The University Of Sheffield.

Evaluating PolyEtherKetoneKetone (PEKK) Polymer used for fabricating Fixed Prosthodontics

By:

Omar Abdullah Alsadon

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

Academic Unit of Restorative Dentistry

School of Clinical Dentistry

The University of Sheffield

February 2017

بسم الله الرحمن الرحيم

In The Name of God, Most Gracious, Most Merciful

I would like to dedicate this thesis to:

My beautiful young sister

"May"

Who sadly passed away November 5th 2015. May God rest your soul in peace as you have always filled our lives with joy and love and will still do so with all your cherished memories

My parents "Loolwah" and "Abdullah"

Your endless inspiring support, love and prayers were behind all the success in my life

My wife "Shahd"

For your loving encouragements when I most needed it and for being there for me every step of the way

And sons "Abdullah" and "Alwaleed"

For filling my life with joy and happiness

Acknowledgments

I would like to acknowledge the valuable support of my supervisors: Dr. Sarah Pollington, Dr. Duncan Wood and Dr. David Patrick for all their encouragement, advice and support in the whole PhD duration. Without their guidance and patience, the completion of this thesis would not have been possible.

A special thank you to Dr. Tony Johnson, Prof. Richard van Noort, Prof. Nicolas Martin and Dr. Robert Moorhead for their valuable consultations that helped me overcome obstacles in my research.

Also a special acknowledgement to my employer, King Saud University, Saudi Arabia, for giving me the opportunity and sponsoring my postgraduate studies in the United Kingdom.

Thank you to Dr. Thierry Copponnex and Cendres+Métaux in Switzerland for providing Pekkton® ivory used in this study and for their kind invitation to present my PhD study at the Pekkton Circle 2016 conference, 16 September 2016, in Biel-Bienne, Switzerland.

Gratitude to fellow students: Haitham, Raad, Saja, Rayan and Abulraouf for their technical help and advice in the laboratory.

And finally, thank you to all my friends, staff and students at the University of Sheffield for their kindness and support in all the past years and making me feel welcomed and at home in the beautiful city of Sheffield.

Summary

Dental alloys, and later zirconia, have been used in dentistry as frameworks for many years in making crowns and bridges veneered with ceramic e.g. feldspathic porcelain. Such methods of restoring teeth have been extensively studied both in the laboratory and clinically. Although such substructures have excellent strength there remains a large properties mismatch between these materials and bone or dentine e.g. elasticity. Furthermore, other drawbacks have been documented such as possible allergies, colouring of alloy margins, veneer chipping and excessive wear to opposing natural dentition.

Polyaryletherketone (PAEK) thermoplastic biomaterial polymers such as polyetheretherketone (PEEK) and polyetherketoneketone (PEKK) have been successfully applied in different medical applications with the latter recently being introduced to dentistry as a restorative material. The material is called Pekkton® ivory (Cendres+Métaux, SA, Switzerland) and is proposed to be used for fabricating both monolithic and bi-layered structures veneered with indirect composite resin.

The manufacturer recommends methods similar to well-established restorations such as alloy and ceramic based crowns which makes it a user friendly material for both dental clinics and laboratories. Furthermore, the material's properties such as high strength, low elastic modulus close to that of dentine, high temperature, chemical, hydrolysis and wear resistance, makes it a promising material for the replacement of tooth material.

There is little published data about this material and hence the aim of this research was to evaluate the manufacturing process, aesthetic properties, structural integrity and durability of bi-layered crowns made from PEKK based thermoplastic high performance polymer (Pekkton® ivory, Cendres+Métaux, SA) and veneered with indirect light cured composite (Vita VM LC, VITA Zahnfabrik H. Rauter GmbH & Co.KG, DE).

The processing route for Pekkton® ivory is either via milling or hot-pressing and the procedures were compared.

The polymer-based restoration was compared to equivalent zirconia and metal based bi-layered restoration systems veneered with either light cured composite resin or feldspathic porcelain.

Optical properties of each crown system were compared using a UV and visible light spectrophotometer. Structural integrity was compared for each system by testing the fracture resistance of the crowns using a universal testing machine and durability was evaluated by testing the fatigue limit and fatigue life using a fatigue chewing apparatus.

The research hypothesis is that the PEKK polymer as an underlying substructure material will perform equivalently to metal and zirconia substructures when veneered with light cured composite in the aspects of optical properties, strength and durability.

The outcome of the study established a pressing protocol for PEKK using a standard ceramic pressing furnace where the pressed samples showed no

significant differences in the CIEL*a*b* colour values, hardness or biaxial flexural strength to those samples produced via milling.

There was no significant optical difference between the systems compared, the study found no evidence of difference in the CIEL*a*b* colour value of PEKK, zirconia or metal based samples when veneered with the same composite veneer. However, zirconia based groups displayed greater translucency with the composite veneer and feldspathic porcelain veneer.

The fracture resistance of the PEKK and metal composite veneered crowns showed to be comparable, whereas zirconia based crowns demonstrated significantly lower fracture resistance.

The durability of the PEKK composite veneered crowns showed the highest fatigue limit in comparison to the zirconia and metal composite veneered crowns. Similarly they showed the highest survival rate in the fatigue life assessment under the same cyclic load. Furthermore, the fracture mode was significantly different than observed with the zirconia and metal based crowns.

The conclusion was that this material is promising for use as a restorative material and that clinical evaluation should be undertaken.

Table of Contents

List of Figures

List of Tables

Chapter 1

Introduction

Producing an ideal restorative material that will mimic the natural tooth's appearance, longevity and durability, is always the aim of dental professionals (Rueggeberg, 2002). In modern dentistry, metal alloys, resin based composites and ceramics are the most significant materials for replacement of tooth tissue, the latter two due to their aesthetic and physical properties being close to that of the natural tooth (Sadowsky, 2006, Conrad et al., 2007).

Dental Technology is the science and art of designing and making medical oral devices and restorations to restore function and improve aesthetic appearance. Such devices range from crowns and bridges to dentures and maxillofacial appliances. The different types of appliances can be classified by type of materials used e.g. polymers, metals or ceramics, and by their purpose e.g. partial or complete dentures, fixed and removable appliances or by their fabrication process.

Indirect restorations are well established in restorative dentistry, with the porcelain fused to metal (PFM) used extensively. PFM restorations were considered the benchmark in fixed dental prostheses, with good clinical survival rates outperforming those of zirconia based porcelain restorations (Sailer et al., 2007, Donovan, 2009, Heintze and Rousson, 2010, Anusavice, 2012). The advantage of PFM restorations is that their underlying framework has higher resilience in comparison with brittle ceramics and hence greater resistance to fractures from generated stresses (Aboushelib et al., 2008). The demand for more aesthetic solutions, concerns regarding the biocompatibility of bonding alloys, discolouring of the restoration margin, the desire to conserve tooth material, and increasingly the environmental impact

of materials have all led to the pursuit of alternatives (Schmalz and Garhammer, 2002, Sadowsky, 2006, Andreiotelli et al., 2009). The most notable are the all-ceramic systems and increasingly resin-based restorations. This development of restorative materials is also associated with a rapid progression of processing technologies, which in turn enables the use of previous unexplored materials.

Recently, in the medical and dental fields, polymeric materials are being used widely as restorative materials replacing materials such as titanium and zirconia (Kurtz, 2012). The advantage is that such materials could be tailored for the purpose of their application e.g. properties close the cortical bone for orthopaedic applications (Kurtz and Devine, 2007). Polyaryletherketone (PAEK) polymers, i.e. polyetheretherketone (PEEK) and polyetherketoneketone (PEKK), are examples of such high performance polymers being used as dental restorative materials and are purposed as alternatives to metal and ceramic based restorations (Tannous et al., 2012, Rosentritt et al., 2015). The latter has been recently developed as a restorative material for fixed prostheses, either monolithic or bi-layered structure where it is veneered with composite resin.

Any restorative material introduced in the market must meet many requirements before clinical use. From a clinical perspective there are certain important factors that influence their choice of restorative materials such as: biocompatibility, aesthetics, strength, longevity and cost. The manufacturing process and ease of manipulation, cost of processing, is of

particular concern to the technician and any new material must improve on those that already exist.

To date there is little published data relating to both laboratory and clinical performance of PEKK polymers, hence the reason for undertaking this research was to assess the aesthetics, structural integrity, and durability of these restorations to support their clinical use.

Chapter 2

Review of Literature

2.1. Dental Crowns: Overview of restorative materials and methods

Through time, dentistry has been practiced in various ways using rudimentary materials and methodology. There is no clear record of dentistry beginning, but evidence in human teeth older than 6000 years suggests beeswax was used as a restorative material (Bernardini et al., 2012). In the 1830s, Elias Wildman used dental ceramic with properties close to that of natural teeth to make aesthetically acceptable appliances (Southan, 1970). In more recent times, an Italian dentist called Guiseppangela Fonzi was the first to introduce single porcelain teeth in the early nineteenth century, and by the mid nineteenth century, Charles Goodyear had produced Vulcanite rubber that led to dental prostheses becoming available to the general population (Little, 1982).

There are now different reasons for restoring or replacing teeth. Restorative work may be undertaken due to caries, trauma or purely for aesthetic reasons (Deligeorgi et al., 2001). The choice of restorative material is complex, but most significantly it should not cause any damage to the surrounding soft tissue or compromise aesthetics (van Noort, 2007).

Dental prostheses are designed and manufactured in a dental laboratory by a dental technologist. They are fabricated using accurate impressions and models or by digital scanning the oral cavity and/or the teeth. Different materials and techniques can be chosen for processing a prosthesis depending on the clinical need, required design and cost.

Dental appliances may be considered as:

- Fixed prostheses: permanently cemented restorations such as crowns, bridges, veneers, partial crowns, inlays and onlays.
- Removable prostheses: removable complete or partial dentures.
- Orthodontic appliances: retainers, habit breaking appliances, space maintainers and active removable appliances.
- Maxillofacial appliances: extra-oral appliances including: artificial nose, ear and eye; and intra-oral appliances such as obturators, splints and surgical stents.
- Dental implants: Comprising of fixture, abutment and restoration supported.

The materials that are typically used include:

- Polymers: Polymers in dentistry can be found in different applications such as: impression materials, cements, removable dentures and fixed restorations.
- Ceramics: Various ceramics are used for different applications and are mainly known in fixed dental restorations e.g. feldspathic porcelain, leucite reinforced ceramics. In addition, these ceramics can be produced by using different techniques and methods e.g. firing, pressing and milled using the CAD/CAM technique.
- Metals: Precious and non-precious alloys can be used in fixed restorations and in removable frameworks (chrome cobalt).

Crowns and bridges became a popular technique for the restoration of severely damaged teeth in the 1970's. The Adult Dental Health survey in the UK (2009) revealed that around 37% of elderly people have had a crown fitted with an average of three crowns per person, which is about 47.6 million crowns (Steele and O'Sullivan, 2011). Such crowns can be made of a single material, which is called a monolithic crown, for example a full gold crown; or of different materials in bilayered crowns, which are composed of a substructure and compatible veneering material.

Full metal crowns are well established for restoring teeth, usually in the posterior region where aesthetics are not essential. Due to their superior strength, full metal crowns are able to be fabricated in thin section (0.5mm), therefore less tooth reduction is required compared to high strength ceramic core restorations such as zirconia, even in patients with a heavy occlusion (Walmsley, 2007). Gold alloy is favoured in constructing full metal crowns due to its biocompatibility, corrosion resistance and accuracy. However, the desire for aesthetic dental restorations has led to the development of dental ceramics.

2.2. Ceramics in Dentistry

In 1903, Land was the first to succeed in producing a full ceramic crown by building feldspathic porcelain on a foil (Land, 1903). Pincus followed the same method for making ceramic veneers for actors in Hollywood in the 1930s (Pincus, 1938). These early all-ceramic attempts and techniques were prone to fracture and chipping.

A stronger ceramic coping was introduced by McLean and Hughes in the 1960's, who combined alumina with feldspathic ceramic, which became known as the porcelain jacket crown (PJC) using foil firing technique (McLean and Hughes, 1965).

At the same time an alternative approach in dental ceramics was being developed by MacCulloch who used a ceramic developed from the cookware industry to cast ceramic teeth (MacCulloch, 1968).

In the 1980s, castable ceramics were introduced to the dental field called Dicor all-ceramic crowns (Dicor, Dentsply International, York, PA, USA) benefiting from improved ceramic properties i.e. strength, biocompatibility and colour stability. This system used the lost-wax technique, giving this technique a foothold in dental clinics and laboratories (Malament and Grossman, 1987, Evans, 1996, Shillingburg, 1997). Dicor copings could be veneered with feldspathic porcelain (sometimes called Willi's glass crowns), after discarding the initial shading method using colorant glass (Geller and Kwiatkowski, 1987). Castable ceramics had some drawbacks such as microporosities leading to restoration cracks and added shrinkage caused by crystallisation heating (Schaerer et al., 1988). Such crowns showed good aesthetics but were susceptible to fracture especially in the posterior region and currently are not used in the field (Anusavice and Phillips, 2003).

In the same period, a significant advancement was being developed in the bonding techniques between the tooth structure and the restoration. Here resin was being used to adhere to an etched (with 5% and 7.5% hydrofluoric

acid) surface of ceramic. This gave rise to the resin bonded ceramic restoration (Horn, 1983, Calamia and Simonsen, 1984), resulting in aesthetic restorations using the underlying tooth to provide the necessary strength for clinical application.

An alternative approach was also being developed creating a high strength ceramic substructure, the In-Ceram systems, where porous ceramic, (either zirconia, alumina or spinel) was originally fabricated on the die using a slip casting technique (now by milling) and heated to form a lightly sintered substructure. This is then infiltrated with lanthanum glass to create a high strength substructure which is veneered with feldspathic porcelain (McLaren, 1998).

Currently ceramic indirect dental restorations may be considered as:

- Metal –Ceramic
- High Strength core ceramic
- Resin bonded ceramic.

Which differ by the type of underlying supporting material (van Noort, 2007). The materials and indications are constantly evolving with new materials not fitting wholly into these categories. For example zirconia may now be used as a full contour restoration. Figure 1 summarises indications, materials and production method of crowns made out of: PFM, high-strength ceramic and resin-bonded ceramics.

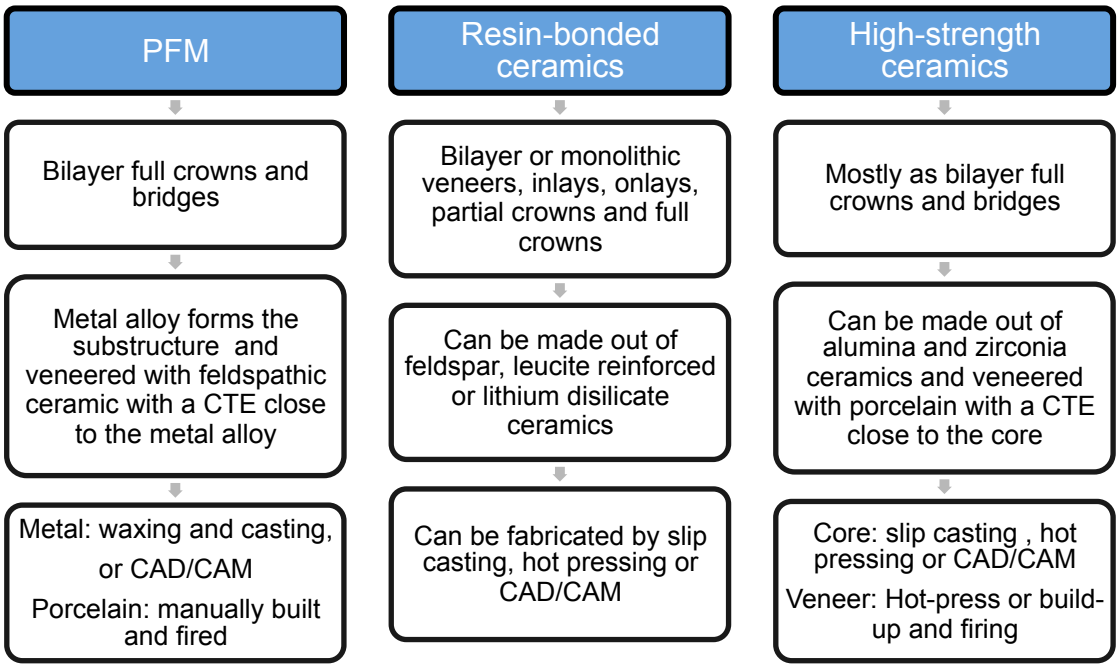


Figure 1: Diagram of indications, materials and production method of PFM, resin-bonded ceramics and high-strength ceramic crowns[*].

2.2.1. Metal Ceramic Systems

Known as porcelain fused to metal (PFM), porcelain veneer crown (PVC), porcelain fused to gold (PFG) and metal ceramic crown (Smith and Howe, 2007). This crown differs to the full metal crown in that a ceramic layer covers most of the metal substructure, improving aesthetics, while the metal substructure provides the necessary strength for the ceramic. The veneering porcelain was developed in the late 1950s by adding leucite crystals to feldspathic ceramic, thus altering the coefficient of thermal expansion (CTE) to match that of the alloy which enabled the veneering porcelain to be bonded to the underlying alloy substructure (Freese, 1959). Ceramics manufacturers have found that porcelain with a slightly less CTE than

[*] Diagram created by the author.

underlying alloy (ranging between 12-14 ($\times 10^{-6}$/°C)) makes it in the state of slight tangential compression and therefore enables greater longevity for the restoration (Kelly and Benetti, 2011).

To produce this type of restoration, the lost wax technique is used to convert a wax pattern of the substructure into a metal substructure. In dentistry, Taggart introduced this method in the early 1900s for fabricating gold inlays, which extended later for making different fixed and removable dental prostheses (Taggart, 1911). With advanced manufacturing methods, wax pattern production may be eliminated and the metal substrate can be milled directly from alloy blocks or sintered using Direct Metal Laser Sintering (DMLS) (van Noort, 2012).

The alloy properties used in making these substructures differ to those used for full metal crowns (Knosp et al., 2003). They have:

- Higher melting temperature, to resist the ceramic sintering temperature.
- Base metal content, promoting ceramic bonding by producing an oxide layer.
- CTE close to that of the ceramic veneer.
- Increase stiffness to match the ceramic to improve its resistance to cracks.

A 7 year clinical follow-up study by Coornaert et al. (1984) resulted in approx. 3% failure rate of all PFM units. According to Scurria et al. (1998), PFM

prostheses are considered reliable due to their low failure rate of just 8% over ten years. Other studies conclude that these prostheses are prone to damage mainly caused in the outer ceramic veneer chipping or fracturing (Diaz-Arnold et al., 1989).

