.

2.3. Research statement

The null hypothesis for this research project is that there is no statistically significant difference between a composite resin bonded to titanium and PEEK.

3. MATERIALS AND METHODS

3.1 Study design

The study is a laboratory-based descriptive study.

3.2 Sample size

A pilot study was conducted to establish the sample size. Using MedCal software, the sample size for the Bland-Altman plot for measure of agreement was estimated to be 51 specimens per group. This calculation is an indication of the number of specimens required to detect clinically relevant differences within a 95% confidence interval with a margin of error of 0.05.

3.3. Specimen preparation and data collection

Preparation of the specimens, shear bond strength testing, microscopic examination of specimens and collection of data was done by a single operator. This was in order to improve internal consistency and reduce biases.

The specimens were prepared at the Wits Oral Health Centre dental laboratory. Shear bond testing was carried out in the Instron room at the Department of Oral Biological Sciences, in the School of Oral Health Sciences. The Instron machine was calibrated prior to data collection. Access to the Instron room was limited to the operator for the duration of the study. Examination of the specimens to determine failure mode was conducted at the School of Anatomical Sciences using a stereo microscope. The settings for the microscope, 16X maginification (WD 24 Nikon, Japan), and the position was the same for every specimen.

3.4. Methods

3.4.1. PEEK and titanium disc preparation

Titanium (grade 5) and PEEK discs were prepared. Grade 5 titanium is a titanium alloy with 90% titanium, 6% aluminium and 4% vanadium. It is stronger than commercially pure titanium. The discs were milled, and therefore standardised, to dimensions of 16mm diameter and 11mm thickness (Figure 1a). The discs were embedded in auto-polymerising acrylic resin increasing the dimensions to 18mm diameter and 12mm thickness (Figure 1b). This was done for the specimen to fit into the stainless-steel frame that secures the specimen in the universal testing machine (Figure 1c).

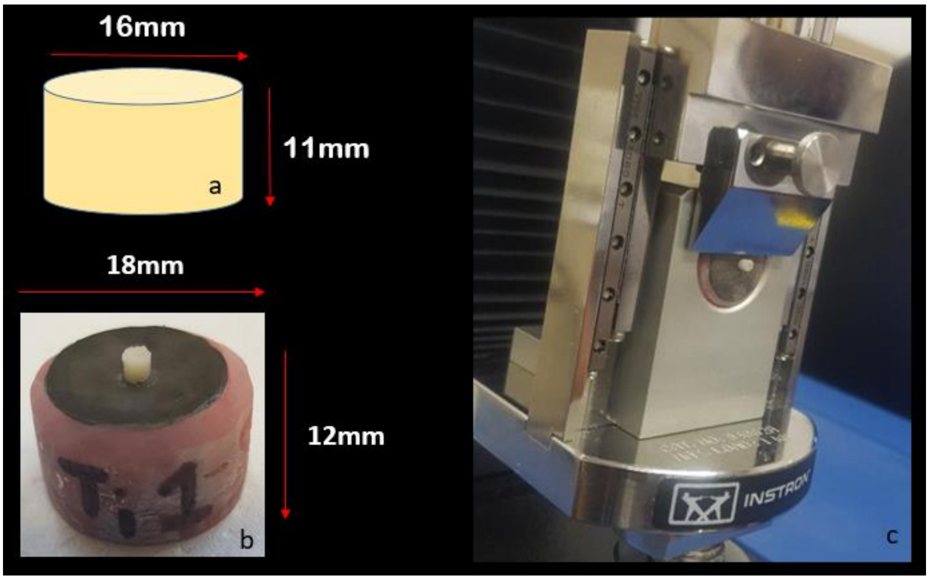


Figure 1: a) Diagrammatic representation of the dimensions of the milled titanium and PEEK discs b) Extension of the dimensions of the milled titanium and PEEK discs with auto-polymerising acrylic resin c) Titanium specimen secured in stainless-steel frame, mounted in the universal testing machine

An impression of the socket in the stainless-steel frame was made using laboratory putty (Figure 2a, b, c). This was poured with type 3 dental stone (yellow plaster) (Figure 2d). Once the plaster had set the putty was removed (Figure 2e).

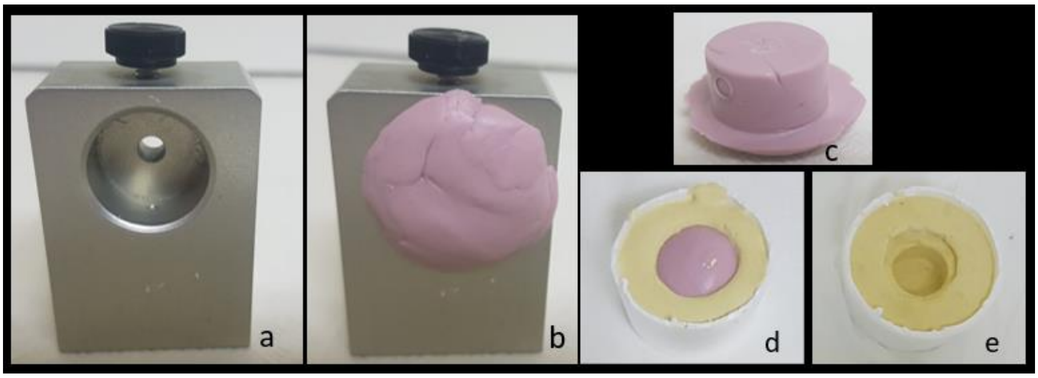


Figure 2: a) Stainless-steel frame that secures the specimen in the Instron machine. b, c) Putty impression of the socket in the stainless-steel frame. d) Putty impression poured in dental stone. e) Concavity after removal of putty impression

The concavity left by the putty was filled (halfway) with auto-polymerising acrylic.