The main disadvantages of PFM crowns are:

- The metal is opaque and not tooth coloured. Therefore an opaque layer of ceramic veneer is required to mask the metal substructure which compromises aesthetics, particularly for anterior teeth (Bello and Jarvis, 1997). Furthermore, the metal substructure may cause blue-gray stains in the surrounding soft tissue caused by corrosion (Venclikova et al., 2007).
- Allergies are a further concern with cast alloys, with reports of patients being sensitive to different elements such as nickel, cobalt, chromium, gold and palladium (Wataha, 2000).
- The extensive amount of tooth reduction required for PFM crowns, 1.2-1.5mm, which can restrict their use in certain cases.

2.2.2. Resin-bonded Ceramic Systems

Eliminating metal to produce all ceramic crowns was the approach to solve the aesthetic, biocompatibility and destructive nature of PFM crowns. The resin-bonded crown is a method of restoring teeth supported by the improvements in bonding techniques, led by Buonocore in the mid 1950s when phosphoric acid was used to modify the enamel surface to enhance bonding (Buonocore, 1955). Later in the 1970s, resin cement was proposed to

cement and support ceramic veneers followed in the 1980s by the advances in dental ceramic etching methods combined with silane coupling agents (Rochette, 1975, Calamia and Simonsen, 1984).

These ceramic restorations are indicated for anterior teeth with high aesthetic demand in low mastication load situations, and are bonded to the remaining tooth for support (Blair et al., 2002). Resin-bonded glass ceramics strengthened with leucite are considered one the most aesthetic dental ceramics (Della Bona and Kelly, 2008). The addition of leucite to feldspathic glass improves the strength of the ceramic without affecting the translucency and hence the aesthetics. Furthermore, leucite is susceptible to selective etching, therefore allowing micromechanical bonding (Kelly and Benetti, 2011).

Resin-bonded ceramic crowns may also be produced from lithium-disilicate ceramics, which have better mechanical properties than leucite reinforced ceramics (Magne et al., 2010). For example, the flexural strength and fracture toughness for lithium-disilicate is around 400 MPa and 3.3 $MPa.m^{1/2}$ respectively in comparison to 112 MPa and 1.3 $MPa.m^{1/2}$ respectively for leucite reinforced ceramics (Holand et al., 2000). These restorations can be in the form of inlays, onlays, veneers, partial crowns and full crowns or short span bridges. Their surface can be micro-mechanically modified allowing bonding of the restoration to the underlying tooth structure enabling minimal tooth preparations to be employed (Smith and Howe, 2007). The micro-mechanical features are created by either etching with hydrofluoric acid or by shot-

blasting with Al_2O_3 particles followed by the application of a silane coupling agent to form chemical bond (Hooshmand et al., 2002).

A failure rate of 4.8% was observed in an 11-year clinical retrospective study by Fradeani and Redemagni (2002), undertaken on 124 leucite reinforced glass ceramic crowns, with a higher failure rate recorded in the posterior (15%) compared to anterior region (1.1%). Burke (2007), in a four year prospective study involving 48 anterior full coverage resin-bonded leucite reinforced ceramic crowns, reported a failure rate of 6%. Lithium disilicate anterior and posterior crowns had a failure rate of about 5% according to a 5-year long clinical observation by Toksavul and Toman (2007) involving 79 crowns and 21 patients.

Table 1 show examples of some resin-bonded ceramic system, their fabrication method and trade names.

Table 1: Typical resin-bonded ceramic systems, materials and their fabrication methods.

Material	Fabrication method	System
Feldspathic glass ceramic	CAD/CAM	Vita® Mark II (Vita Zahnfabrik H. Rauter GmbH & Co, Germany)
Leucite reinforced glass ceramic	Hot-press	IPS Empress® 1 (Ivoclar Vivadent AG, Liechtenstein)
Lithium disilicate glass ceramic	Hot-press or CAD/CAM	IPS e.max® (Ivoclar Vivadent AG, Liechtenstein)

2.2.3. High-strength Core Ceramics

All-ceramic restorations may also be produced with a strong ceramic core to support a porcelain veneer rather than a metal substructure. One of the first attempts was in the mid 1960s resulting in the porcelain jacket crown (PJC) with added alumina (about 50%) to feldspathic porcelain, supported and fired on a platinum foil and later a refractory cast (McLean and Hughes, 1965, van Noort, 2007).

A later development in the 1980s was the addition of more alumina (about 70%) to strengthen the substructure, which was processed using the slip-casting technique and infiltrated with lanthanum glass before veneering with conventional porcelain (Scotti et al., 1995). This In-Ceram technique (Vita Zahnfabrik H. Rauter GmbH & Co, Germany) produced a porous coping, which was infiltrated with molten glass (Denry, 1996). The glass infiltration step was necessary to seal off the porosities of fired alumina which also improved the overall strength of the structure with a biaxial flexural strength of about 350 MPa, flexural strength of about 440 MPa and fracture toughness of about 4.5 $MPa.m^{1/2}$ (Probster and Diehl, 1992, Seghi and Sorensen, 1995, Wagner and Chu, 1996).

VITA introduced further variants of In-Ceram; Spinel using magnesium aluminate spinel instead of alumina, which gave better aesthetics results but was weaker than the In-Ceram Alumina with a flexural strength of 378 MPa (Seghi and Sorensen, 1995, Kelly et al., 1996). Later a zirconia- alumina matrix was added to the range with improved strength with a flexural strength of

about 600 MPa (Seghi and Sorensen, 1995, Rimmer, 2006). The In-Ceram Alumina, Spinel and Zirconia ceramics all used slip-casting as a production method and later CAD/CAM production was used for milling these ceramics in their green stage before sintering at high temperatures.

At approximately the same time, pure alumina-based substructures were introduced enabled by advanced manufacturing technologies. Procera AllCeram™ (Nobel Biocare AB, Sweden) produce an over sized alumina coping from a CAD file which contracted to the required size during firing at approximately 1600°C. (Kelly, 2004, Rimmer, 2006).

Each of these systems may be considered as high strength ceramic substructure systems, supporting weaker veneering ceramics and relying on mechanical retention rather than adhesive bonding.

A six year study conducted by Segal (2001) on In-Ceram Alumina crowns made using the slip-casting production method found a failure rate of approximately 1.1% for 177 anterior crowns, and about 0.8% for 369 posterior crowns. Another study observing 101 In-Ceram Alumina crowns produced via the CAD/CAM production route demonstrated a failure rate of around 3% for anterior crowns and 12% for posterior crowns in a five years study by Kokubo et al. (2011). Forty slip-casted In-Ceram Spinel anterior crowns showed a failure rate of about 2.5% according to Fradeani et al. (2002) in a 5 year study. The failure rate was higher at about 8% in another five-year study by Bindl and Mormann (2004) on 18 anterior In-Ceram Spinel crowns produced using CAD/CAM method. A six-year study on Procera Alumina crowns showed a

failure rate of about 3% for 61 anterior crowns, and about 8.5% for 46 posterior crowns (Walter et al., 2006).

2.2.3.1. Zirconia

The most recent addition to the high strength ceramic systems is zirconia. Due to its desirable mechanical properties, zirconia can be found in different applications from industrial machinery, to furnaces and aerospace manufacturing (Lee and Rainforth, 1994). It is also considered as a biocompatible material and hence it is widely used in the medical field in fabrication of different body implants (Della Bona et al., 2015). By the end of the 1990s, about 300,000 hip joints made of zirconia in Europe and USA were implanted (Ghevalier et al., 1997).

The first use of zirconia was in the 18th century where a chemist in Germany called Martin Heinrich Klaproth discovered zirconium oxide (Vagkopoulou et al., 2009). In the medical field, zirconia was suggested for fabricating femoral heads implants from the late 1960's, replacing titanium and alumina (Helmer and Driskell, 1969). Hundreds of thousands of zirconia femoral heads were widely used around the world until the early 2000s when the failure of hundreds of them in a short time frame caused a severe drop in demand. Despite that, dental professionals at the same time started using zirconia for prosthodontics because of its aesthetics and mechanical properties, unconcerned with the failure associated with femoral heads (Chevalier, 2006).

Zirconia high strength ceramic (BFS of 1000 MPa) with its major component as zirconium oxide (ZrO_2) is usually stabilised with different oxides such as yttrium oxide (Y_2O_3) and magnesium oxide (MgO) (Denry and Kelly, 2008, Ozcan et al., 2011).

Pure zirconia undergoes phase changes when heated and cooled. At room temperature it demonstrates a monoclinic structure and when heated to 1170°C it changes to tetragonal and then to cubic phase at temperatures exceeding 2370°C. When left to cool, a reverse phase transformation takes place from tetragonal to monoclinic phase causing expansion that stimulate stresses which eventually may cause the zirconia to fail (Piconi and Maccauro, 1999).

Stabilising zirconia with metal oxides such as calcium, magnesium and yttrium oxides, prevents failure caused by this phase-to-phase reverse transformation by stabilising the tetragonal zirconia at room temperature, preventing cracks from generating and simultaneously improving its mechanical properties (Heuer et al., 1986, Kelly and Denry, 2008).

The mechanical properties of zirconia are also dependent on its grain size, having increased strength with smaller grain size, and larger grain size increasing toughness (Ruiz and Readey, 1996). The heat treatment (sintering) temperature and duration can affect the stability and mechanical properties of the final zirconia structure e.g. larger grains are associated with higher and longer heating rates (Ruiz and Readey, 1996, Chevalier, 2006).

In its application for prosthodontics, yttria partially stabilized tetragonal zirconia (Y-TZP) is one of the most commonly used zirconia ceramic for fabricating substructures due its favourable mechanical properties (Kosmac et al., 2000).

CAD/CAM has enabled the fabrication of zirconia dental restorations by allowing the material to be milled in a green (pre-sintered) state from either a block or disc shaped blanks before sintering (Figure 2). The alternative is to mill fully sintered blocks that are hard-milled using a CAD/CAM system e.g. Everest ZH, KaVo Dental GmbH, Germany.

The soft-milled zirconia has to be sintered in a furnace rising at a steady rate until reaching approximately 1500°C. This process reduces pores between the particles, causing the structure to shrink (Figure 3) and increases the strength (Lee and Rainforth, 1994).

Figure 2: Different shapes of zirconia blanks (Vita In-Ceram YZ) for different CAD/CAM systems and applications.

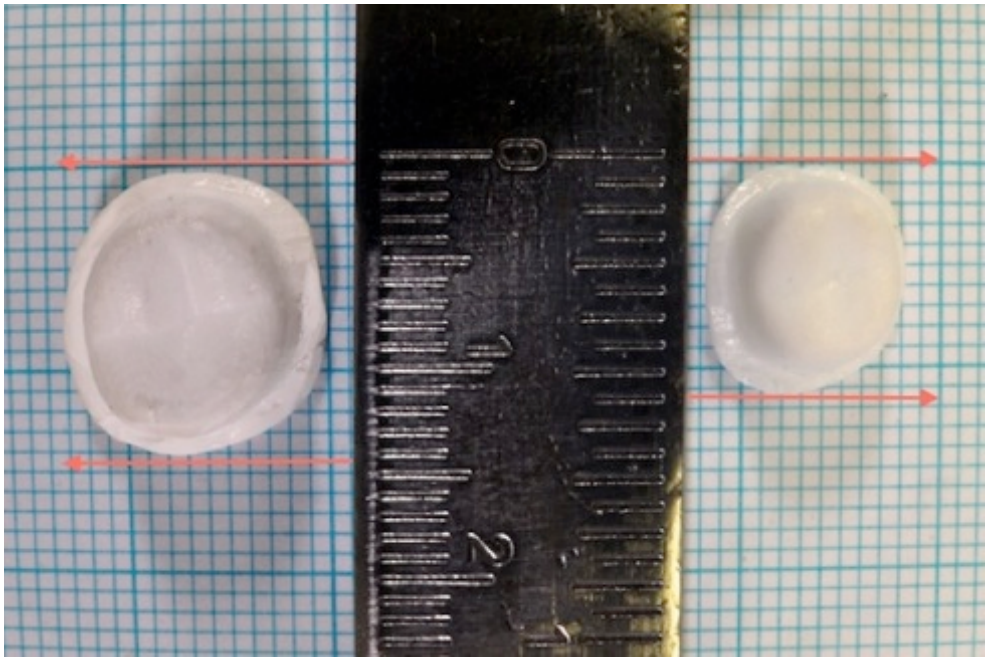


Figure 3: Zirconia substructure before sintering on the left and after sintering on the right showing about 20% reduction in volume (Alsadon, 2012).

The sintered zirconia colour is opaque white, which is the reason behind veneering them with feldspathic porcelain (Kim and Kim, 2014). The high crystallinity and density of zirconia causes this high opacity (Harada et al., 2015). However, it could be considered as semi-translucent ceramic as it allows some light to pass through it (Baldissara et al., 2010).

Zirconia's high opacity could be considered as one of the downsides with zirconia based restorations when in comes to replacing anterior teeth (Zhang, 2014). On the other hand, the opacity of substructures is sometimes advantageous, for example when masking dark coloured teeth or metal posts (Baldissara et al., 2010).

The zirconia substructure can be shaded to allow the translucent porcelain veneer better aesthetics or can be used as a monolithic restoration when glazed and polished. This eliminates any risk of the veneer chipping and is particularly suitable for the posterior region were these restorations shows an acceptable level of aesthetics for patients requiring non-metal crowns (Marchack et al., 2011).

Zirconia shading is achieved via different approaches such as mixing metal oxide with zirconia powder and by immersing the milled zirconia restoration in chloride solutions with different elements such as nickel, iron and erbium, for a period of time depending on the required shade before the sintering procedure (Suttor et al., 2004, Shah et al., 2008).

An additional technique for fabricating zirconia substructures (with cerium-tetragonal polycrystal), is via an additive technique called electrophoretic

deposition (EPD) (Vagkopoulou et al., 2009). This technique uses electricity charges to pack ceramic particles to build the desired shape out of green-stage zirconia which is then sintered to create a highly dense ceramic structure (Moritz et al., 2006).

A common procedure in dentistry is modifying the ceramic surface for either bonding or cementing purposes. These require shot-blasting or grinding which may stimulate the reverse transformation and hence cause residual stresses (Chevalier, 2006, Denry and Kelly, 2008). Forming microcracks is a concern in zirconia due to aging or low temperature degradation (LTD) (Swab, 1991). This phenomena is stimulated in wet environments which slowly changes the zirconia's tetragonal to monoclinic phase transformation causing microcracks (Piconi et al., 1998). To prevent such a problem, it is highly recommended to ensure full ceramic veneer coverage to the zirconia substructure to protect from the surrounding oral fluids (Koutayas et al., 2009).

Studies suggest that zirconia can be used for fixed bridges in the posterior region, as stated by Suarez after a 3 year study involving 18 zirconia fixed bridges resulting in one failure which was caused by root fracture (Suarez et al., 2004). Veneering with feldspathic porcelain improves the restoration appearance but has the downside of being prone to failure (Koutayas et al., 2009). The veneer failure mode is mostly chipping and is considered as a common problem in zirconia fixed partial dentures (Sailer et al., 2006, Manicone et al., 2007, Hammond, 2009, Koutayas et al., 2009, Sailer et al., 2015). Such failure is thought to be caused by the interface between the

veneer and substructure failing due to several reasons (Aboushelib et al., 2007). One suggested reason is the mismatch of CTE between the veneer and substructure. Rekow et al. (2011) postulated that the porcelain veneer CTE mismatch causes added residual stress to the already existing stresses caused by the zirconia's transformation toughening, and hence raise the chance of veneer failure.

Ceramics for zirconia veneering have a very similar CTE to that of zirconia and because of that it is thought by Denry and Kelly (2008) that this small difference in CTE between veneer and substructure is an implausible cause to failure.

Further causes that can be related to the ceramic veneer include veneer shrinkage associated with firing and low wetting to the zirconia substructure (Aboushelib et al., 2006). Poor designing of the zirconia substructure and the ratio between substructure and ceramic veneer is also thought to be a logical reason for the veneer failure (Denry and Kelly, 2008).

Other potential concerns regarding zirconia based restorations are the wear they could cause on the antagonist natural teeth (Stawarczyk et al., 2011).

In addition, the un-etchable zirconia surface can cause a poor marginal fit to the restoration and hence leakage (Ozcan et al., 2008). This can be associated with CAD/CAM ceramic restorations, where the error could occur while configuring the margin in the scanning and designing stage, plus the machining of the irregular crown shape and the later sintering shrinkage can affect the internal fitting of the crown (Reich et al., 2005).

A systematic review by Heintze and Rousson (2010) on zirconia and PFM restorations showed in studies including both systems that veneer chipping over three years was approximately 54% for zirconia cores and 34% for PFM and, when taking all grades of veneer chipping into account, the survival rate was 90% for zirconia and 97% for PFM restorations.

Table 2 shows examples of commercially available zirconia for prosthodontics and their fabrications process.

Table 2: Typical zirconia systems, materials and used CAD/CAM system (information from these companies' websites).

Brand	Material	CAD/CAM system
Denzir (Cad esthetics AB, Sweden)	Pre-sintered blanks of: Hot isostatic pressed yttrium oxide stabilized zirconium dioxide	• Milled in company's centre.
Ceramill zi (Amann Girrbach AG, Austria)	Pre-sintered blanks of: zirconia oxide with yttria stabilized tetragonal zirconia polycrystals.	• Ceramill motion® • Milled in company's centre.
Cercon Zirconia (DeguDent GmbH, Germany)	Pre-sintered blanks of: Yttria stabilized tetragonal zirconia.	• Cercon® CAD/CAM • Milled in company's centre.
ZS KaVo (KaVo Dental GmbH, Germany)	Pre-sintered blanks of: yttrium stabilised zirconium oxide	• KaVo Everest®. • KaVo Arctica®.
Vita In-Ceram YZ (Vita Zahnfabrik H. Rauter GmbH & Co, Germany)	Pre-sintered blanks of: yttria partially stabilized zirconia	• Sirona® inlab CAD/CAM. • Open source CAD/CAMs.
Lava Frame Zirconia (3M ESPE AG, Germany)	Pre-sintered blanks of: Yttria stabilized tetragonal zirconia.	• Lava™ All-Ceramic CAD/CAM system.

2.3. Manufacturing Procedures for Indirect Restoration

Rapid changes in restorative materials have led to the use of advanced manufacturing techniques to fabricate dental restorations. The porcelain fused to metal (PFM) manufacturing route is relevant as a comparison to other newer materials and equipment. Following tooth preparation, an accurate impression of the prepared tooth is made. A Class IV die stone is used to produce a sectional model. The crown pattern is manually formed using wax before using the lost wax process to create the metal structure via casting. After cooling, the metal substructure is prepared by shot-blasting with alumina particles and finished with burs, e.g. carbide burs. The framework surface is prepared for bonding by heating in a vacuum furnace at about 900°C to create an oxide layer. Three main parts form the ceramic veneer: opaque (masks the metal colour and improves the bond), dentine (form the coloured crown shape) and enamel (translucency along the edges). In addition, staining colours can be added to the crown to mimic the natural adjacent teeth. The crown is then glazed to shine and seal any porosity.

Replacing the metal substrate with ceramic may be achieved using the same lost-wax technique, however a ceramic ingot (lithium disilicate) is heated and pressed into the mould rather than a metal cast.

2.3.1. Hot-Pressing Technique

The coping is produced in wax and invested in a phosphate bonded material and heated in a furnace for wax elimination. A pressing furnace (Figure 4) is then used to heat and press the ceramic in the heated ring after placing the

ceramic ingot and a plunger (usually made of Al_2O_3) in the furnace. Hot pressed high strength ceramics crowns can be used as a monolithic structure or veneered with feldspathic porcelain in a similar manner to PFM crowns. Early attempts can be traced to the late 1960's when Droge used flask and investment material following a complete dentures fabrication concept to press ceramic. Later in the 1980's, the IPS Empress system was produced as a result of collaboration between the University of Zurich and Ivoclar dental company (Dong et al., 1992). The ceramic in this system was provided as an ingot comprising of feldspathic porcelain combined with leucite crystals (Beham, 1991). In the late 1990s, a newer generation was introduced, the IPS Empress 2 (lithium disilicate glass ceramic) as an improved ceramic, which can be used for short span bridges (Culp, 1999). The currently available lithium disilicate ceramic is under the name IPS e.max (Ivoclar Vivadent Inc).

Figure 5 summarises the steps involved in crown manufacturing via hot pressing.

An alternative production route for fabricating crowns (including all-ceramics) is the CAD/CAM technology.

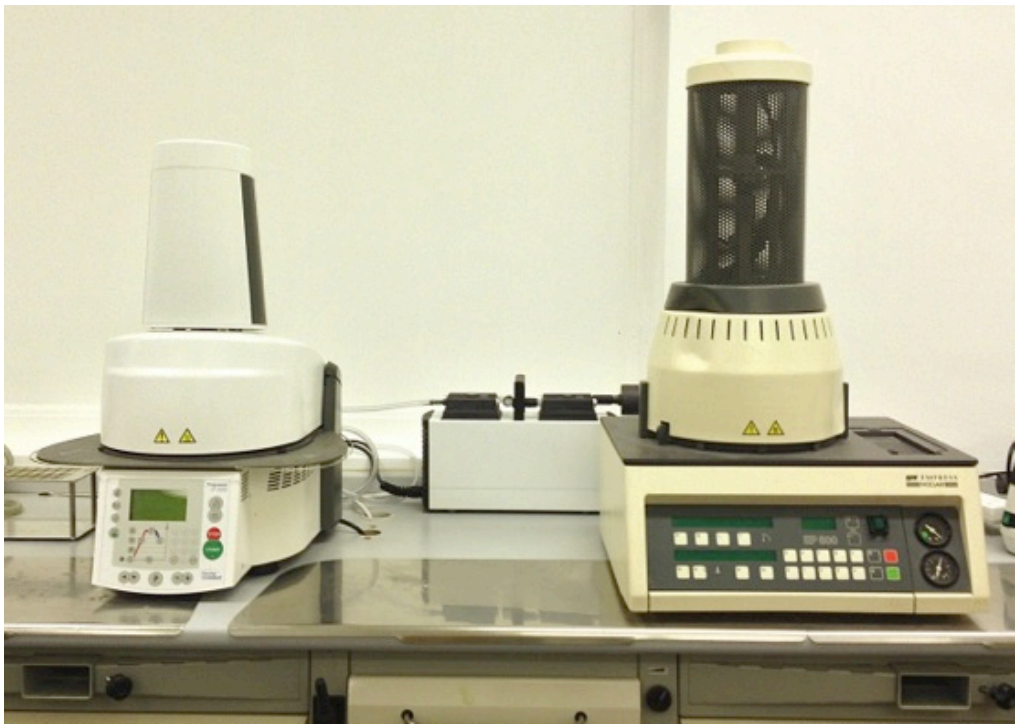


Figure 4: Pressing furnaces (Ivoclar EP300 left and IPS Empress Ivoclar right).

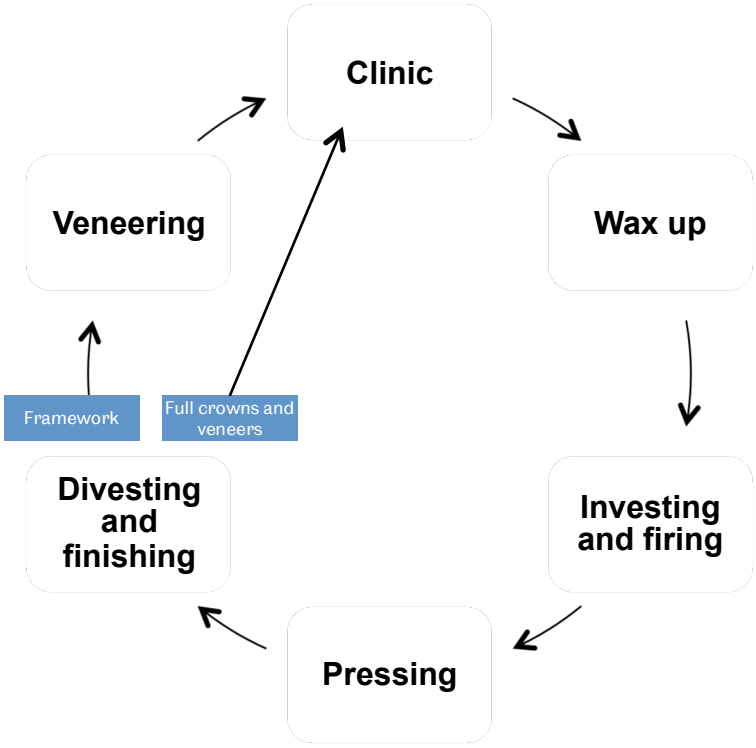


Figure 5: Restoration fabrication process when using hot-pressing method*.

* Diagram created by the author.

2.3.2. CAD/CAM

CAD stands for Computer Aided Design and CAM is for Computer Aided Manufacture. This fabrication method depends on three main parts:

- Data acquisition: using intra or extra-oral scanner.
- Restoration design: using CAD software.
- Restoration production: CAM of advanced manufacturing.

Such technology was first used in industry more than 60 years ago (Rekow, 2006). In the 1970s, CAD/CAM was introduced for dental applications but with limitations such as primitive camera resolution of scanners, chipping of sharp margins and large, high priced machines (Miyazaki et al., 2009). One of the earliest CAD/CAM systems was called Sopha and was developed in the early 1970s establishing the technology in the field of Prosthodontics (Duret and Preston, 1991). The CEREC system was introduced in the mid 1980s as a clinical based machine capturing the preparation inside the mouth using an intra-oral camera before processing the ceramic restoration (Mormann et al., 1989).

Procera, developed later in the 1980s, utilising the technology by scanning the model and milling at the company's central processing centre rather than in the dental laboratory or clinic (Andersson and Oden, 1993).

The restoration fabrication procedure is similar to that described for a PFM with individual steps utilising different technologies. The impression step can be replaced by scanning the prepared tooth with an intra-oral camera. The data may also be gained from the stone model using an extra oral scanner.

The pattern is produced digitally using design software. The design is then used to manufacture via milling the chosen material from a block or disc blank or via advanced manufacturing using selective electron beam melting, laser powder forming and inkjet printing (van Noort, 2012).

The milled material may be simply polished and fitted or require further processing by the dental technologist e.g. sintering and veneering (Figure 6). The range of materials is continually expanding, and varies depending on the required restoration e.g. monolithic crowns or substructures to be veneered. Types of materials this range can include are:

- Alloys (e.g. titanium).
- Glass ceramics (e.g. feldspathic ceramic Vita Mark II and lithium disilicate IPS e.max CAD).
- High-strength ceramics (e.g. yttria stabilised zirconia In-Ceram YZ).
- Polymers (e.g. Fibre reinforced polymer Everest C-Temp)
- Wax (For lost wax investing to create alloy restorations e.g. the acrylic Vita CAD-waxx).

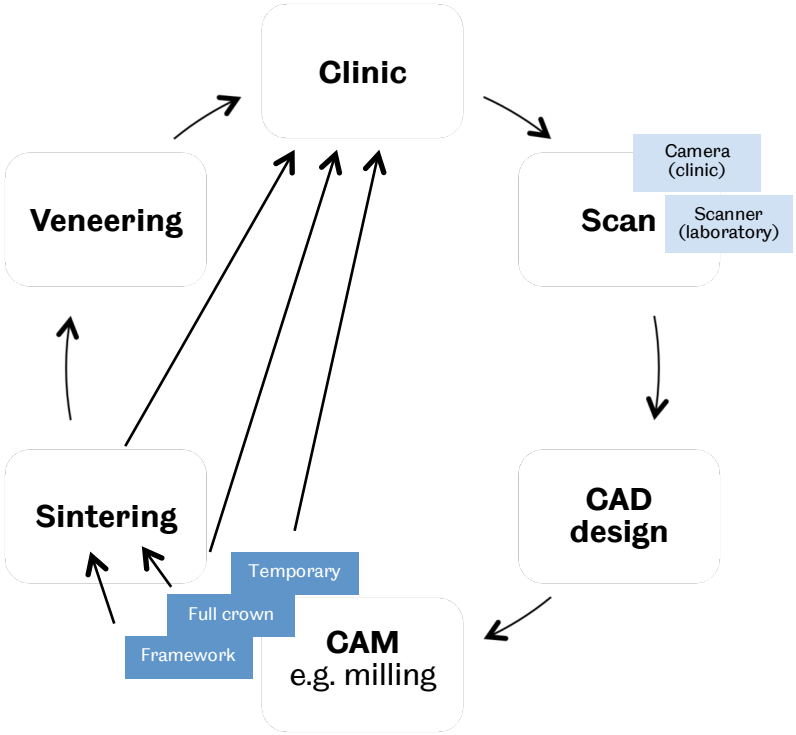


Figure 6: Restoration fabrication process when using CAD/CAM method*.

CAD/CAM systems may be categorised depending on manufacturing CAM or milling to:

- Chair-side: Based in the clinic with no need for the dental laboratory, which saves time and can have the restoration ready for the patient in one visit. This route is limited to single units such as crowns, inlays and onlays made out of ceramics and composites.
- Laboratory-based: This enables much more flexibility in the restoration designs (e.g. crowns, fixed and removable dentures) and in the selection of materials (e.g. alloys, high-strength ceramics and polymers). Also, ceramic and composite can be used to veneer the milled substructure

* Diagram created by the author.

using dental technology conventional methods e.g. build-up and firing, ceramic hot pressing and light curing composites.

- Milling centres: In this method, the stone model or the digital scanned prepared tooth or designed restoration is sent to a certified production centre where the restoration is milled. Most cases are for substructures where they are sent back to the dental laboratory to be veneered. This method could be useful for dental practises that cannot afford the cost of milling units or CAD/CAM systems.

CAD/CAM can be a closed or open system. Closed systems (Figure 7) are usually sold as a complete set comprising of a scanner, software and milling unit, where they work in closed circuit not allowing the use of other software or devices of other brands. Open systems, where data files can transfer between devices allowing usage of different scanners, designing software and milling units (Figure 8).

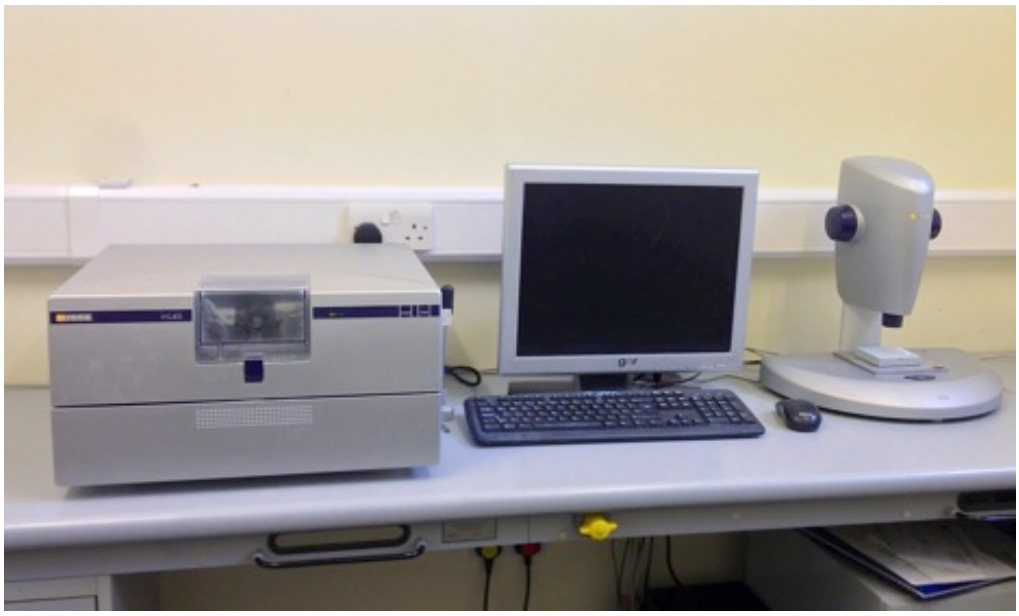


Figure 7: Typical example of closed CAD/CAM system is the CEREC inLab (Sirona Dental Systems LLC) showing the scanner on the right and the 2-axis milling box on the left.

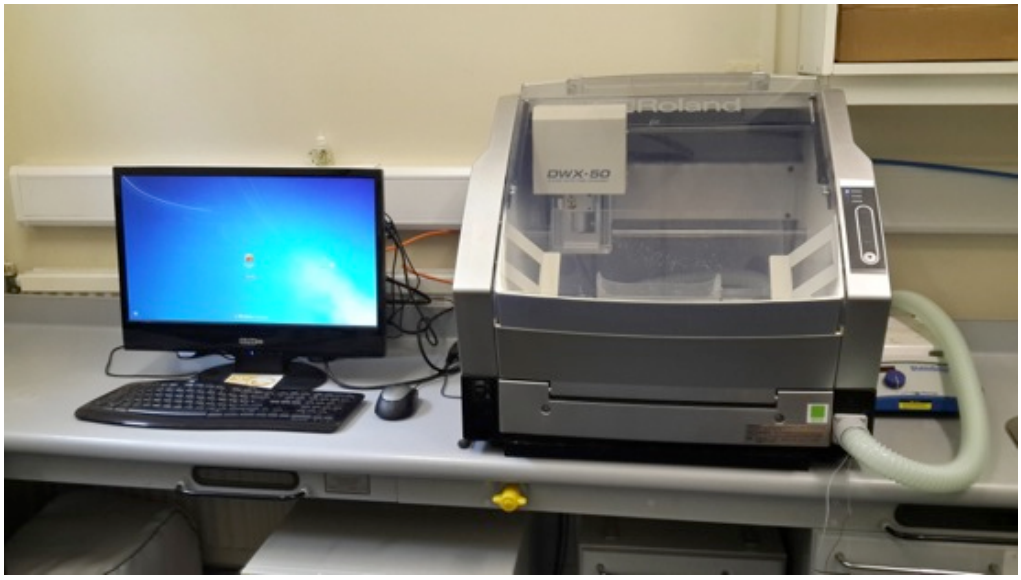


Figure 8: Typical example of open source CAD/CAM is the Roland DWX-50 (Roland DGA Corporation) showing the 5-Axis milling box on the right.

2.4. Polymers in Dentistry

Polymers are used extensively in dentistry for different applications from impression materials to base materials for dentures and as direct composite restorative materials. The idea of using plastic materials for replacing teeth goes back many years, but rarely have they fulfilled the ideal properties for fixed prosthesis particularly in terms of rigidity and colour instability (Peyton and Craig, 1963). An affordable removable denture in the mid 1800s was made by Goodyear using hard rubber called vulcanite (Gorgas, 1891). In 1869, Celluloid was developed as an affordable restorative material (Bremner, 1959). In the late 1890s, gutta-percha was used in dentistry as a restorative material and crown fabrications benefitting from the hard and light flexible rubber like texture, plus the high melting temperature (Anusavice and Phillips, 2003, Rueggeberg, 2002).

Vulcanite denture material was replaced in mid 1930s by a superior material activated by heat called Vernonite, also known as polymethylmethacrylate (PMMA). It was used for constructing dentures and by the 1940s its application had extended to fixed indirect restorations (Peyton, 1975). This growth in application was expanded considerably with the production of cold cured acrylics allowing polymerisation at room temperature (Glenn, 1982). PMMA is a thermosetting polymer material that consists of a polymer powder and monomer liquid. The powder comprises:

- PMMA beads: critical for the resin structure.
- Benzoyl peroxide: polymerisation initiator.

- Colorants: mimic oral tissue.

The liquid comprises:

- Monomer (Methyl methacrylate): Building blocks for polymerisation.
- Glycol dimethacrylate: cross-linking agent.
- Hydroquinone: inhibitor to prevent adverting polymerisation.

After mixing the liquid and powder, the dough like structure is processed most commonly by pack moulding or by injection moulding. Thermosetting polymers, when subjected to heat, undergo a chemical reaction hardening the polymer to the desired shape after cooling. It cannot be reshaped when heated again to the same temperature as it does not soften.

Thermoplastic polymers differ to thermosetting polymers in their behaviour at high temperatures. They soften when heated to glass transition temperature (T_g) and can be formed to the desired shape before cooling to harden again and can be again softened and reshaped without being damaged. In the past, different restorative thermoplastic materials were introduced for fabricating removable dentures and orthodontic appliances (Eid, 1971, Ponitz, 1971). Negrutiu et al. (2005) stated that thermoplastic materials were commercially available in dentistry by mid 20th century and an example is a material called Flexiplast (Bredent, Germany). The material's flexibility was an advantage to patients but the material could not withstand occlusal loads, thus could not be used in areas with direct masticatory loads (Lindauer and Shoff, 1998, Phoenix et al., 2004).

2.4.1.1. Polyaryletherketone (PAEK) High-Performance Thermoplastic Polymers

Polyaryletherketones (PAEK) are high performance thermoplastic polymers renown for different industrial applications due to their physical and chemical stability and high melting temperature (Margolis, 1985). Polyetherketoneketone (PEKK) was the first PAEK family member to be introduced in 1962 (Bonner, 1962). PAEK polymers are formed from an aromatic backbone molecular chain with ketone and ether groups shaping the structure. In the 1980s, PAEK thermoplastic polymers extended their industrial uses to the medical field as a biocompatible material (Williams et al., 1987). These polymers are synthesised and processed in two main ways: electrophilic or nucleophilic methods. Electrophilic techniques are considered expensive and may result in a thermally unstable outcome and other techniques achieve thermal stable products but lack biocompatibility (Kurtz, 2012). The nucleophilic processing route is considered an easier way to produce PAEK polymers and is the most used commercially (Kemmish, 2010). The produced raw polymer is available in the form of powder or pellets, which then can be shaped to the desired shape by either injection moulding or machining.

These polymers benefit from the ability to modify their properties depending on the proposed application by adding different elements such as carbon fibres (Jones et al., 1985). They exhibit high temperature resistance with both the glass transition temperature T_g and melt temperature T_m exceeding

above 100°C making these polymers applicable in many different fields from engine parts to body implants (Green and Schlegel, 2001, Kemmish, 2010).