PEEK and titanium discs were inserted allowing excess acrylic to overflow (Figure 3a).

Once set the acrylic and PEEK/titanium specimens were removed from the plaster then trimmed to fit into the stainless-steel frame (Figure 3 b. c)

Figure 3: a) PEEK and titnium discs embedded in auto-polymerise acrylic; b) The acrylic PEEK/titanium specimen once removed from the plaster; c) The trimmed specimen, ready for shearing with the bonded composite

3.4.2. Surface treatment

All specimens were ground with 600 –and 1000-grit silicon carbide papers. The surfaces were sandblasted with 110µm grain size alumina particles and then lightly air blown. The air pressure for sandblasting was 0.45MPa with the nozzle 10 mm away from the specimen for 15 seconds (Fuhrmann et al., 2014; Egoshi et al., 2013; Hallmann et al., 2012). Then a MDP containing primer and adhesive (One Coat 7 Universal, Coltene, Switzerland) was applied to the titanium and PEEK surfaces according to the manufacturer’s instructions. Using a disposable brush, the adhesive was applied for 20 seconds onto the titanium and PEEK surfaces, then gently air dried for 5 seconds with oil-free compressed air. This was followed by light curing (LED Polymerisation units with a light output of >800 mW/cm2) for 10 seconds. Composite resin was applied after surface treatment of the specimens.

3.4.3. Bonding

The composite resin (Gradia® Plus Heavy body paste, GC, Europe) was bonded to the specimens using an Ultradent bonding mould, on an Ultradent bonding clamp (Ultradent, South Jordan, UT, USA) (Figure 2a, 2b). The composite was packed in the opening at the centre of the bonding mould (Figure 2b) using the smaller end of a non-serrated amalgam plugger and cured at an angle perpendicular to the surface for 40 seconds. A composite specimen with a diameter of 2 mm and 3 mm height was created (Figure 2c).

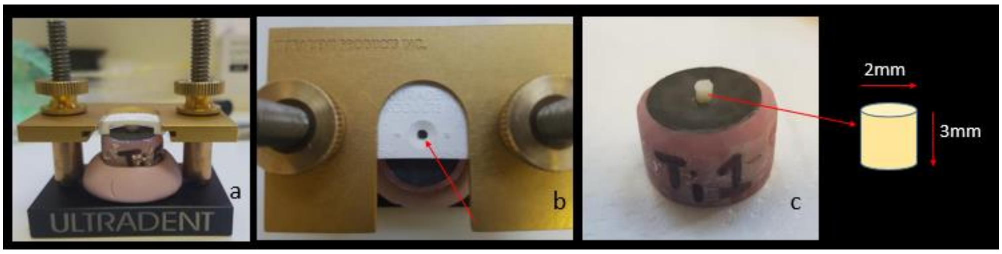


Figure 4: a) The titanium disc mounted in the bonding mould and bonding clamp; b) Arrow indicating space in the bonding mould through which composite will be packed; c) Dimension of the composite bonded to titanium disc

3.4.4. Shear testing

Each specimen was fitted to a test base clamp on the Instron (Instron, UK) universal testing machine. SBS was determined using an Instron shear test apparatus using a 2kN load cell with the shearing load parallel to the bonded surface at a crosshead speed of 1mm/min (Figure 3). The force was applied continuously until the composite was sheared off the PEEK or titanium.

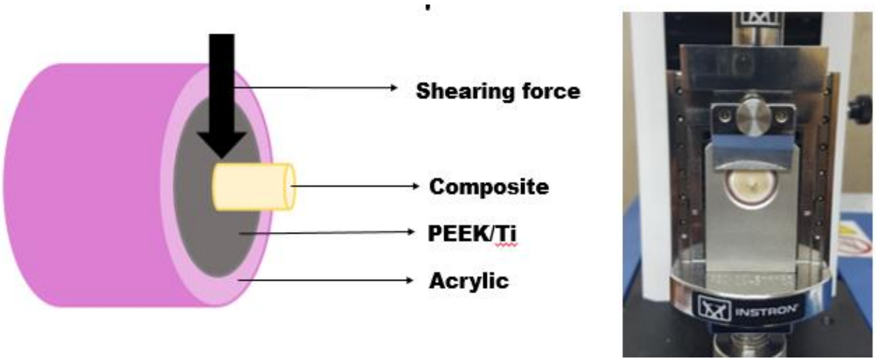


Figure 5: Illustration of the different components of the study and a representation of a PEEK specimen in the universal testing machine

3.4.5. Evaluation of failure mode

Following shear failure, all specimens were inspected under a stereo microscope (Nikon SMZ 1500, Johannesburg, South Africa) at 16X magnification (Figure 6) to determine the failure mode (adhesive, cohesive or mixed). This step was to analyse the fractured interface resulting from the shearing test. Adhesive failure occurs at the composite and PEEK/titanium interface. Cohesive failure is a fracture within the composite, and mixed failure is a combination of adhesive and cohesive failure. The microscope delivers true images of the specimens in colour (Figures 9 and 10).