Such materials are in their brittle form below the glass transition temperature but can still show some flexibility depending on the processing circumstances (Kurtz, 2012). PAEK polymers are almost identical in their structure (Figure 9) with greater ketone content resulting in higher glass transition temperatures T_g. PAEK variants of PEEK, PEK and PEKK have similar thermal properties as shown in Table 3. Furthermore, the melting point T_m could be lowered by reduced crystallinity and crystal size that also could affect their properties such as fatigue and chemical resistance (Kemmish, 2010).

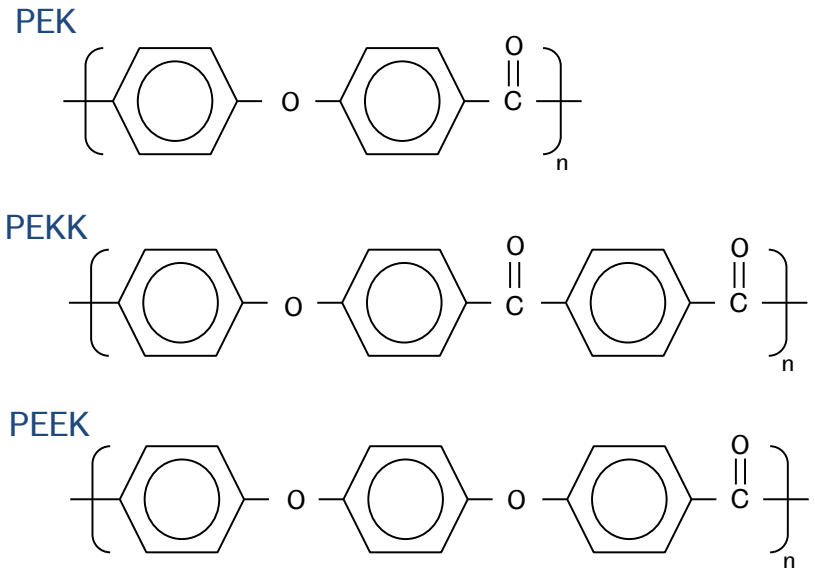


Figure 9: Schematic structure of PEK, PEKK and PEEK polymers*.

* Diagram created by the author.

Table 3: Thermal properties of some PAEK polymers (Shibata et al., 1997).

Material	Glass transition temperature (T_g) C°	Melting temperature (T_m) C°
PEEK	143	334
PEK	152	365
PEKK	165	386

Polyetheretherketone (PEEK) is the most common member of the PAEK family being utilised for its stiffness and biocompatibility properties. It is now commonly used for internal fixation plates for bone fracture and orthopaedic and spinal implants (Kurtz and Devine, 2007, Skinner, 1988). It was first produced in the 1970s by Imperial Chemical Industries and in the late 1990s it was produced as an implantable biomaterial by Invibio Ltd (Attwood et al., 1981, Green and Schlegel, 2001). PEEK is one of the main substitutes for metals in implants such as orthopaedic and trauma applications (Corvelli et al., 1997). Mechanical properties, biocompatiblity and the radiopacity of these implantable materials can be tailored by adding different fillers such as carbon fibers and barium sulphate thus forming a composite material. For example the material can have its elasticity modified to match bone (18 GPa) or alloy (110 GPa) by adding carbon fibers (Skinner, 1988). Furthermore, a study by Schwitalla et al. (2015) tested the flexural strength of commercially available PEEK materials with different fillers and the results varied between 170 to 1000 MPa. In general, few important factors can influence the performance of such polymers (Gardner et al., 1994, Kurtz, 2012):

1) Crystallinity, where higher crystallinity increases the elastic modulus, density and dimensional stability but decreases the impact strength, tendency to creep and thermal expansion.

2) Ketone content, where higher ketone content increases the polymer's chains stiffness e.g. the ketone percentage in the ketone/ether linkage ratio in PEEK and PEKK are 33% and 67% respectively and hence relates to the thermal and mechanical difference between PEEK and PEKK.

3) The filler's strength, shape, amount and adhesion to the polymer matrix also plays an important role in determining the mechanical properties of the final product.

Polyetherketoneketone (PEKK) is the oldest PAEK member and is easy to process with a high glass transition and melting temperatures (Attwood et al., 1981). Currently PEKK is available as a high performance thermoplastic used for different applications such as aeroplanes interiors. Oxford Performance Materials, Inc. USA (acquired originally from Arkema Group, France) produces PEKK under the brand OXPEKK® for medical and industrial applications.

When compared with other PAEKs, PEKK shows better mechanical results against PEEK (pure and glass-reinforced) as can be seen in Table 4. PEEK's stiffness, flexural and compressive strength lowers when stored in 50C° water for nine months by about 70%, 65% and 55% respectively, whereas only a slight declination in PEKK's stiffness (20%) and flexural strength (31%) with no change in it's compressive strength (Copponnex and DeCarmine, 2009).

PAEK based polymers products will have their mechanical properties data provided by the manufacturer. However, this data may vary depending on different methodology, design of specimens and applications (Jones et al., 1985).

Table 4: Comparison of mechanical properties of pure and glass fibres filled crystalline PEKK and PEEK polymers (Bagley and Bell, 2002).

Property	Pure polymer		Filled with 30% glass fibres	
	PEKK	**PEEK**	**PEKK**	**PEEK**
Tensile strength (MPa)	110	93	186	171
Flexural strength (MPa)	193	170	255	233
Compressive strength (MPa)	206	117	--	--

2.4.2. PAEKs in dentistry

In dentistry, PEEK and PEKK polymers have been launched in the field as high performance thermoplastic restorative materials with both materials exhibiting high strength exceeding the minimum strength requirements for dental plastic restorative material of 65 MPa i.e. PEEK showing flexural strength of 165 MPa and PEKK of 200 MPa. PEEK was the first to be used for the fabrication of dental implants (Cook and Rust-Dawicki, 1995) and later, removable partial dentures and obturators (Tannous et al., 2012, Costa-Palau et al., 2014), fixed partial dentures and crowns (Tetelman and Babbush, 2008) and most recently, orthodontic wires (Maekawa et al., 2015). Due to preferred properties, PEEK has been suggested and studied as a viable substitute to well-established restorative materials such as titanium, zirconia and acrylics (Schwitalla and Muller, 2013). However, no clinical studies have been found to support the longevity of PEEK fixed and removable prostheses restorations (Najeeb et al., 2016).

Commercially, high performance thermoplastic polymers based on PEEK have been introduced in the field for fabricating fixed and removable prostheses (Table 5). They can be provided as pellets for injection moulding, ingots for hot pressing or blanks to be milled via CAD/CAM.

Table 5: Typical PEEK based restorative material for prosthodontics with brand names, processing methods and properties (from the companies' websites*).

Brand	BioHPP®	Ceramill® PEEK	VESTAKEEP ® D4 R	PEEK-OPTIMA® Natural LT1	LuxaCam PEEK	Dentokeep peek
Company	Bredent GmbH & Co.KG, Germany	Amann Girrbach AG, Austria	Evonik Industries AG, Germany	Invibio Ltd., United Kingdom	DMG GmbH, Germany	nt-trading GmbH & Co. KG, Germany
Fabrication	Milling and hot pressing	Milling	Milling and Injection moulding	Milling and Injection moulding	Milling	Milling
Properties						
E-modulus (GPa)	4	4	4	4.1	3.8	3.8
Flexural strength (MPa)	150	170	165	165	150	--
Tensile strength (MPa)	--	--	110	100	--	--
Glass transition temperature T_g (°C)	140	--	--	--	--	--
Melting temperature T_m (°C)	340	343	340	340	--	343

2.4.2.1. Pekkton ivory: PEKK Based Restorative Material

A restorative material called Pekkton® ivory (Cendres+Métaux SA, Switzerland) has recently been marketed as a high performance thermoplastic polymer for fixed prostheses. This material is formed from an implantable grade polymer, (PEKK) and is supplied as a material for surgical implants called OXPEKK® (Oxford Performance Materials, Inc., USA).

Titanium dioxide is added to improve the mechanical properties and optimise the aesthetic appearance of the restorative thermoplastic material and hence is beige in colour and opaque when viewed.

* According to the following websites that were last accessed in 11.04.2017: www.bredent.com, www.amanngirrbach.com, corporate.evonik.com, www.invibio.com, www.dmg-dental.com and www.nt-trading.com.

The company suggest that this restorative material can be a substitute for alloys and zirconia in a bilayered restoration with a veneering material of composite resin. Furthermore, the aesthetics and adjustability intra-orally of the composite veneer is an added attraction to the PEKK material.

The mechanical and thermal properties of Pekkton ivory restorative material can be seen summarised in Table 6.

Table 6: Mechanical and thermal properties of PEKK based restorative material (Pekkton® ivory, Cendres+Métaux, SA) from the company's website.

Properties	Value
E-modulus (GPa)	5.1
Flexural strength (MPa)	200
Compression strength (MPa)	246
Tensile strength (MPa)	115
Hardness (MPa)	252
Glass transition temperature T_g (°C)	163
Melting temperature T_m (°C)	363

According to the U.S. Food and Drug Administration (FDA), (application 510(K) no. K123638), Pekkton ivory base material is the same as the base material for an FDA approved implantable device called KMD-Mark1 (Kent Medical Devices, Inc, USA). OXPEKK®-IG (Oxford Performance Materials, USA), PEKK polymer containing barium sulphate $BaSO_4$ is the base material for the implantable device.

The processing method for Pekkton® ivory is either via hot pressing polymer ingots (Figure 10) or CAD/CAM milling. The polymer can be used to form monolithic single crowns or substructure to be veneered with light cured

composite resin (Figure 11). Furthermore, Pekkton® ivory can be used for fabricating frameworks on implants. The manufacturer's guide for cementing is to use any eugenol-free conventional cement as recommended for metal free restorations.

Figure 10: Pekkton ivory ingots for hot-pressing.

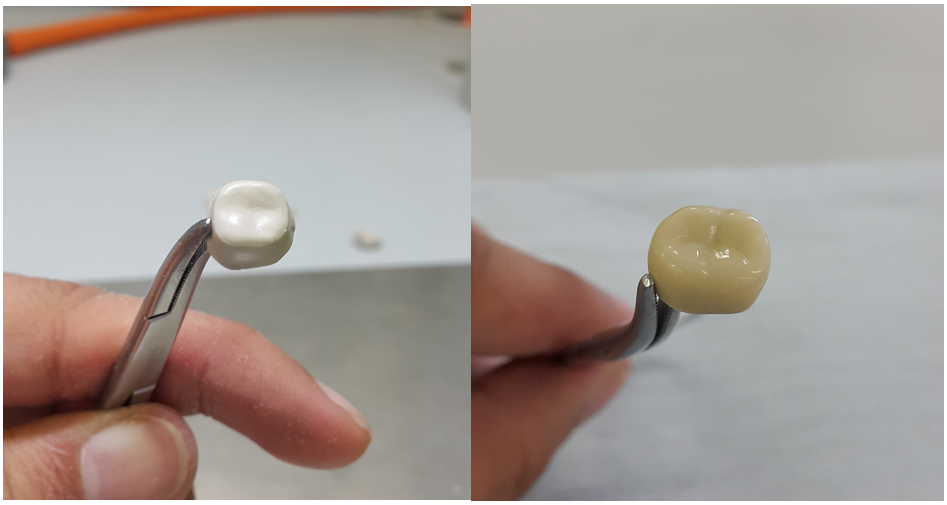


Figure 11: PEKK coping (left) before and after building composite veneer (right).

It has been claimed in non peer-reviewed journals that PEKK showed 80% higher compressive strength than PEEK (Copponnex, 2011) and that full contour PEKK crowns can withstand a static facture load of approximately 1700 N and can survive a 1.2 million cyclic loads test with 500 N upper load, but there are no further details nor data about veneered specimens (Copponnex and DeCarmine, 2009).

The only details of veneered PEKK crowns was found in the manufacturer's manual, where it claims good bond between the PEKK substructure and the composite veneers and shows different values comparing composites and bonding techniques.

At the outset of this study, one study was found in a peer-reviewed journal relating to the use of PEKK in dentistry (Tannous et al., 2012). They investigated the "Retentive forces and fatigue resistance of thermoplastic resin clasps" where retentive forces of PEKK and PEEK clasps for removable partial dentures were compared to CrCo alloy. The authors concluded that the latter showed significantly higher retentive forces after simulating 10 years of use.

A further six publications relating to the use of PEKK in prosthodontics have been found:

Fuhrmann et al. (2014) investigated the resin bonding to three types of polyaryletherketones (PAEKs) and investigated durability and influence of surface conditioning. The study recommended applying two primers: universal primer (Monobond Plus, Ivoclar Vivadent AG, Liechtenstein) and

adhesive primer (Luxatemp Glaze & Bond, DMG, Hamburg, Germany) after shot-blasting of the polymer surface (both PEEK and PEKK) with alumina particles (Rocatec Pre, 3M Espe, Germany).

Keilig (2014) investigated the fatigue of crowns made from high performance polymer (PEKK) with different abutments when subjected to cyclic loading. The author concluded that PEKK crowns showed fatigue limit above 600 N exceeding clinical limits.

Bae et al. (2016) compared the marginal and internal fit of molar copings fabricated from PEKK and zirconia. They concluded that PEKK copings showed better marginal and internal fit (51.6 µm and 36.1 µm respectively) than the zirconia counterpart (55.7 µm and 40.4 µm respectively) and that both had a marginal fit within clinical acceptable range of around 39–120 µm.

Furthermore, a study by Park et al. (2016) compared the fit of interim implant restorations of different materials made using different fabrication methods by measuring the marginal and internal discrepancies using a 2D cross-sectional approach. In their findings, the milled PEKK crowns showed average marginal and internal discrepancies of 58 µm and 96 µm respectively between crowns and implant abutments, which are in the range of clinically acceptable figures.

A study by Passia et al. (2016) entitled “Long-term retention behaviour of resin matrix attachment systems for over dentures” concluded that PEKK attachments showed superior results after testing in a chewing simulator against polyethylene attachments.

A study by Han et al. (2016) entitled “Implant and tooth-supported fixed prostheses using a high-performance polymer (Pekkton) framework” reporting implant and tooth-supported fixed restorations made out of PEKK frameworks for a fully edentulous maxilla and partially edentulous mandible.

Related studies will be referred to and reviewed accordingly in the discussion part in chapters to follow.

The search for the studies was done through different databases such as “Ovid MEDLINE”, “Web of Science” and “Google scholar” and the terms used were “polyetherketoneketone”, “PEKK”, “Pekkton” and “Pektton ivory”. All the relevant studies published in peer-reviewed journals were mentioned above.

In dental resins and polymers the colour of the material can be modified by incorporating additive pigments such as titanium oxides but this is often at the expense of the material’s translucency being reduced (Johnston et al., 1995, Yu et al., 2009b). Furthermore, crystalline materials are denser and less transparent than the more translucent amorphous materials. PAEK polymers are considered as a linear, aromatic semi-crystalline polymers and hence do appear as opaque materials (Kurtz, 2012).

Similar to PEKK, PEEK restorative materials also use titanium dioxide to improve colour (Ma and Tang, 2014, Schwitalla et al., 2016) and both PEKK and PEEK can be considered as an opaque restorative materials. Hence, the Pekkton® ivory is purposed by the manufacturer as a substructure materials to be veneered with light cured composite for achieving an aesthetic restorations.

The same reasoning could also be applied for veneering substructures made out of the similar polymer of PEEK (Stawarczyk et al., 2013a, Stawarczyk et al., 2014b, Rosentritt et al., 2015).

2.4.3. Dental Composite Resins

Improvements in polymer technology have led to resins that are easily cured at oral temperature and with shades close to natural teeth due to coloured pigments and fillers. This had led to the resin's application being extended to different uses such as restorative material, indirect restoration and veneering material for alloy and ceramic substructures.

Composite resins are the most common direct restorative material used in the field of dentistry with outstanding aesthetic properties when compared with the alternative options. The material is versatile and may be used both as a direct restorative material and as a laboratory produced indirect restoration. Dental composites have been used for approximately fifty years (Bowen, 1962). In the 1950s, acrylic resins, based on PMMA, with shades close to a natural tooth, were developed but with drawbacks such as limited wear resistance and shrinkage after curing. Later, in the 1960s, newer composite resins were introduced based on bisphenol A glycidyl methacrylate (bis-GMA), dimethacrylate resin and organic silane coupling agents to create the bond between the filler particles and the resin matrix (Anusavice and Phillips, 2003).

Composite resins are formed from a mixture of two or more different components engineered to fulfil certain features (Ferracane, 1995). In the past, dental practitioners used amalgam and acrylic resins as direct restorative materials, both of which do not fulfil the ideal requirements of a restorative material (Craig and Powers, 2002). The mercury in amalgam was

a concern plus amalgam restorations require a preparation that may frequently be destructive to tooth structure (Hengchang et al., 1990, Bates, 2006). Acrylic resins are relatively weak, stain easily and when used as a restorative material, frequently exhibit marginal gaps (Fusayama et al., 1971). Composite resins surpass acrylic resins as they are more aesthetic, easy to apply and handle, have good wear characteristics and require minimal preparation (Shahdad and Kennedy, 1998, Rathke et al., 2009).

There are three main constituents of composite resin: an organic matrix, an inorganic filler and a coupling agent. Composite resins can be polymerised chemically by having the filler in the powder and liquid activate reaction (Peutzfeldt, 1997). Alternatively they can be polymerised using ultraviolet light, having benzoin methyl ether as initiator for the activation. Also the visible light method for polymerising uses a mixture of amine and dikitone as an initiator (McCabe and Walls, 2008).

Ultraviolet light cured composite resins have problems with depth of cure, which is partly resolved by the visible light cured composite resins (Alvim et al., 2007). This method was introduced in the 1970s and benefits include a longer working time and control of the hardening point (Mount and Hume, 1998, Walmsley, 2007). The distance between light source and composite resin surface can affect light curing, and the shade of the composite resin can affect the depth of cure with darker shades taking longer to cure. Curing units produce light with a wavelength of around 470nm, the point where camphoroquinone absorbs the light and initiates polymerisation of the composite (Alvim et al., 2007). These units are fitted with halogen bulbs and

are available as a desktop box or a hand held device. A light emitting diode also can be used, which generate less heat and allow control of the desired light spectrum range (McCabe and Walls, 2008).

2.4.3.1. Composite resins for veneering substructures

The strength and durability of bond between the underlying substructure and the outer veneer is important for the success of any bilayered restoration. Factors that could affect this bond and how long it will last after being subjected to aging and cyclic stresses includes property differences between the two layers and the surface finish in mechanical bonding, and the compounds used for chemical bonding.