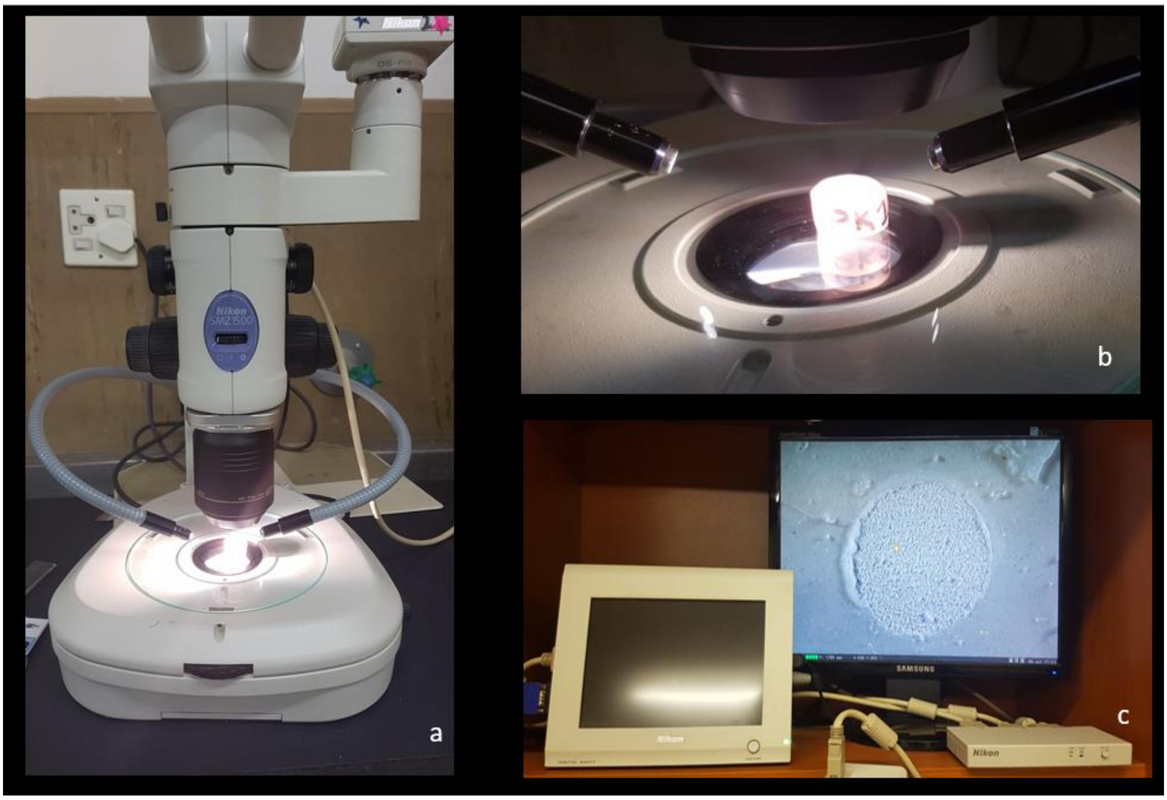


Figure 6: a) Stereo Microscope (Nikon SMZ 1500, Johannesburg, South Africa). b) Failure mode being inspected on a PEEK specimen. View of specimen at 16X magnification projected on monitor

3.5. Data analysis

The data was subjected to descriptive and inferential statistical analyses.

3.5.1 Descriptive statistics

The mean and standard deviation was used to summarise the compressive stress at maximum compressive load or SBS for PEEK and titanium by way of a bar graph (Figure 7). The average, minimum and maximum SBS (MPa) for titanium and PEEK is also presented.

3.5.2 Inferential statistics

A Shapiro Wilk test was used to determine whether the data was normally distributed.

The t-test selected was used to analyse the differences between the SBS of PEEK versus titanium to composite. The p-values measured reflect the extent of their differences at a significance level set at $p<0.05$.

The Pearson correlation was also used to determine the relationship between PEEK and titanium.

The analyses were performed by using the IBM SPSS statistic 25 ® software.

Table 2: Summary of materials and methods

Material	Surface treatment	Veneering material	Shear bond testing (Instron, UK)	Failure mode assessment (Nikon SMZ 1500)
Titanium and PEEK	Sandblasting 110µm + MDP containing adhesive system (One Coat 7 Universal Adhesive	Composite resin (Gradia® Plus)	2kN load cell at a crosshead speed of 1mm/ min	Adhesive/cohesive/mixed