Composite resins could be used as a laboratory based veneering material to produce restorations. The material will mask other restorative materials such as acrylics, amalgam, alloys and zirconia (Goldstein, 1985, Gordon et al., 1985, Solow, 1999). The advantages of composite resin as a veneering material for substructures are (Barzilay et al., 1988, Yoshida et al., 1993):

- Ease of handling and repairing both in the laboratory and intra-orally.
- Abrasion to opposing teeth close to that of natural tooth
- Aesthetics and colour stability.
- Biocompatibility to surrounding tissue.

Composite veneers may be bonded to metal substructures by mechanical means e.g. beads and undercuts which has been considered an inferior method (Matsumura et al., 1991). Micro-mechanical bonding, e.g. acid etching technique and the use of chemical bonding promoters such as silane coupling

agents and primers, aid the bonding between the materials. Currently primers include the addition of an etching component allowing bonding chemically and micro-mechanically at the same time. Therefore bonding to non-precious metals can be achieved by etching to create a micro-mechanical surface texture or by using a silane-coupling agent after silica layer formation (McCabe and Walls, 2008). Another method is shot-blasting the alloy surface with Al_2O_3 particles releasing oxides that will eventually interact chemically with primers containing carboxylic or phosphoric acid functional monomers (Sarafianou et al., 2008). The achieved bond following such method has been proven to improve the bond between composite and alloy up to clinically acceptable level exceeding 25 MPa (Tarozzo et al., 2003, Petridis et al., 2004).

Furthermore, composite veneers could be bonded to ceramic substructures e.g. zirconia that are considered unetchable with hydrofluoric acid because of their glass-free structure. This could be achieved by using primers containing adhesive phosphate monomers, which can link chemically to ceramics containing metal oxides as well as increasing its surface wettability and thus enhancing bonding (Blatz et al., 2003, Kern et al., 2009).

Attempts have been made to change the zirconia surface characteristics by shot-blasting with silica coated alumina particles to form a silica layer before using silane coupling agents for bonding (Matinlinna et al., 2006). This air-borne abrasion has been thought to cause micro crack growth in the zirconia leading to weakness of the core material (Ozcan et al., 2008, Ural et al., 2010). On the other hand, this modification of the zirconia surface can increase the

bonding surface area and promote the mechanical bonding with the other material (Guazzato et al., 2005, Ozcan et al., 2008, Vagkopoulou et al., 2009).

Additionally, some researchers have concluded that the best bonding method for bonding resin to zirconia was combining shot-blasting with alumina particles with the application of universal primer (Kern et al., 2009, Yun et al., 2010, Attia et al., 2011).

As the use of PAEKs in dentistry is relatively recent, few studies were found focusing on the bonding between resin cements and PEEK substructures (Schmidlin et al., 2010, Kern and Lehmann, 2012, Liebermann et al., 2013, Uhrenbacher et al., 2014, Sproesser et al., 2014) and very limited studies about composite veneering PEEK substructures (Stawarczyk et al., 2015, Rosentritt et al., 2015, Keul et al., 2014).

For bonding composite veneers to the PEKK substructure, Pekkton® ivory manufacturer's manual recommends using composite primers to condition the PEKK surface after shot-blasting with 110µm Al_2O_3 particle under 2 bar pressure before applying the composite veneer. The manual also shows different bonding strength values between PEKK and composite veneer using different primer and composite brands ranging from 14 to 28 MPa,

One relevant study on PEKK conducted by Fuhrmann et al. (2014) focused on the bonding between different PEEK and PEKK substructures and resin cement. These studies evaluated the effect on the quality of the bond of different pre-treatment procedures varying from standard dental procedures such as shot blasting with Al_2O_3 particles of different sizes, silica

coating, sulfuric acid etching and priming, to new techniques such as plasma coating. They have concluded that using a combination of silica coating and conditioning the polymer's surface with universal and resin primers gave the best results of about 18 MPa for PEKK. Also PEKK showed a durable bond even after storage in water at 37°C for up to 150 days. It was also suggested that silica coating had the same affect as shot-blasting with Al_2O_3 particles by roughening the polymer's surface, allowing primers containing multifunctional methacrylates to penetrate the roughened polymer surface and create a chemical and micromechanical bonding.

This finding of PEKK and PEEK composite bonding agrees with other studies that tested the resin to PEEK bonding using multifunctional methacrylates containing primers (Stawarczyk et al., 2013b, Stawarczyk et al., 2015, Stawarczyk et al., 2014a, Keul et al., 2014, Rosentritt et al., 2015).

It is of note that where it has been thought that studies of resin cement bonding to substructures could be applied to resin composite veneer bonding, Rosentritt et al. (2015) demonstrated wide variations between them and recommended conducting separate evaluations when testing veneer/substructure bonding.

Plasma coating is of particular interest as it improves bonding by raising the surface energy of the substructure using ionised gas such as oxygen, nitrogen helium and argon (Liebermann et al., 2013). Studies have evaluated effects of plasma coating on bonding to substructure materials and it was found to improve the bond between zirconia and both porcelain veneer and resin

cement (Lee et al., 2016, Derand et al., 2005); in contrast, no effect was found in bonding resin cement to PMMA and PEEK with plasma coating (Liebermann et al., 2013, Stawarczyk et al., 2014a, Stawarczyk et al., 2015).

2.5. Aesthetics and Optical properties

Aesthetics is a key issue in dentistry and this requires choosing the right material that can mimic natural teeth (Lee et al., 2005) especially when it comes to restorations replacing anterior teeth (Khashayar et al., 2014, Al Wazzan, 2004).

Restoring teeth requires precision in the techniques used and materials selected to meet clinically acceptable results for natural teeth and it is commonly composites and ceramics upon which we call for these situations (Khashayar et al., 2014).

When restoring teeth, different factors can affect the appearance of the restoration such as optical properties of the material used, the background colour of the tooth or substructure material as well as the ambient light (Vichi et al., 2011).

Light is a visible electromagnetic radiation falling in the range of 380 to 780nm of the spectrum (Figure 12). Vision is determined by light reflected by surrounding objects. This reflected light is influenced by: colour, translucency and opacity, and texture of the object.

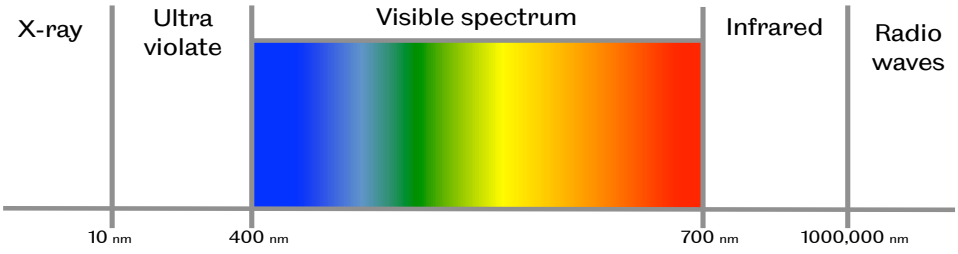


Figure 12: Visible light spectrum*.

* Diagram created by the author and collated from the literature (Anusavice and Phillips, 2003, van Noort, 2007, Sakaguchi and Powers, 2012).

In the early 20th century, an artist from Massachusetts called A.H Munsell created a method to describe colour depending on hue, chroma and value (Nickerson, 1976). Hue represents the colour family, chroma the strength and value to describe how bright or dark the colour.

A colour measuring method which is now used in dentistry was developed by the Commission Internationale de l'E Clairage (CIE) in 1931, and revised in 1976 allows colour to be mapped on a scale (CIEL*a*b*) where L* represents lightness and chromaticity coordinates, a* represents red to green axis, and b* represents yellow to blue axis (Joiner, 2004), as shown in Figure 13.

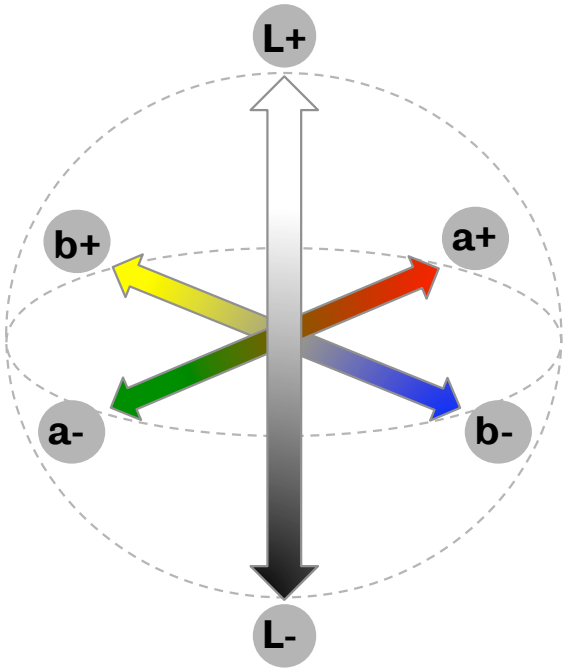


Figure 13: CIE L*a*b* colour space*.

* Diagram created by the author and collated from the literature (Anusavice and Phillips, 2003, van Noort, 2007, Sakaguchi and Powers, 2012).

The advantage of plotting colours using these coordinates is that two colour samples can be compared by calculating the colour difference (ΔE) between CIE L*a*b* values using the following equation (Azzopardi et al., 2009):

$$\Delta E = \sqrt{\Delta L *^2 + \Delta a *^2 + \Delta b *^2}$$

Colour coordinates can be determined using a colorimeter or visible light spectrophotometer. In spectrophotometers, illuminants are controlled as they play a major part in determining the colour of samples since it is this light source that is reflected from the objects surface. Several illuminants standards are characterised by the CIE for different applications. In dentistry D65 illuminant is used as this is a standardised 'day light'.

Translucency, or opacity, is a further optical property that can again be quantified using a spectrophotometer. An opaque material is a material that blocks light from passing through, whereas translucent materials permit the passage of light as scattered or directly transmitted light and examples of translucent restorative materials are ceramics and composite resins (Sakaguchi and Powers, 2012). A material's translucency can be determined in numerous ways:

a) By calculating the translucency parameter (TP) that is determined from the colour difference of a material when measured with black and white background (Johnston et al., 1995). Higher TP values indicate higher translucency and lower values indicating the opposite up to a value of 0.00 indicating a completely opaque material (Paravina et al., 2002).

b) A material's opacity may also be expressed as the Contrast Ratio; the ratio of the material's reflectance when tested with black and white backgrounds (Vichi et al., 2004). The opacity may also be described in percentages after multiplying the CR by 100 (Shiraishi et al., 2011).

Both methods serve the same purpose as they are significantly correlated i.e. high TP correlates to low CR meaning higher translucency and vice versa. This is confirmed in some studies performed on enamel and dentine (Yu et al., 2009a) and different ceramic systems (Barizon et al., 2013) where they concluded a significant negative correlation between TP and CR values with a correlation coefficient ranging between -0.78 and -0.99.

The natural tooth colour is determined by the dentine and enamel, with the latter playing an important role in the tooth's translucency, which decreases as the enamel thickness reduces towards the cervical part of the tooth. Hence, understanding these properties plays an important role in achieving aesthetics when replacing or repairing damaged tooth structure. Dental professionals use shade guides to subjectively assess the colour of damaged teeth to be replaced or the adjacent teeth so it can guide the dental technologist fabricating the restoration. The shade guide has the range of ceramics available in tooth form in a systematic arrangement.

Several surrounding conditions may affect accuracy of assessment environmental light, individual's experience, distracting colours and eye condition all alter the perception of colour. An alternative is to use an objective assessment method using hand-held devices to measure the

patient's tooth shade such as camera shade guides or dental tooth colorimeter. An example is the Vita Easy Shade, which is a spectrophotometer that can display different values such as value, chroma and hue.

Some spectrophotometers are equipped with integrated spheres allowing them to measure the reflectance and colour under two modes depending on the specular mode to: specular component included (SCI) and specular component excludes (SCE).

A spectrophotometer (CM-2600d Konica Minolta Sensing, Inc., Japan) uses two light sources to simultaneously measure under both modes SCI and SCE, unlike conventional spectrophotometer where it should be done mechanically by switching the optical trap inside the integrating sphere every time changing between SCI and SCE and vice versa.

This is achieved by having the first light flashing with the chosen illumination type and the first measurement with SCI is recorded. Then the second light flashes measuring the reflected light from the sample in comparison with the first light flash to calculate the SCE mode (Figure 14).

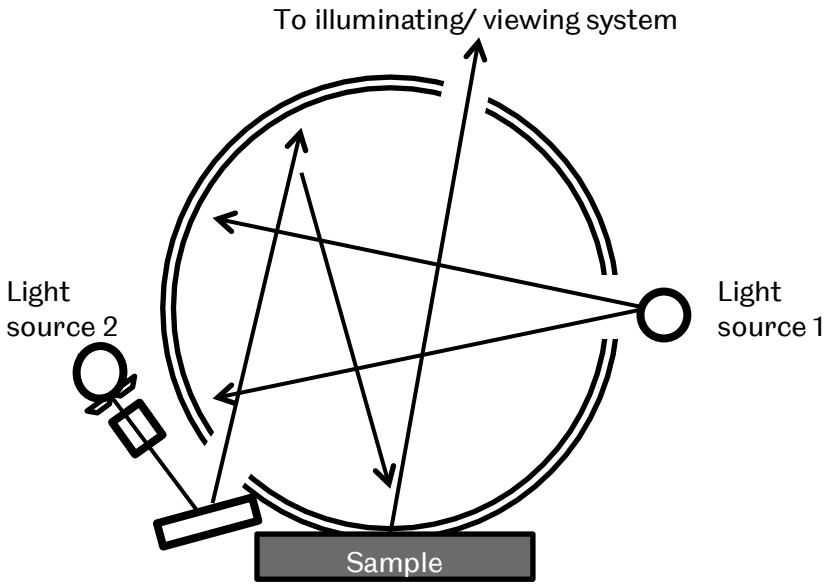


Figure 14: Schematic of a Spectrophotometer*.

It is not clear which mode is more relevant to clinical research, but in general, the SCE mode represents the view of the natural eye and the SCI mode is a more in depth approach for analysing an object's colour and hence can be used when comparing the colour of different materials such as composites (Hosoya et al., 2009, Hosoya et al., 2010). Some investigators suggest relying on the SCE mode for restorative materials as it takes into account the surface finishing and therefore is more accurate when comparing groups of different surface roughness (Lee et al., 2002, Kim and Kim, 2014, Choi et al., 2005).

* Diagram created by the author and derived from the spectrophotometer's user's manual (CM-2600d Konica Minolta Sensing, Inc., Japan).

2.6. Mechanical Properties

Mechanical properties can be described as the physical science related to measuring the resistance of a material to distortion or fracture under an applied force (Anusavice and Phillips, 2003). The mechanical properties of any restorative material play an important role in choosing the appropriate material for the application. This is widely applied in the engineering and manufacturing of many products and industries where these properties are determined through standardised tests in the laboratory using different testing machines.

In restorative dentistry, the understanding of these mechanical properties, in addition to the physical, optical and biocompatibility properties, are essential in choosing their application and hence durability of their service inside the oral cavity.

Standardised mechanical laboratory evaluations are helpful in providing an initial understanding of a material. However it is the combination of requirements and the intended application that is significant in order to make prediction of clinical performance (Sarrett, 2005, Ferracane, 2013) e.g. limitations of amalgam due to lack of adhesion in comparison to composite and poor wear characteristics of early composite resins placed in posterior teeth (Dunne et al., 1997).

Stress (force per unit in a cross-sectional area of a material in action) and strain (the fractional change in dimensions caused by the force) form the basis of the mechanical properties (van Noort, 2007). Figure 15 shows typical

stress-strain curve for different materials such as ceramics, metals and polymers. Stress can be divided into three types: tensile stress, compressive stress and shear stress (Figure 16).

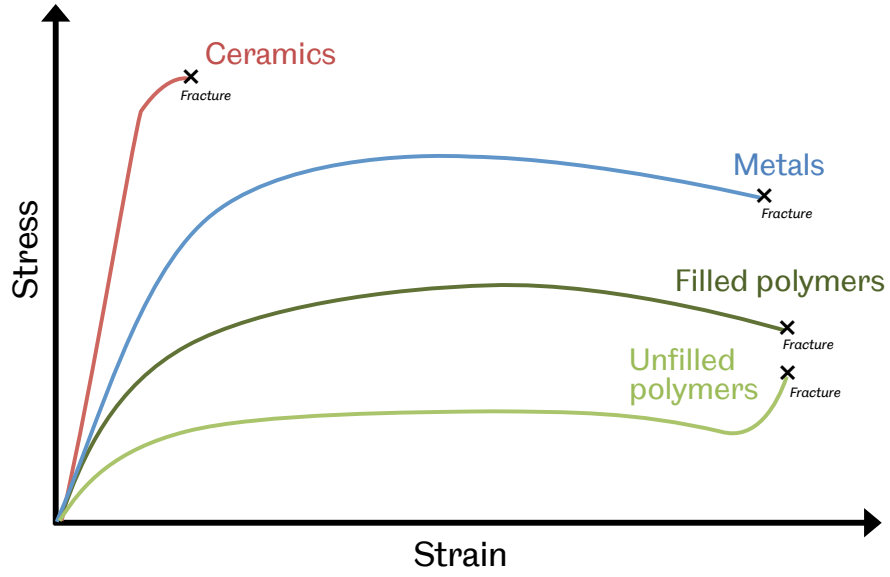


Figure 15: Example of stress-strain curve of ceramic, metals and polymers*.

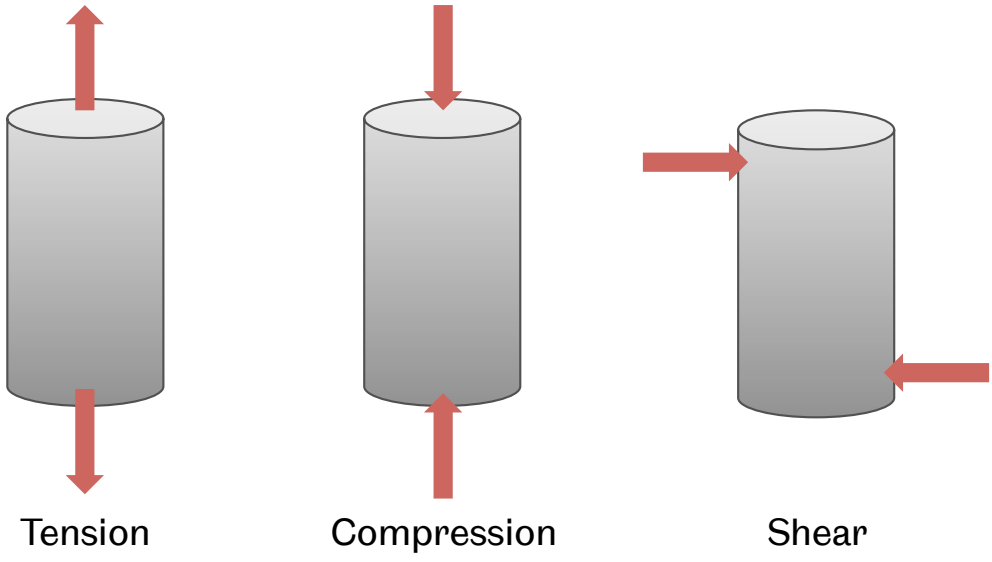


Figure 16: Illustration of tensile stress, compression stress and shear stress*.