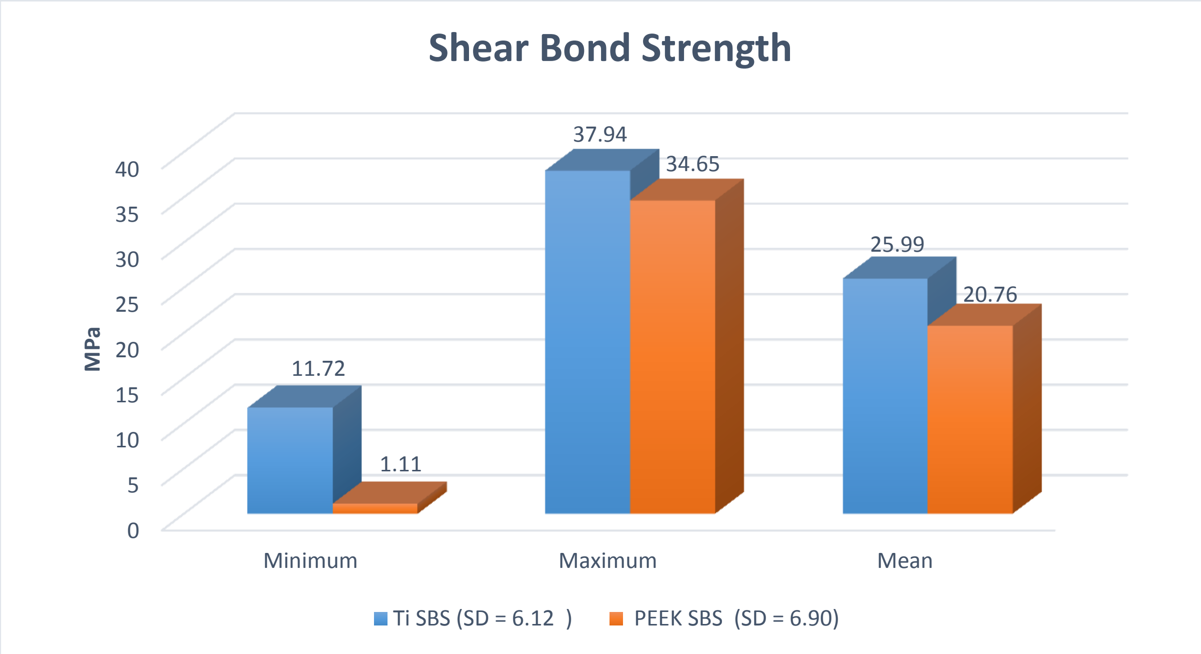
4. RESULTS

4.1. Descriptive statistics

4.1.1. Descriptive statistics for shear bond strength in MPa

The average SBS for titanium and PEEK was 25.99±6.12 MPa and 20.76±6.90 MPa respectively, as shown in Figure. 7.

The mean difference of the maximum compressive load between the PEEK and titanium was 5.23±7.77 (95%CI of -9.99 – 20.46) as shown in Table 3.



*SD = Standard deviation

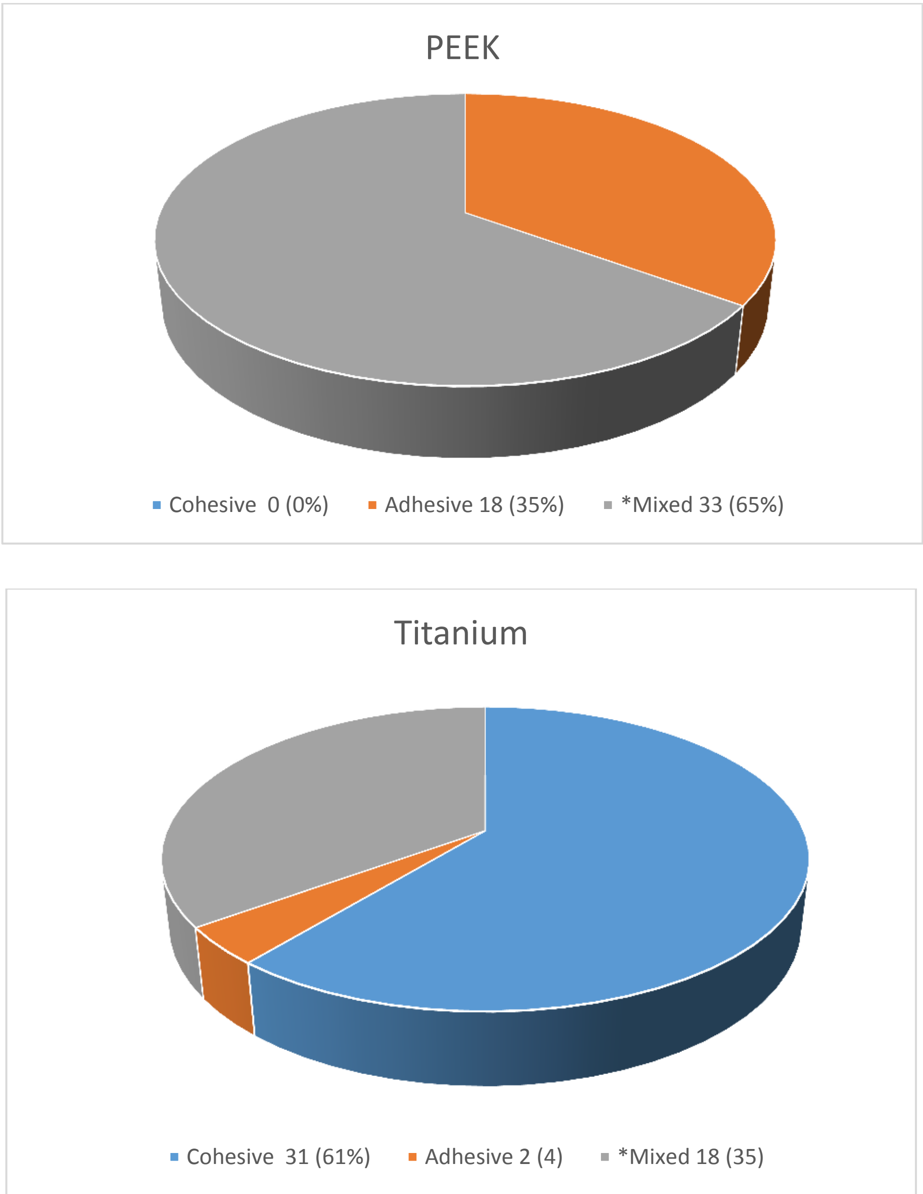
Figure 7: Bar graph depicting the SBS for PEEK and titanium

Table 3: Mean difference and average of the PEEK and titanium

			95%CI	
Mean difference	**Mean**	**SD**	**Lower bound**	**Upper bound**
MPa	5.23	7.77	-9.99	20.46
Average				
MPa	23.38	5.24	33.65	13.11

4.1.2. Failure mode

The images were saved so that the analysis is repeatable (Figures 9 and 10). The results are depicted in a pie chart in Figure 8. The predominant failure mode was mixed failure with 33 out of the 51 PEEK specimens showing mixed failure. Followed by 31 out of 51 titanium specimens producing cohesive failure. There were zero PEEK specimens that purely displayed cohesive failure.



* This group represents specimen that presented with a combination of cohesive and adhesive failure.

Figure 8: Pie charts depicting failure mode results for PEEK and titanium

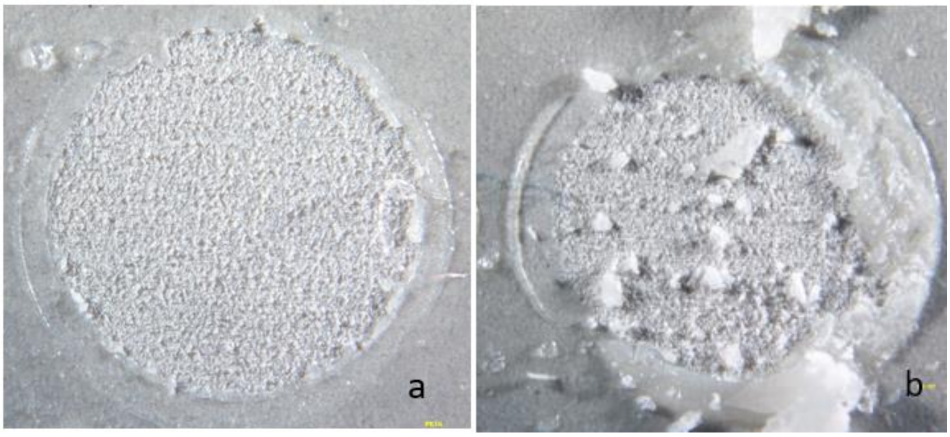


Figure 9: View of PEEK specimen at 16X magnification showing examples of different failure modes a) Adhesive b) Mixture of cohesive and adhesive failure. No PEEK specimen showed purely cohesive failure

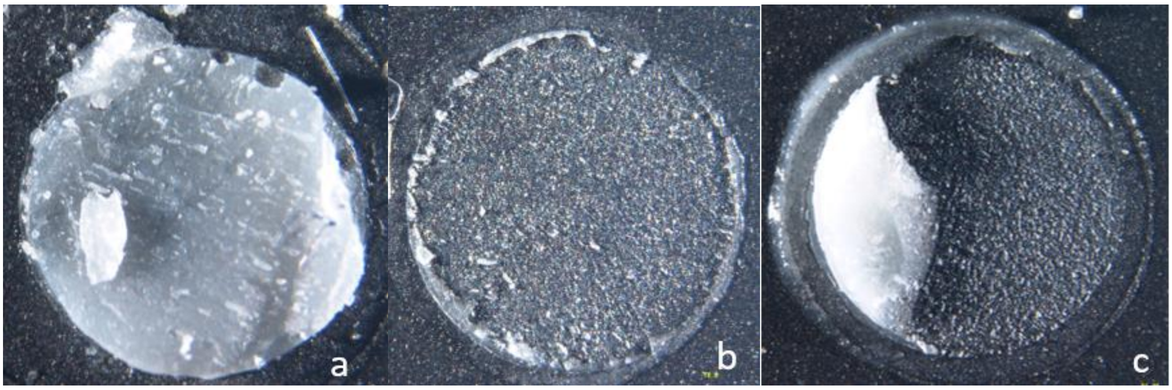


Figure 10: View of titanium specimen at 16X magnification showing examples of different failure modes a) Cohesive b) Adhesive c) Mixture of cohesive and adhesive failure

4.2. Inferential statistics

4.2.1. Pearson correlation between PEEK and titanium

Pearson correlation coefficient showed that there was a significantly weak positive relationship between the SBS of PEEK and titanium (p=0.29, p=0.037) as shown in Table 4.

Table 4: Pearson correlation between PEEK and titanium

Pearson		Compressive stress load (MPa) Titanium	Compressive stress load (MPa) PEEK
Compressive stress load (MPa) Titanium	Correlation Coefficient	1	0.292*
	Sig. (2-tailed)	.	0.037
	N	51	51
Compressive stress load (MPa) PEEK	Correlation Coefficient	0.292*	1
	Sig. (2-tailed)	0.037	.
	N	51	51

4.2.2. One sample t-test

With the test value at 0, one sample t-test of the mean difference between the PEEK and the titanium showed that there was a statistically significant difference and therefore shows that the two measurements are significantly different from one another, p-value=0.00 (Table 5).