* Diagrams created by the author and collated from the literature (Anusavice and Phillips, 2003, van Noort, 2007, Sakaguchi and Powers, 2012).

Knowing the stress and strain allow us to define the most common and important mechanical properties related to understanding materials behaviour:

- Brittleness: Ability of a material to fracture without the tendency to deform plastically.
- Ductility: Ability of a material to deform plastically under tension before failure.
- Elastic modulus: Is the relative stiffness of a material and measured as the resistance to non-permanent deformation when subjected to force. It is also called Young's modulus and modulus of elasticity.
- Hardness: Resistance of a material to plastic deformation on the surface under an indentation load.
- Strength: Maximum force a structure can withstand before failure (plastic deformation or fracture).
- Compressive strength: Maximum stresses a material can withstand when subjected to compression loading before failure. This property could be useful in comparing brittle poor tension materials e.g. composite resins.
- Tensile strength: Maximum stress a material can resist when subjected to tension loads before failure. It can also be termed ultimate strength.
- Shear strength: Maximum stress a material can resist when subjected to shear loading before failure.
- Flexural strength: Maximum stress when subjected to flexural loading required to fracture a material. It can also be termed bending strength and fracture strength. With disc shaped samples supported with metallic

ring or three balls, it is referred to as biaxial flexural strength, which could combine compressive (top surface), tensile (lower surface) and shear (near supporting points) stresses (Anusavice and Phillips, 2003).

- Toughness: Ability of a material to absorb elastic energy and to deform plastically before fracture.
- Fracture toughness: Material resistance to brittle fracture in the presence of a crack e.g. higher fracture toughness means more resistance to catastrophic facture than materials with lower fracture toughness.

Standardising the tests used in determining such parameters is important to allow reproducibility and allow direct comparison of different materials. For example, the International Organisation for Standardisation (ISO) offers some guidelines in evaluating dental materials such as the ISO 6872 standard for dental ceramics, the ISO 22674 standard for metallic materials for dental restorations and the ISO 4049 standard for polymer-based restorative materials.

Nevertheless, the strength data provided for certain materials do not necessary reflect the actual material performance when tested in different shapes and different environments (Jones et al., 1985, Kelly, 1995, Padipatvuthikul and Mair, 2008).

Consequently such tests do not necessarily correlate to clinical performance of restorations produced from these materials (Oh and Anusavice, 2002, Heintze, 2007, Bayne, 2007, Bayne, 2012).

Ferracane (2013) have summarised in Table 7 some of the important mechanical properties required in evaluating dental materials and his thoughts on their relevance to clinical performance.

Table 7: Restorative material's important mechanical properties and their clinical relevance according to Ferracane (2013).

Property	What it relates to	Ferracane's opinion on the possible relation to clinical performance
Elastic modulus	Elastic deformation under force	Intuitively important to maintain form, especially under high forces (easy to test)
Fatigue resistance	Repeated mechanical stressing	Important – likely many failures due to fatigue (difficult to test)
Flexure strength	Fracture – includes tensile and compressive components	Important – has tensile aspect and failures likely due to tensile stresses; some correlation with wear (easy to test)
Fracture toughness	Chipping and bulk fracture	Important – many failures due to fracture; not geometry dependent (more difficult to test)
Hardness	Resistance to indentation	Intuitively important, but only limited correlation with wear (easy to test)
Tensile strength	Fracture in tension	Important – failures likely due to tensile stresses (difficult to test)
Wear	Volume loss due to abrasion and opposing contact stresses	Important – abrasive and occlusal contact stresses (difficult to test)

Mechanical properties of metal based restorations such as strength, modulus of elasticity and fracture toughness might be consistent with the restoration's clinical performance but this is not necessarily the case with ceramic based ones (Bonfante and Coelho, 2016, Rosentritt et al., 2016). On the other hand, composite resins' mechanical properties do not correlate with their fatigue resistance behaviour (Lohbauer et al., 2003). A study by Belli et al. (2014) that involved different composite materials concluded that the elastic modulus

and fracture toughness values do not correlate to their respective fatigue results and hence should not be used to speculate on their clinical performance. Nevertheless, such properties could correlate to the clinical wear performance of composite restorations (Heintze et al., 2007).

Researchers have attempted to develop laboratory tests to evaluate dental materials under conditions closer to the intended use of the material. Ideally a testing regime would simulate all of the conditions found in the oral cavity and the results would reflect clinical observations. No laboratory experiment fully reproduces the clinical situation however one approach is testing a material when constructed into the definitive restoration. This test takes into account the processing of the material, the complex geometry of the restoration, the multiple materials and the supporting structures.

2.6.1. Occlusal Fracture Resistance (Crown Structural Integrity)

Fracture resistance tests are useful as an initial evaluation of innovative restoration designs and restorative materials in comparison with well-established dental restorations. Generally, the tests are performed using a universal testing machine to apply axial (occlusal) load through an indenter (ball, bar or antagonist tooth) to a dental restoration bonded to a tooth and fixed into a bone-socket like base (Preis et al., 2012).

This evaluation takes into consideration different factors that have an affect on the strength of any dental restoration such as the processing methodology, finishing and bonding of the restoration which may include polishing, heat treatments, shot-blasting, etching, bonding to other materials

e.g. substructure, abutment, veneer and cement (Scherrer and de Rijk, 1992). Furthermore, the different restoration designs, tooth preparations and layer thicknesses e.g. substructures and veneers can also be considered in such evaluations (Mahmood et al., 2011, Casson et al., 2001).

The supporting abutment plays an important role in the fracture resistance performance of tested crowns. Several abutment materials have been used in different studies. Extracted natural teeth have been used in a number of studies (Burke, 1999, Burke and Watts, 1994, Rosentritt et al., 2009a) metal abutments by (Kilicarslan et al., 2004, Tinschert et al., 2001, Al-Makramani et al., 2009), gypsum abutments in other studies (Vallittu, 1998, Al-Wahadni and Gutteridge, 2002, Al-Hazaimeh and Gutteridge, 2001) and resin abutments of different types, epoxy resin (Zahran et al., 2008), PMMA (Grieznis et al., 2006), acrylic resin (Zhi-Yue and Yu-Xing, 2003), high filler resin (Neiva et al., 1998) and reinforced polyurethane (Kohorst et al., 2007).

Ideally natural teeth should be used as an abutment, however these present further variables and difficulties including but not limited to: difficulties and time required in acquiring them, the possible inconsistency of size, difficulties in producing the same size of sample, anatomy problems with size of pulp and thickness of dentine, storage circumstances and time of preservation (Michalakis et al., 2009, Wimmer et al., 2014, Rosentritt et al., 2006).

These variables lead to the consistency of samples being reduced. As a result, many studies use a single material for abutments to ensure consistency,

allowing direct comparison between different tested groups (Kilicarslan et al., 2004).

Using abutments with a much higher elastic modulus than that of dentine (e.g. metal), can contribute to higher fracture resistance values of tested crowns than if tested with extracted teeth or abutments with mechanical properties close to dentine e.g. resin based abutments (Larsson et al., 2012, Wimmer et al., 2014, Mahmood et al., 2011). Therefore abutment materials with properties close to that of dentine are selected for better representation of natural teeth (Dittmer et al., 2010, Oh and Anusavice, 2002).

A further consideration that increases the representation of the natural teeth is to simulate the presence of the periodontal ligament (PDL) to allow the abutments appropriate mobility. Soares et al. (2005), evaluated simulating the PDL using different materials when carrying out fracture resistance tests. The study described a technique of applying the layer simulating PDL using a wooden base and X-ray film. The roots were embedded in wax and removed after they had been mounted in base material to create the space for the PDL material. Brosh et al. (2011), evaluated different impression materials to simulate the PDL and concluded that the light body impression material was the most appropriate.

Any restoration must be able to resist the loads applied during function while in situ and several researchers have studied the forces of mastication. This leads to the question firstly to define how much force a restoration should be

designed to resist. Furthermore, once this has been defined, what is the relevance of results that demonstrate a greater resistance to fracture?

Masticatory forces vary between different genders and age groups with generally higher mastication force in the molar region than incisor teeth (Tinschert et al., 2001). This is supported by Ferrario et al. (2004), where they concluded that maximum forces were recorded on the first molar and males exhibited greater biting forces than females. It was recorded that the biting force for natural first molar tooth can range from 8 to 800 N (Bates et al., 1976).

Körber and Ludwig recommended that any restoration in the molar area should be able to sustain an occlusal load of approximately 500 N (Körber and Ludwig, 1983). Although Mehl et al. (2010) concludes that an in-vitro evaluation of molar crown restorations should withstand an occlusal force of at least 1000 N, with the assumption that the masticatory forces in the moist oral environment may weaken the restoration up to half its known fracture resistance force.

The irregular shape of dental restoration samples can affect the results of any evaluation in comparison with regular shaped samples (Casson et al., 2001) and hence fracture resistance tests are a useful evaluation tool in developing new dental restorations, materials and fabrication techniques. Nevertheless, such testing is under debate as to whether it is a useful tool to test the performance of brittle ceramics, and how relevant it is to the behaviour of the crown in the mouth (Isgro et al., 2011). Therefore, results of

such testing could not be interpreted as clinical behaviour predictors and hence the restoration's longevity as there are many factors supporting this, such as: larger forces, different force magnitudes from mastication and different mode of failure than recorded clinically (Kelly, 1999).

An attempt to bridge the gap between such evaluations and clinical trials is creating more clinical relevant tests that more closely resemble mastication forces in the oral cavity, for example by subjecting crowns to fatigue cycling loading under a wet environment (Tinschert et al., 2001).

2.6.2. Fatigue Testing (Crown Durability)

Evaluating a restoration's material, design and fabrication technique prior performing clinical trials is challenging as there is no experiment which completely recreates the environment and forces in the oral cavity. Most mechanical tests use symmetrical shaped samples and do not necessarily predict the longevity of dental restorations. Similarly static loading fracture testing of anatomically shaped crowns and restorations have their limitations (Kelly et al., 2012, Heintze et al., 2017).

Ideally restorations should be evaluated using randomised controlled clinical trials. However the challenges associated with clinical trials such as time consuming (many years), high cost and ethical considerations has led to the development of experiments closely simulating the oral environment (DeLong and Douglas, 1991).

Therefore, the use of fatigue chewing machines that subject the prostheses to cycling loading under thermocycled or temperature controlled water

simultaneously is a useful evaluation method before starting with any clinical trials (Rosentritt et al., 2006, Steiner et al., 2009, Silva et al., 2010, Coray et al., 2016). Such method is useful in evaluating and predicting the longevity of different restorative materials when processed, bonded to different materials, and shaped to their final prosthetic designs (Baran et al., 2001, Rosentritt et al., 2016).

Fatigue failure is one of the problems associated with dental prostheses and is caused by microscopic cracks growing with the cyclic loading stresses, even below the ultimate tensile strength, until the prosthesis fractures (Anusavice and Phillips, 2003). Dental restoration fractures are uncommon in the short-term and are usually related to defects in the design or material. However, most restoration failures occur after several years of functioning inside the mouth (Wiskott et al., 1995).

Hence, fatigue testing is considered to relate to clinical conditions closer than static-loading experiments as aggregated cracks can build-up causing failure from cyclic loading. Stress and number of cycles is an inverse relationship meaning that for a restoration to fail, higher stress requires less number of cycles to reach failure and hence the number of cycles is defined when expressing fatigue strength (Powers et al., 2006).

Different fatigue chewing simulator machines were found to be used in the literature and with different test configurations. Some used machines were commercially available (Kheradmandan et al., 2001, Butz et al., 2005, Steiner et al., 2009, Lorenzoni et al., 2010, Nawafleh et al., 2016) and others were

custom built (DeLong and Douglas, 1991, Orr and Mitchell, 1996, Bakaeen et al., 2001, Truninger et al., 2012, Stawarczyk et al., 2012, Guo et al., 2014, Aboushelib and Elsafi, 2016). Furthermore, variables in test configurations could include and are not limited to (Rosentritt et al., 2006):

- The range and frequency of the used loads.
- Type of abutments.
- Antagonist indenter type and movement.

For designing a life predictive experiment of dental materials and restorations, Wiskott et al. (1995), suggested:

- For dental researchers, a fail or not-fail approach should be used as an easy method to perform and to describe.
- To achieve a clinically relevant prediction, at least 1,000,000 cycles should be carried out.
- It is recommended to use negative stress ratio (back and forth) with dental restorations.
- Staircase approach is the easiest way for evaluating fatigue of prosthodontics.

In the dental field, different laboratory techniques have been described in the literature to evaluate the effect of fatigue on dental restorations and the two most common approaches are:

1. Accelerated lifetime testing: Commonly referred to as step-stress-accelerated-life-testing (SSALT) or step stress method and is used for predicting fatigue life. In this method, samples are divided into three different stress levels from low, moderate and aggressive and are determined according to the failure value of static loading test.

   For example, a group of 16 samples is divided as: n=2 static loading, n=7 profile I (mild), n=4 profile II (moderate) and n=3 profile III (aggressive) (Baldassarri et al., 2011, Bonfante et al., 2010, Nelson, 2009, Coelho et al., 2009b).

2. Fatigue limit and fatigue life: Restoration fatigue behaviour is determined by subjecting the specimens to cyclic stresses to distinguish these two parameters (Padipatvuthikul and Mair, 2008):

   - Fatigue limit: Determines the stress cycles upper and lower limits that the sample will withstand before failure.
   - Fatigue life: Is how long the sample will withstand for a set stress value and is measured in number of cycles that is interpreted to lifetime inside the mouth.

2.6.2.1. Fatigue Limit

The most common technique used for determining a sample's fatigue limit is the staircase method, also referred to as the up and down method, and is the approved method by the British, French and Japanese standard (Lin et al., 2001).

The fatigue limit is determined by subjecting a sample to a certain force level for a set number of cycles or until fracture. The next sample will be subjected to a different force level, higher if the previous sample survived and lower if the previous sample fractured. This gives rise to the up and down method. Once a regular fracture pattern is achieved, a fatigue limit sequence can be generated in a diagram using the force levels for each sample. Furthermore, the mean fatigue limit and the standard deviation can be calculated based on the lowest load level considered in the evaluation (X_0), fixed stress level increments (d), stress level (i) and the number of failure or survival at a certain stress level (n_i) (Dieter, 1961, Garoushi et al., 2007, Lohbauer et al., 2003, Bae et al., 2004, Koyama et al., 2012).

$$Fatigue\ Limit = X_0 + d\left(\frac{\sum in_i}{\sum n_i} \pm 0.5\right)$$

$$Standard\ Deviation = 1.62d\left(\frac{\sum n_i \sum i^2 n_i - (\sum in_i)^2}{(\sum n_i)^2} + 0.029\right)$$

2.6.2.2. Fatigue Life

The fatigue limit force (stress level) is used to establish the load used for evaluating the fatigue life. The samples are subjected to cyclic loading at this force for a set number of cycles (1,000,000 cycles or more) and failure or survival of each sample is recorded.

The number of cycles is interpreted as years in service and a commonly used value is 250,000 cycles as equivalent to one year of chewing (Sakaguchi et al.,

1986, Zankuli et al., 2015, Delong and Douglas, 1983, Barcellos et al., 2013, Att et al., 2006, Kassem et al., 2012, Kern et al., 1993).

The collected data is then analysed using probability distribution plots such as Weibull analysis, which can be performed using special statistical software (Abernethy, 2008, Rinne, 2009). The software generates Weibull Parameters, beta (β) and alpha (α), that dictate the Weibull distribution and visual graphs may be generated (Figure 17 and Figure 18). The α indicates the characteristic life scale of a group and the value is interpreted as the average number of survived cycles. The β value indicates the group's failure rate, for example, it can indicate the following:

β < 1.0 indicates early failures (infant mortality).

β = 1.0 indicates normal failures (independent of age).

β > 1.0 indicates late failures (wear out failures).

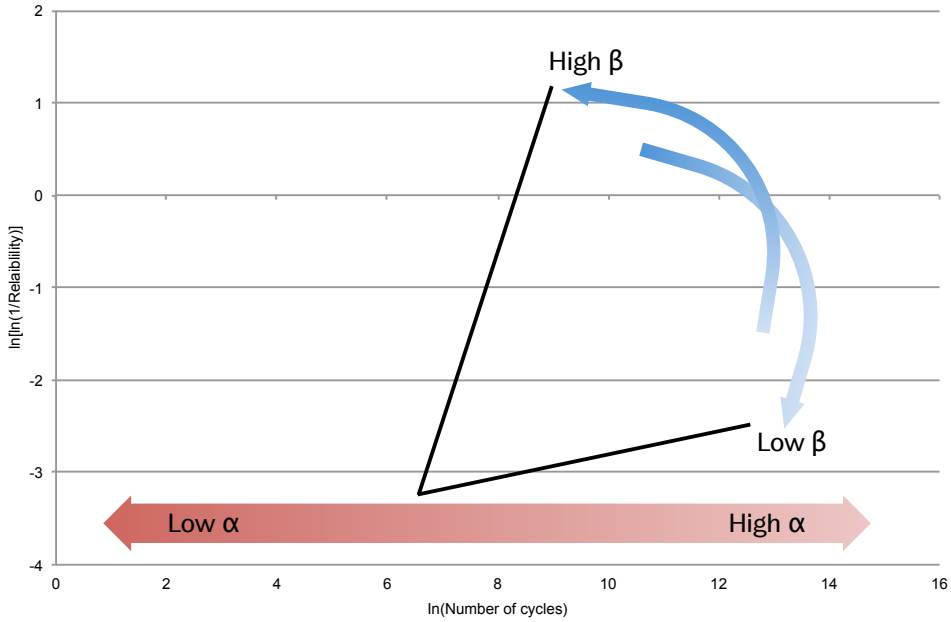


Figure 17: Relation between shape parameter β and scale parameter α in a Weibull probability plot*.