Table 5: One sample t-test

	Test Value = 0					
One-Sample Test	**t**	**df**	**Sig. (2-tailed)**	**Mean Difference**	**95% Confidence Interval of the Difference**	
					Lower	Upper
Mean difference MPa	4.806	50	0.000	5.23098	3.045	7.417

Table 6: Summary of results

Test group	Mean (*SD) MPa	P-value	Failure mode (%)
PEEK	20.76 (6.90)	0.00**	Adhesive 35 Cohesive 0 Combination 65
Titanium	25.99 (6.12)	0.00**	Adhesive 4 Cohesive 61 Combination 35

*SD= Standard deviation' **Statistically significant difference

5. DISCUSSION

This study investigated the SBS of a veneering composite resin to titanium and PEEK. The SBS of the titanium group was statistically significantly higher (p-value=0.00) than the PEEK group. Therefore, the null hypothesis was rejected.

This outcome is contrary to the findings by Jin et al., (2019). Their study however compared the SBS of composite to titanium and a modified PEEK variant BioHPP (bio high performance polymer) which is a new PEEK based polymer. It is possible that BioHPP performs differently to and super to PEEK. Further research can be conducted in future to compare BioHPP to PEEK. Also, commercially pure titanium was used in their study whereas this study used grade 5 titanium which is a titanium alloy that is stronger and less reactive. Titanium's reactive nature leads to corrosion which can adversely affect its mechanical properties. Fatigue strength and eventually tensile strength of titanium can be severely compromised by corrosion therefore causing mechanical failure. Titanium alloying elements are responsible for the formation of a continuous TiO_2 film on the surface making it more stable and biocompatible (Bhola et al., 2011).

Failure mode for the fractured interfaces was evaluated and classified. Cohesive failure was the predominant mode of failure in the titanium group with 61% of the specimens fracturing within the composite. This is the more favourable mode of failure. It indicates the strong bond between the titanium and composite resin, stronger than the bond of the particles within the composite. The titanium group was the group with the higher SBS values of the two groups under investigation. Similarly, groups with specimens that displayed more cohesive failure, were the groups with the higher bond strengths in the study by Fuhrmann et al., (2013). Therefore, it can be inferred that the bond strength of the adhesive/titanium interface exceeds the cohesive strength of the veneering composite resin. This supports the recommendation from previous studies to select MDP-containing primers or adhesive systems to obtain strong and durable bonding of composite resin to titanium (Tsuchimoto et al., 2006; Almilhatti et al., 2013; Egoshi et al., 2013). Only two titanium specimens (= 4%) presented with adhesive failure in this study. This may be attributed to an error in specimen preparation.

Most of the PEEK specimens presented with mixed failure at 65% (Figure 8). The remaining 35% showed adhesive failure. There was no purely cohesive failure in the PEEK group. It should be noted, however, that in many of the PEEK specimens categorised as ‘mixed’, a greater ratio (or proportion) of the surface showed adhesive failure. Another study reported adhesive failure as the predominant mode of failure when bonding composite to PEEK, despite the use of an MMA- containing primer (Fuhrmann et al., 2013).

Through a pilot study the optimal alumina size and sandblasting pressure was determined. The 110µm alumina grain size at 0.45MPa air pressure as in Almasri et al., (2013) was found to be optimal and therefore implemented in this study. Stawarczyk et al., (2013a) reported that PEEK specimens after air abrasion with 50 and 110µm alumina particles yielded higher roughness with the coarser 110 µm alumina particles. Subsequently, these showed higher SBS values because the higher the surface roughness, the better the bond strength. The contact area for materials to bond to is increased by the irregularities on the surface which in turn increase the mechanical retention and bond strength. The smaller grain (50µm) sizes produce adequate bond strength when coupled with acid etching as a surface treatment (Egoshi et al., 2013; Hallmann et al., 2012).

A durable bond between veneering materials and the framework is a requirement for longevity and clinical success. For PEEK and titanium frameworks, this can be achieved with chemical or mechanical surface treatment or various combinations of treatments (Egoshi et al., 2013; Hallman et al., 2012). Acid etching does increase the surface roughness and functional groups /surface polarity; however, the combination of sand blasting and the use of an adhesive without etching, as adopted in the present study, yielded sufficient roughness to produce clinically acceptable bond strength values (Jin et al., 2019; Amilhatti et al., 2013).

Many of the etchants used in the literature are strong acids in high concentrations such as 98% sulphuric acid (Stawarczyk et al., 2013a) and 50% sulphuric acid + 50% hydrogen peroxide (Hallmann et al., 2012). These acids require very specific handling, protective glasses, and apparel and fume chambers, as they are extremely hazardous. There are currently no commercially available preparations, and application of these acids cannot be accomplished safely in the dental practice or laboratory. For reasons described above, this study therefore, did not include acid etching as a surface treatment

There is a complex interaction between the substrate and the adhesive. With PEEK and titanium surfaces being the substrates in this study, a strong bond forms when the adhesive integrates with the surface and dissipates most of the energy. A strong and durable bond is an important property for adhesive bonding that can be achieved when the surface and the adhesive have reactive groups. The roughness of the surface is an important factor since it improves the mechanical anchorage of the adhesive to its substrate due to the increase in surface contact (Cognard, 2006 cited by Hallman et al., 2012). The more extensive the contact surface the more functional groups there are, leading to better cross-linking of polymers (Hallman et al., 2012). In this study, sandblasting of the PEEK and titanium surfaces improved the mechanical anchorage for the adhesive enabling the adhesive to integrate with the surface. The mechanical bonds formed are stronger than chemical bonds; they are not as susceptible to degradation and are not as sensitive to moisture (Cognard, 2006 cited by Hallman et al., 2012).