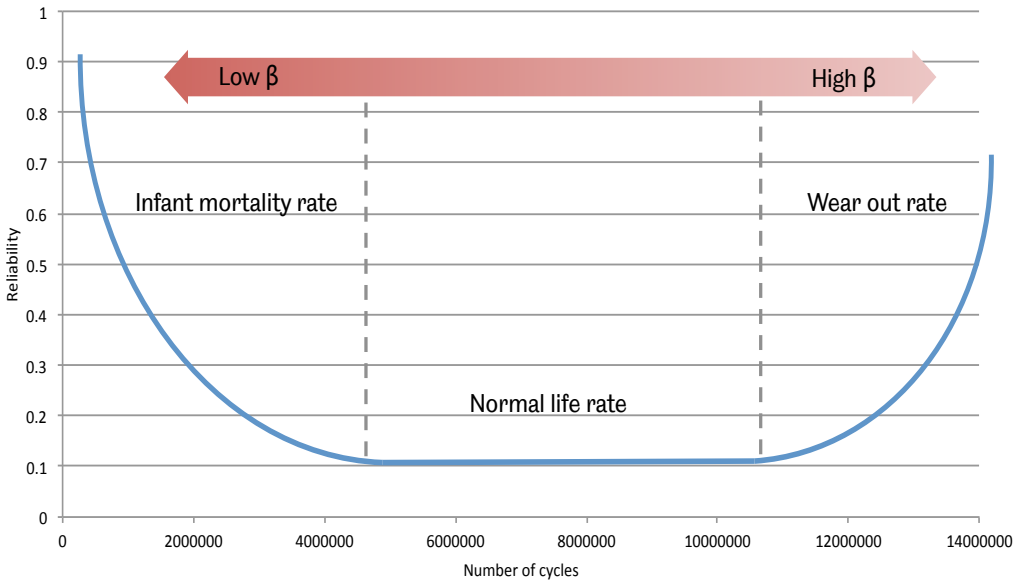


Figure 18: Predicted reliability curve showing the three general sequences of any product failure rates over time, commonly referred to as the bathtub curve*.

* Diagrams created by the author. Derived and collated from the literature (Abernethy, 2008, Rinne, 2009).

Chapter 3

Summary of the literature review

A common solution for restoring teeth in dentistry is using fixed prostheses, e.g. porcelain fused to metal, resin-bonded ceramic, or high strength ceramic substructure crowns. Dental ceramics have desirable features such as good aesthetic properties and biocompatibility with the oral cavity, although they have some disadvantages such as brittleness, which may lead to chipping of the veneer and abrasiveness that leads to wear to opposing natural teeth. Fractured ceramic may be repaired intra-orally with light cured composite involving sensitive techniques but with limited success.

Dental polymers play an essential role in the field of dentistry with different uses and indications. In dental fixed prostheses, the application of polymers has been limited due to the relative weakness, shrinkage and staining. However the PAEK family of thermoplastic high performance biomaterial polymers are being successfully used in the medical field as a substitute for some titanium, with PEKK polymer recently being introduced as a dental restorative material. They can be processed by either hot-pressing or CAD/CAM techniques and veneered with light cured composite resin.

Composite resins are well-established in restorative dentistry as a direct restorative material and as veneering material for metal or zirconia substructure as indirect fixed prostheses. Composite veneers could be considered more convenient because of ease of handling making them an intra-orally repairable material avoiding further tooth preparation. Also these veneers can mask opaque underlying substrate making the prosthesis aesthetically acceptable to the matching surrounding teeth and oral tissue.

Advantages of using PEKK, e.g. fabrication method in accordance with well established dental technology production techniques, combined with the aesthetic and adaptable light cure composite resin veneers shows great potential in the field of fixed dental restorations. Very limited data is available about PEKK's prospective for use in dentistry and hence more investigations should take place and the novel reason for this thesis.

Chapter 4

Aim and Objectives

4.1. Aim

To investigate the manufacturing processes, aesthetics properties, structural integrity and durability of PEKK high performance polymer based bi-layered crowns veneered with light cured composite in comparison to equivalent zirconia and metal based bi-layered crowns.

4.2. Objectives

- To press PEKK using standard dental laboratory pressing furnace.
- To evaluate the optical properties of the PEKK/composite bi-layered system in comparison with other zirconia and metal based bi-layered groups.
- To compare the occlusal fracture resistance of the PEKK/composite crowns in comparison to zirconia based and metal based bi-layered crowns.
- To compare the durability of the PEKK/ composite bi-layered crowns to zirconia based and metal based bi-layered crowns using fatigue testing methodology.

Chapter 5

Pressing Methodology: Optimising pressing parameters*

* Work from this chapter was presented at the Pekkton® Circle Conference 2016, 16 September 2016, Biel-Bienne, Switzerland. Oral presentation titled: Composite Veneered Pekkton® Crowns: How do they compare?

5.1. Introduction

The hot pressing technique is a well-established dental technology procedure for fabricating restorations. This procedure utilises the lost wax process whereby a wax pattern is invested in a phosphate-bonded material to create a mould. The mould is heated in a furnace at about 800°C for wax elimination. A pressing furnace is used to heat and press a material, typically ceramic, in to the preheated mould after placing the material ingot and a plunger (usually made of Al_2O_3) in the furnace. An example of such a system is Ivoclar Vivadent's IPS Empress® and IPS e.max® (Ivoclar Vivadent AG, Liechtenstein).

High performance thermoplastic polymers such as PEEK and PEKK, take advantage of this processing route. Having been introduced for the production of fixed and removable prostheses, fabrication using these materials in the dental laboratory often relies upon special equipment recommended by the manufacturer.

Pekkton® ivory (Cendres+Métaux SA) has recently been marketed as a high performance thermoplastic polymer for fixed prostheses which may either be fabricated via hot pressing of polymer ingots or by milling.

For the pressing procedure, the manufacturer recommends using a specific pressing furnace (Austromat press-i-dent DEKEMA furnace or PEKKtherm furnace from Cendres+Métaux), which allows the muffle to be cooled while pressing. Commonly used pressing furnaces for ceramics are tailored for

ceramic and are not generally fully programmable to allow cooling while actively pressing.

5.2. Aim

To examine a range of pressing parameters for Pekkton® ivory using a standard laboratory ceramic pressing furnace.

5.3. Objectives

- To establish a processing method for hot pressing using parameters available on a standard ceramic pressing furnace (Ivoclar Programat EP3000, Ivoclar Vivadent, Liechtenstein).
- To compare the mechanical and optical properties of samples produced via established pressing methodology to those produced via CAD/CAM milling.

5.4. Methods

Wax patterns of 12mm diameter and 1.0mm thick disc samples were used for the first pressing trials as simple shaped samples (for IVO PR1 and IVO PR2 pressings).

Furthermore, wax copings were prepared for pressing to evaluate the press of such samples with their complex shapes and thin margins (for IVO PR3, IVO PR4 and IVO PR5 pressings). A digital first molar coping design was produced via CAD/CAM milling (Roland DWX50, Roland DGA Corp. USA) to produce 8.0 mm thick wax copings.

Preparation of wax patterns and sprueing were carried out in accordance to the manufactures instruction. The investment material used was IPS PressVEST Speed (Ivoclar Vivadent AG) as recommended in the Pekkton manual.

Pressing programs for Pekkton® ivory in a 100g size ring using DEKEMA furnaces (AUSTROMAT® 654 press-i-dent and AUSTROMAT® 3001 press-i-dent, DEKEMA Dental-Keramiköfen GmbH Germany) were used as a baseline.

The programmes are shown in Figure 19 and the codes in the programme were clarified (highlighted in red) using the operating instructions for the DEKEMA furnace resulting in the following cycle:

Wax burnout in preheating furnace at 850°C for 45 minutes then place mould in the DEKEMA furnace and start for cooling program at 390°C for 20 minutes to stabilise the mould's temperature from 850°C before melting and pressing

PEKK. Then the furnace door opens allowing access to place the ingot and plunger before the pressing step. The furnace then melts the PEKK ingot at 380°C for 9.5 minutes (for the AUSTROMAT® 654) or 390°C for 10 minutes (for AUSTROMAT® 3001) and then starts pressing and cooling at the same time. This is achieved by operating the vacuum to allow air in the pressing chamber till it drops to 250°C before partially opening of the pressing chamber till reaching 200°C and ending the programme.

Program overview

Manufacturer	Furnace		Program
DEKEMA	Austromat 654 press-i-dent	100 g	L9 T20.C380 V0 T570 L92 T40 V.C250 L8 V.C200 C0 L0 T5
		200 g	L9 T20.C385 V0 T780 L92 T40 V.C250 L8 V.C200 C0 L0 T5
		380 g (Trixpress)	L9 T20.C395 V0 T1200 L92 T40 V.C250 L8 V.C200 C0 L0 T5
	Austromat 3001 press-i-dent	100 g	L9 T20.C390 V0 T600 L92 T40 V.C250 L8 V.C200 C0 L0 T5
		200 g	L9 T20.C395 V0 T1200 L92 T40 V.C250 L8 V.C200 C0 L0 T5
		380 g (Trixpress)	L9 T20.C395 V0 T1200 L92 T40 V.C250 L8 V.C200 C0 L0 T5

Figure 19: Pressing program for DEKEMA furnaces from Pekkton® ivory manual and the clarified programmes highlighted in red.

For the IVOCLAR EP3000 furnace, the changeable parameters (Table 8) for pressing are: standby temperature, temperature increase rate, holding temperature, holding time and abort speed. The lower the abort speed rate, the longer the plunger presses before release.

Table 8: Pressing parameters for IVOCLAR EP3000.

Symbol	Parameter	Value range
B	Standby temperature	100-700 °C
t	Temperature increase rate	10-140 °C/min
T	Holding temperature	100-1200 °C
H	Holding time (min:sec)	00:00-60:00
E	Abort speed	0-100000 µm/min

The IVOCLAR EP3000 differs to the DEKEMA furnace in the inability to programme the vacuum to cool the pressing chamber while pressing.

The pressing regimes that were used are shown in table 8. The regimes differ in plunger type and size, burnout time and temperature and pressing temperature.

Table 9: Baseline pressing programme using DEKEMA AUSTROMAT press-i-dent furnace (highlighted in red) and summarised performed PEKK pressing trials using the IVOCLAR EP3000 furnace.

Trials	Ring size & plunger	Wax burn-out in preheating furnace (temp. & time)	Stabilising mould's temperature before pressing	PEKK melting and pressing
BASELINE	100g & Pekkton disposable plunger	850°C 45 min	390°C ➔20 min➔ end program	390°C (Holding temp.) ➔10 min➔ press & cool till 200°C ➔ end program
IVO PR1 (Try outs)	100g (e.max set) & Alox plunger	850°C 45 min	Left to cool on bench till reaches 390°C using electrical thermometer	380/390°C (standby & holding temp.) ➔9.5/10min➔ press (abort speed 100)
IVO PR2 (Different pressing plungers)	100g (e.max set) & Alox and disposable plunger	850°C 45 min	390°C for 20 min (Preheat furnace)	380°C (standby & holding temp.) ➔10min➔ press (abort speed 100)
IVO PR3 (Different temperatures for cooling and pressing)	100g (Empress 1 set) & Pekkton disposable plunger	850°C 45 min	360/370/380/390°C (standby & holding temp.) ➔20min➔ end program (IVOCLAR EP3000)	360/370/380/390°C (standby & holding temp.) ➔10min➔ press (abort speed 100)
IVO PR4 (Lower temperature for wax-burnout)	100g (Empress 1 set) & Pekkton disposable plunger	750°C 45 min	365°C (standby & holding temp.) ➔20min➔ end program (IVOCLAR EP3000)	365°C (standby & holding temp.) ➔10min➔ press (abort speed 100)
IVO PR5 (Best parameters)	100g (Empress 1 set) & Pekkton disposable plunger	850°C 45 min	365°C (standby & holding temp.) ➔20min➔ end program (IVOCLAR EP3000)	365°C (standby & holding temp.) ➔10 min➔ press (abort speed 100)

The pressing parameters were altered depending on the result of the previous regime.

5.4.1. Pressing Regime 1 (IVO PR1):

After the wax burn-out at 850°C, the mould was left till reaching 390°C on the bench with the use of electrical thermometer before proceeding to the pressing procedure (Figure 20).

Figure 20: Electrical thermometer measuring the ring's temperature.

The IVOCLAR EP3000 furnace was programmed for using a 100g ring set as follows (Table 10) resulting in a heating regime of: 380°C standby and holding temperature for 9.5 minutes before pressing. This was programmed following the DEKEMA Austromat 654 100g program as much as can be achieved with the IVOCLAR EP3000. The same process was repeated again with changing the standby and holding temperature to 390°C for 10 minutes following the Austromat 3001 programme.

Table 10: Main pressing parameters used in Pressing Regime 1 (IVO PR1) in comparison to baseline pressing parameters.

Prog.	Sample	Ring size & plunger	Wax burn-out	Stabilising mould's temperature	Pressing
BASELINE (DEKEMA)	--	100g Pekkton plunger	850°C 45 min	390°C ➔20 min➔ end program	380°C (Holding temp.) ➔9.5 min➔ press & cool till 200°C ➔ end program
IVO PR1	Wax disc	100g (e.max set) Alox plunger	850°C 45 min	Left to cool on bench till reaches 390°C using electrical thermometer	380°C (standby & holding temp.) ➔9.5 min➔ press (abort speed 100)

The difference in this pressing trial to the baseline pressing programme, besides the cooling while pressing, is:

- Alox plunger, with a wider diameter, which fits the e.max 100g perfectly.
- Stabilising the mould on the bench after wax burn-out.

5.4.2. Pressing Regime 2 (IVO PR2) Different pressing plungers:

The pressing regime 2 parameters are summarised in Table 11 in comparison to the DEKEMA baseline programme.

Table 11: Main pressing parameters and difference in trials (highlighted in blue) used in Pressing Regime 2 (IVO PR2) in comparison to baseline pressing parameters.

Prog.	Sample	Ring size & plunger	Wax burn-out	Stabilising mould's temperature	Pressing
BASELINE (DEKEMA)	--	100g Pekkton plunger	850°C 45 min	390°C ➔20 min➔ end program	380°C (Holding temp.) ➔9.5 min➔ press & cool till 200°C ➔ end program
IVO PR2	Wax disc	100g (e.max set) & Alox plunger+ metal weight	850°C 45 min	390°C for 20 min (Preheat furnace)	380°C (standby & holding temp.) ➔10min➔ press (abort speed 100)
IVO PR2	Wax disc	100g (e.max set) & disposable plunger+ metal weight	850°C 45 min	390°C for 20 min (Preheat furnace)	380°C (standby & holding temp.) ➔10min➔ press (abort speed 100)
IVO PR2	Wax disc	100g (e.max set) & disposable plunger	850°C 45 min	390°C for 20 min (Preheat furnace)	380°C (standby & holding temp.) ➔10min➔ press (abort speed 100)

The difference from the first pressing regime was cooling of the mould after wax-burn-out in a preheat furnace at 390°C for 20 minutes, unlike before when the specimen was left on the bench to cool before the pressing procedure.

Three trials were pressed using this regime involving two different pressing plungers, Alox plunger with rubber cap (from Pekkton's disposable plunger) and the custom-made refractory disposable plunger.

The refractory plunger was created by duplicating the wider diameter Alox plunger using silicon-moulding material (Dublisil 15, Dreve Dentamid GmbH, Germany) and using the same mould investment material to produce a disposable plunger capped with the rubber seal that was part of the Pekkton disposable plungers equipment (Figure 21). The reason for doing that is to have a firm fit to the e.max 100 g ring set to allow direct comparison to the Alox plunger.

Following the same steps for pressing, the moulds were removed from the furnace after the pressing had finished and left to cool on a bench as follows:

- Alox plunger with metal weight (1.5 Kg) placed on top for 15 minutes.
- Custom-made disposable plunger with metal weight placed on top for 15 minutes.
- Custom-made disposable plunger without metal weight placed on top.

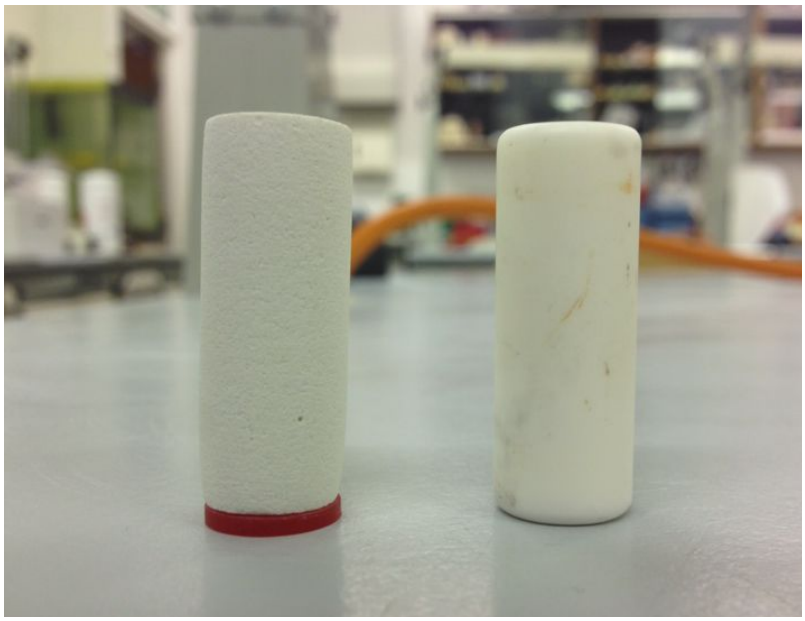


Figure 21: Refractory disposable pressing plunger with rubber seal on the left and Alox pressing plunger on right.

5.4.3. Pressing Regime 3 (IVO PR3) Different stabilising and pressing temperatures:

The pressing regime 3 parameters are summarised in Table 12 in comparison to the DEKEMA baseline programme.

Table 12: Main pressing parameters and difference in trials (highlighted in blue) used in Pressing Regime 3 (IVO PR3) in comparison to baseline pressing parameters.

Prog.	Sample	Ring size & plunger	Wax burn-out	Stabilising mould's temperature	Pressing
BASELINE (DEKEMA)	--	100g Pekkton plunger	850°C 45 min	390°C ➔20 min➔ end program	380°C (Holding temp.) ➔9.5 min➔ press & cool till 200°C ➔ end program
IVO PR3	Wax coping	100g Pekkton plunger	850°C 45 min	390°C (standby & holding temp.) ➔20min➔ end program (IVOCLAR EP3000)	390°C (standby & holding temp.) ➔10min➔ press (abort speed 100)
IVO PR3	Wax coping	100g Pekkton plunger	850°C 45 min	380°C (standby & holding temp.) ➔20min➔ end program (IVOCLAR EP3000)	380°C (standby & holding temp.) ➔10min➔ press (abort speed 100)
IVO PR3	Wax coping	100g Pekkton plunger	850°C 45 min	370°C (standby & holding temp.) ➔20min➔ end program (IVOCLAR EP3000)	370°C (standby & holding temp.) ➔10min➔ press (abort speed 100)
IVO PR3	Wax coping	100g Pekkton plunger	850°C 45 min	360°C (standby & holding temp.) ➔20min➔ end program (IVOCLAR EP3000)	360°C (standby & holding temp.) ➔10min➔ press (abort speed 100)

The differences in regime 3 to regime 2 were:

- Pressing wax copings using the Empress1 100g ring set to form the investment ring enabling the use of C+M disposable plungers (Figure 22).
- Using the IVOCLAR EP3000 to cool down the ring from 850°C before pressing by programming a firing program for 20 minutes. After the firing programme finishes, the door opens allowing access to place Pekkton ingot and pressing plunger in the mould before switching to the pressing program.