Adhesive systems have an influence on the chemical bond between the veneering composite resin and the framework material. Several studies have reported that adhesive systems that contain MDP were able to constitute a sufficiently strong bond to titanium (Egoshi et al., 2013; Tsuchimoto et al., 2006). Almilhatti et al., (2013) observed that the effectiveness of metal conditioners on the SBS of commercially pure titanium was enhanced by conditioners with phosphoric acid in their composition. The chemical affinity of the phosphoric acid group for aluminium oxide particles on the sandblasted surface enhances the bond strength (Özcan et al., 1998).

The adhesive system used in this study (One Coat 7 Universal) contains MDP. This fact may account for the high SBS values. The highest reading obtained was 37.94 MPa (Figure 7), for titanium. The same adhesive was applied on the PEEK surfaces. Although the differences between PEEK and titanium are statistically significant (p-value=0.00), the SBS values for PEEK, with a mean of 20.76 MPa, were well above the clinically acceptable value of ≥10 MPa (Behr et al., 2011).Many studies have demonstrated that the application of an MMA-containing adhesive for bonding composite to PEEK gives optimal results (Fuhrmann et al., 2013; Stawarczyk et al., 2013b; Stawarczyk et al., 2014). The use of an MMA- containing adhesive for PEEK surfaces instead of the MDP- containing one, in this study, may have yielded different outcomes. The PEEK specimen with the minimum value of 1.11 MPa (Figure 7) was probably a premature failure, but it did not have a significant effect on the overall outcome, and it was included in the analysis. Of the 51 specimens only two had SBS values below 11MPa. Their values were 1.11 and 2.23 MPa, which could be sheared off by exerting very little force. The premature failure could be due to an error during specimen preparation.

The outcome of this study shows statistically significant differences in the bond strength between composite resins bonded to titanium and PEEK. However the SBS values for both materials is well above the minimum clinically acceptable value (≥10 MPa). This proves that the combination of mechanical retention through sandblasting and chemical bonding through the use of adhesive systems, produce high bond strengths when composite is bonded to titanium and PEEK. The results reiterate what has been widely shown in the literature about the use of MDP- containing adhesive systems for optimal bonding to titanium (Tsuchimoto et al., 2006; Almilhatti et al., 2013; Egoshi et al., 2013). Repeating the study only using an MMA-containing adhesive for the PEEK surfaces may be a valuable research opportunity.

The rationale for testing SBS is because shear forces are dominant during function, and best represent the clinical scenario (Behr et al., 2003). This study only attempted to mimic the intra-oral shearing forces. There was no further attempt at creating clinical conditions such as ageing and thermocycling. The clinical performance of the materials under investigation cannot be extrapolated to the clinical scenario. While inferences can be made, clinical trials are required.

Because the mean SBS results for both groups are well above the minium clinical requirement in this study, PEEK could be used as a framework material instead of titanium particularly in cases of high aesthetic demand. This is within the clinician's discretion informed by evaluation of other variables such as parafunction or the opposing dentition.

6. CONCLUSION AND RECOMMENDATIONS

6.1. Conclusion and recommendations

The outcome of this study showed statistically significant differences in the bond strength between composite resin bonded to titanium and PEEK, which resulted in the rejection of the null hypothesis.

Within the limitations of the study, the following conclusions were drawn, and recommendations made.

1. The SBS of composite resin to titanium was greater than that of composite bonded to PEEK when the surfaces pre-treated with sandblasting and a universal adhesive.

2. The use of MDP-containing adhesive systems creates the greatest bond between composites and titanium.

3. Although titanium bonding proved to be superior, PEEK is a suitable alternative to titanium and other metals as a framework material veneered with composite resin. PEEK results exceeded the minimum clinically acceptable bond strength. Indications for its use can be established through further clinical trials.

4. Although high SBS values were obtained for PEEK, further investigations with the same methodology but using an MMA-containing adhesive system for PEEK surfaces are recommended.

7. REFERENCES

Academy of Prosthodontics. The Glossary of Prosthodontic Terms, 9th ed. J Prosthet Dent, 2017; 117(5S), pp e1-e105.

Almasri R, Drago CJ, Siegel SC and Hardigan PC. Volumetric misfit in CAD/CAM and cast implant frameworks: a university laboratory study. J Prosthodont, 2011; 20: 267-274.

Almihatti HJ, Neppelenbroek KH, Vergani CE, et al. Adhesive bonding of resin composite to various titanium surfaces using different metal conditioners and a surface modification system. J Appl Oral Sci, 2013; 21(6): 590-596.

Behr M, Proff P, Kolbeck C, et al. The bond strength of the resin-to-zirconia interface using different bonding concepts. J Mech Behav Biomed Mater, 2011; 4: 2–8.

Behr M, Rosentritt M, Gröger G and Handel G. Adhesive bond of veneering composite on various metal surfaces using silicoating, titanium-coating or functional monomers. J Dent, 2003; 31: 33-42.

Bhola R, Bhola SM, Mishra B and Olson DL. Corrosion in Titanium Dental Implants/Prostheses - A Review. Trends Biomater. Artif. Organs, 2011; 25(1), 34-46.

Dawson JH, Hyde B, Hurst M, et al. Polyetherketoneketone (PEKK), a framework material for complete fixed and removable dental prostheses: A clinical report. J Prosthet Dent, 2018; 119: 867-72.

Egoshi T, Taira Y, Soeno K. et al. Effects of sandblasting, $H2SO_4$/HCl etching, and phosphate primer application on bond strength of veneering resin composite to commercially pure titanium grade 4. Dent Mater J, 2013; 32(2): 219–227.

Fuhrmann G, Steiner M, Freitag-Wolf S, et al. Resin bonding to three types of polyaryletherketones (PAEKs) durability and influence of surface conditioning. Dent Mater, 2014; 30: 357-363.

Hallmann L, Mehl A, Sereno N, et al. The improvement of adhesive properties of PEEK through different pre-treatments. Applied Surface Science, 2012; 258: 7213–7218.

Hunter A, Archer CW, Walker PS, et al. Attachment and proliferation of osteoblasts and fibroblasts on biomaterials for orthopaedic use. Biomater, 1995; 16: 287-295.

Jin H, Teng M, Wang Z et al. Comparative evaluation of BioHPP and titanium as a framework veneered with composite resin for implant-supported fixed dental prostheses. J Prosthet Dent, 2019; 122: 383-388.

Kurtz SM and Devine JN. PEEK biomaterials in trauma, orthopedic, and spinal implants. Biomaterials, 2007; 28: 4845–4869.

Lee EY, Jun SG, Wright RF, Park EJ. Comparative study of the shear bond strength of various veneering materials on grade II commercially pure titanium. J Adv Prosthodont, 2015; 7: 69-75.

Lee K, Shin M, Lee J, et al. Shear bond strength of composite resin to high performance polymer PEKK according to surface treatments and bonding materials. J Adv Prosthodont, 2017; 9: 350-357.

Madfa AA, AL-Sanabani FA, Al-Qudami NH, et al. Use of Zirconia in Dentistry: An Overview. Open Biomater J, 2014; 5: 1-9.

Özcan M, Pfeiffer P and Nergiz I. A brief history and current status of metal and ceramic surface-conditioning concepts for resin bonding in dentistry. Quintessence Int, 1998; 29: 713-724.

Prasad S, Ehrensberger M, Prasad Gibson M, et al. Biomaterial properties of titanium in dentistry. J Oral Biosciences, 2015; 57:192–199.

Roach M. Base metal alloys used for dental restorations and implants. Dent Clin North Am, 2007; 51: 603–27 vi.

Santing HJ, Meijer HJ, Raghoebar GM, et al. Fracture strength and failure mode of maxillary implant-supported provisional single crowns: A comparison of composite resin crowns fabricated directly over PEEK abutments and solid titanium abutments. Clin Implant Dent Relat Res, 2012; 14: 882–889.

Schmidlin PR, Stawarczyk B, Wieland M, et al. Effect of different surface pre-treatments and luting materials on shear bond strength to PEEK. Dent Mater, 2010; 26(6): 553-559.

Schwitalla A and Müller W. PEEK Dental implants: A Review of the Literature. J Oral Implantol, 2013; 39: 743-749.

Stawarczyk B, Bähr N, Beuer F, et al. Influence of plasma pre-treatment on shear bond strength of self-adhesive resin cements to polyetheretherketone. Clin Oral Invest 2014; 18: 163–170.

Stawarczyk B, Beuer F, Wimmer T, et al. Polyetheretherketone-A suitable material for fixed dental prostheses. J Biomed Mater Res B Appl Biomater, 2013a; 101: 1209-1216.

Stawarczyk B, Keul C, Beuer F, et al. Tensile bond strength of veneering resin to PEEK: impact of different adhesives. Dent Mater J, 2013b; 32: 441-448.

Stawarczyk B, Thrun H, Eichberger M, et al. Effect of different surface pre-treatments and adhesives on the load-bearing capacity of veneered 3-unit PEEK FDPs. J Prosthet Dent, 2015; 114: 666-673.

Tiossi R, Gomes EA, Faria ACL, et al. Biomechanical behavior of titanium and zirconia frameworks for implant-supported full-arch fixed dental prosthesis. Clin Implant Dent Relat Res, 2017; 19: 860–866.

Tsuchimoto Y, Yoshida Y, Mine A, et al. Effect of 4-MET- and 10-MDP-based primers on resin bonding to titanium. Dent Mater J, 2006; 25: 120-124.

Yanagida H, Matsumura H, Taira Y, et al. Adhesive bonding of composite material to cast titanium with varying surface preparations. J Oral Rehabil, 2002; 29: 121-126.

Zoidis P, Papathanasiou I and Polyzois G. The use of a modified Poly-Ether-Ether-Ketone (PEEK) as an alternative framework material for removable dental prostheses. A clinical report. J Prosthodont, 2016; 25: 580–584.

Cited references

Cognard J. Some recent progress in adhesion technology and science. Comptes Rendus Chemie, 2006; 9: 13–24 cited by Hallmann L, Mehl A, Sereno N, et al. The improvement of adhesive properties of PEEK through different pre-treatments. Applied Surface Science, 2012; 258: 7213– 7218.

APPENDIX A – Turnitin report

510877:Final_research_submission.docx

ORIGINALITY REPORT

3%	4%	5%	4%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	wiredspace.wits.ac.za Internet Source	2%
2	Lubica Hallmann, Albert Mehl, Nuno Sereno, Christoph H.F. Hämmerle. "The improvement of adhesive properties of PEEK through different pre-treatments", Applied Surface Science, 2012 Publication	2%

Exclude quotes	Off	Exclude matches	< 2%
Exclude bibliography	Off		