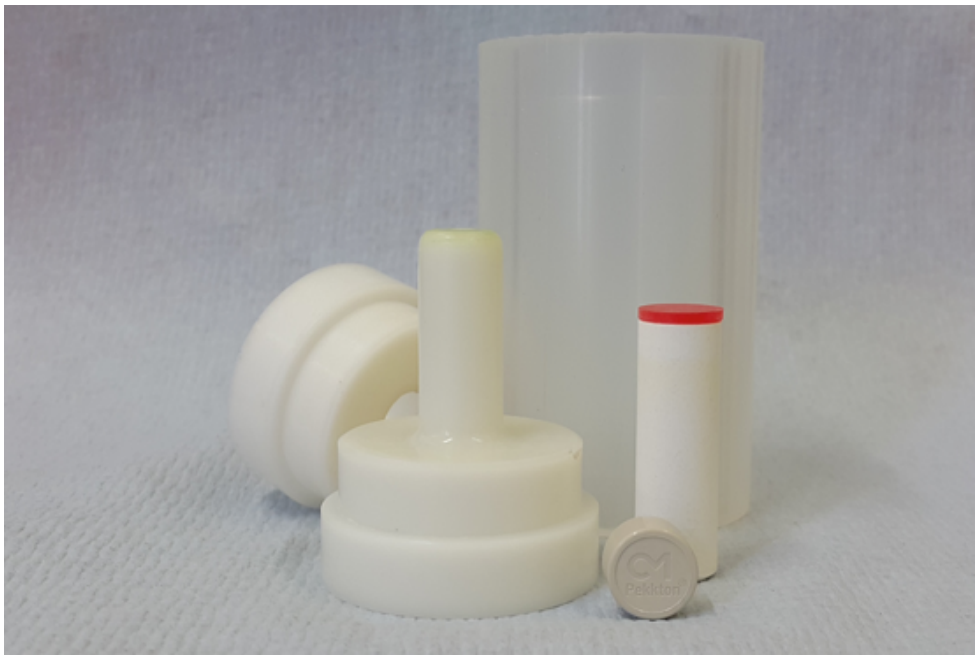


Figure 22: Empress 1 ring set, Pekkton's disposable pressing plunger and Pekkton® ivory ingot.

Four trials were pressed using this regime differing in the stabilising and pressing temperatures (highlighted in blue in Table 12) as follows:

- Stabilising and pressing at 390°C.
- Stabilising and pressing at 380°C.

- Stabilising and pressing at 370°C.
- Stabilising and pressing at 360°C.

5.4.4. Pressing Regime 4 (IVO PR4) Lower temperature for wax-burnout:

The pressing regime 4 parameters are summarised in Table 13 in comparison to the DEKEMA baseline programme.

Table 13: Main pressing parameters used in Pressing Regime 4 (IVO PR4) in comparison to baseline pressing parameters.

Prog.	Sample	Ring size & plunger	Wax burn-out	Stabilising mould's temperature	Pressing
BASELINE (DEKEMA)	--	100g Pekkton plunger	850°C 45 min	390°C ➔20 min➔ end program	380°C (Holding temp.) ➔9.5 min➔ press & cool till 200°C ➔ end program
IVO PR4	Wax coping	100g Pekkton plunger	750°C 45 min	365°C (standby & holding temp.) ➔20min➔ end program (IVOCLAR EP3000)	365°C (standby & holding temp.) ➔10min➔ press (abort speed 100)

The differences in regime 4 to regime 3 were:

- The lower burnout temperature of 750°C.
- Stabilising and pressing temperatures were set at 365°C.

5.4.5. Pressing Regime 5 (IVO PR5) Best pressing parameters

The pressing regime 5 parameters are summarised in Table 14 in comparison to the DEKEMA baseline programme.

Table 14: Main pressing parameters used in Pressing Regime 5 (IVO PR5) in comparison to baseline pressing parameters.

Prog.	Sample	Ring size & plunger	Wax burn-out	Stabilising mould's temperature	Pressing
BASELINE (DEKEMA)	--	100g Pekkton plunger	850°C 45 min	390°C ➔20 min➔ end program	380°C (Holding temp.) ➔9.5 min➔ press & cool till 200°C ➔ end program
IVO PR5	Wax coping	100g Pekkton plunger	850°C 45 min	365°C (standby & holding temp.) ➔20min➔ end program (IVOCLAR EP3000)	365°C (standby & holding temp.) ➔10min➔ press (abort speed 100)

The main difference in this pressing regime to regime 4 was setting the wax burnout temperature to 850°C instead of 750°C.

5.5. Results and Discussion

First attempts to press Pekkton using IVO PR1 pressing regime was to examine the material's behaviour when heated and pressed using the available equipment in the laboratory that are mainly designed for pressing ceramics at much higher temperatures (>700 °C) than required for pressing PEKK (<400 °C).

This resulted in a very poor outcome with little mould filling when using Alox plunger (Figure 23).

Figure 23: 100g ring (e-max set) with Alox plunger after pressing.

For IVO PR2 pressings, the results of the disposable plunger were good with (Figure 24) and without (Figure 25) the extra weight on top of the plunger while cooling and without any cracks in either the ring or plunger. The Alox

plunger ring resulted in incomplete pressing even with the rubber cap and the weight placed after pressing (Figure 26).

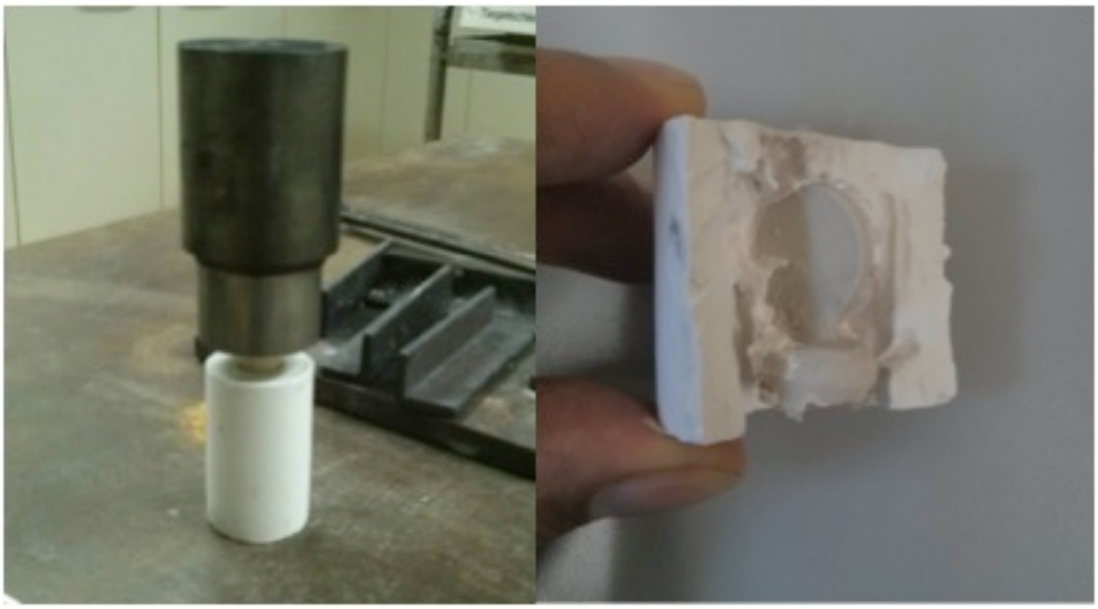


Figure 24: 100g ring after pressing with a bigger disposable ring.

Figure 25: Pressed disc with a bigger disposable plunger without the metal weight when cooling.

Figure 26: incomplete press with Alox plunger and metal weight when cooling.

From these different pressings trials, it was evident that the best method of pressing was with the disposable refractory plunger capped with a rubber seal, resulting in good press with no visible porosity, voids or distortion of any sort. A possible explanation of the better press could be the even cooling rate in both the plunger and the mould, which are made of the same material unlike the Alox plunger.

Using wax copings with the IVO PR3 regime, the different pressings were performed by using the IVOCLAR EP3000 to cool down the ring from 850°C before pressing to reduce the number of steps and eliminate any causes of ring cracks due to the shift in temperatures when transferred between three furnaces with different temperatures.

All pressing resulted in a fully pressed coping but with roughened surface of micro-bubbles in areas. It was clear that the lower the temperature, the less micro-bubbles occurred. This can be seen in the pressed copings under 390°C (Figure 27), 380°C (Figure 28), 370°C (Figure 29) and 360°C (Figure 30). The pressing under 360°C resulted in a smooth pressed coping but with small miss press in the coping's margin that could indicate that the polymer cooled to soon.

Figure 27: Coping pressed under 390°C.

Figure 28: Coping pressed under 380°C.

Figure 29: Coping pressed under 370°C.

Figure 30: Coping pressed under 360°C.

From the results of the IVO PR3 pressings, the cooling and pressing temperatures for IVO PR4 pressing were set at 365°C, as it was thought to be a suitable temperature between the slightly over pressed coping at 370°C and the slightly under pressed coping at 360°C.

Another change was the wax burn-out temperature to 750°C instead of 850°C. Reaching higher temperature was thought unnecessary for this press as the polymer is pressed at temperatures much lower than required for pressing ceramics (700-900°C).

Following the described steps, the result was a smooth complete pressed coping (Figure 31).

The pressing regime was repeated with copings made out of different types of wax and it was noticed that the 3D printed wax copings were pressed but with a rough layer covering the coping that could be removed by shot blasting with Al_2O_3 particles (Figure 32). In addition, it was noticed after wax burn-out of such copings under 750°C temperature caused a blackish colour around the ring's opening as illustrated in Figure 33.

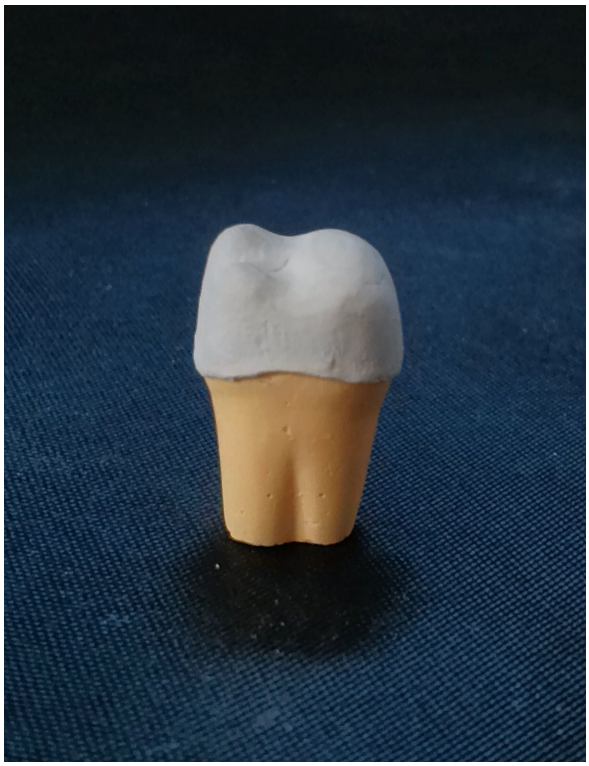


Figure 31: Coping pressed under 365°C.

Figure 32: Pressed sample with rough surface (left) and after shot blasted with 110µm Al_2O_3 (right).

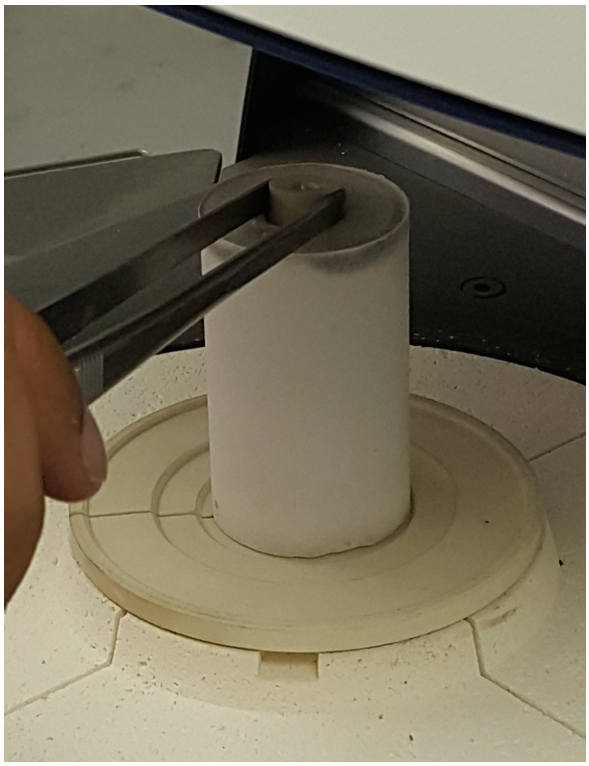


Figure 33: Blackish colour of a 3D printed wax coping's ring after burn-out at 750 °C.

Examples of failures in the previous pressing trials and the causes could be seen summarised in Table 15.

Table 15: Some of the problems and causes found in the early pressing trials.

Problem	**Cause**
Incomplete press	Using alox plunger
Ingot destroyed or pressed crown distorted.	Mould too hot
Incomplete press.	Mould too cold
Rough layer forms on the crowns surface on some types of wax (e.g. 3D printed wax) that could be removed after shotblasting.	Wax burnout at temperatures lower than 850 °C.

The IVO PR5 pressings were repeating IVO PR4 pressing regime but with a raised wax burnout temperature to 850°C to ensure full elimination of any traces of wax in the mould that might have caused the blackish colour around the ring's opening and the roughened pressed polymer surface.

This change solved the problem and the pressed coping was smooth without the rough layer as seen before.

This regime was repeated with different samples and wax types and always resulted in fully pressed polymer samples (Figure 34).

The final PEKK pressing procedure could be seen described in Table 16.

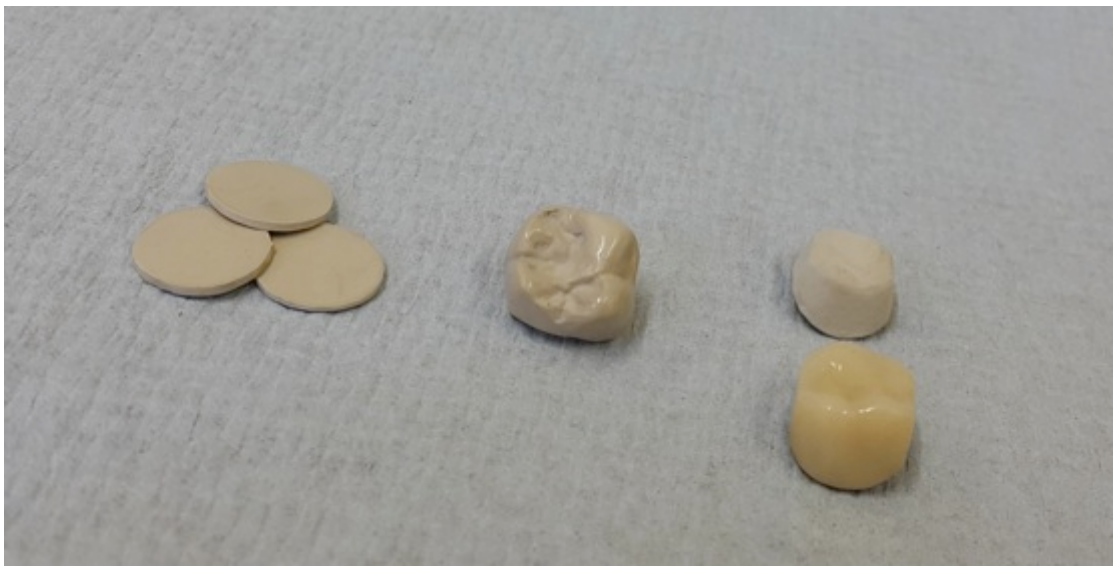


Figure 34: some samples produced using the pressing protocol: discs, crown and un-veneered coping and composite veneer coping respectively.

Table 16: Summarised finalised pressing protocol steps using 100g ring set.

Stage	Description
Sample prep.	Prepare the wax sample and sprue following standard dental laboratory steps
	Fix the wax samples in the proper ring set to allow the use of the disposable plunger with the plastic cab from Cendres+Métaux
Investing and wax burnout	Carry out the investment step following the manufacturer guidelines
	Leave the investment to set and then remove the formers
	Place the ring in the burnout furnace at 850°C and leave for 45 minutes
PEKK hot-pressing	Edit and save a program for firing the following parameters: Firing cycle to be set at 365°C for 20 minutes to cool the mould after wax burnout and to the right temperature before the pressing step
	Edit and save a program for pressing using the following parameters: Pressing cycle to be set at 365°C for standby temperature, 365°C for the holding temperature, 10 minutes holding time and 100 for the abort speed
	Place the preheated mould in the Programat® EP3000 and start the saved firing program
	After the firing program ends, the door opens automatically allowing access to place Pekkton® ivory ingot and plunger in ring and switch to the pressing program and start the customised programme
	After the program ends, remove the ring and leave to cool down
Divesting	Divest the ring following normal procedures and clean the pressed restoration by shotblasting
	Cut the sprue and finish following manufacturer guidelines

5.6. Comparison of samples produced via developed pressing protocol

The IVO PR5 pressing regime was successfully repeated 10 times to produce copings and discs samples. This protocol was developed before Pekkton® ivory blanks for CAD/CAM milling were produced in the market.

The IVO PR5 pressing regime was used again to produce disc samples in order to compare them with equivalent samples produced out of Pekkton® ivory CAD/CAM blank

All results of pressed and milled PEKK samples will be compared using IBM SPSS Statistics 23 software in a paired T-test and significant difference level was determined at $p<0.05$.

5.6.1. Comparison methods and results:

17 disc shaped wax samples were hot pressed using the Ivoclar pressing furnace (Programat EP3000, Ivoclar Vivadent, Liechtenstein). Pekkton® ivory ingots (Lot. No. 175701) was used following IVO PR5 pressing regime.

Another 17 discs were produced using a five-axis milling machine (Roland DWX50, Roland DGA Corp. USA) out of Pekkton® ivory experimental blocks provided by Cendres+Métaux (Figure 35).

All discs, pressed and milled, were polished under water using carbide abrasive paper P400 and P600 respectively in rotating polishing disc

(Metaserv Buehler, UK). For the hardness samples (n=4) extra polishing at P1000 and 1 µm diamond paste to a thickness of 1.4mm.

A digital calliper (PK-0505, Mitutoyo Corporation, Japan) was used to ensure sample thickness.

Figure 35: Pekkton® ivory CAD/CAM blank used for milling PEKK samples.

5.6.1.1. CIE L*a*b colour values

Three samples (12mm x 1mm) were used to record 9 CIE L*a*b readings for each group (pressed and milled) using a spectrophotometer (CM-2600d Konica Minolta Sensing, Inc., Japan) with a 3mm target mask opening, a D65 illuminant and white background (details of used methodology can be found in the next chapter 6.4).

The average recordings of the CIE L*a*b* colour values can be seen in Table 17 showing no significant difference in L* (p=0.9), a* (p=0.67) and b* (p=0.74) colour values.

Table 17: L*a*b* colour values of veneered PEKK (pressed and milled) samples.

Group	L* (p=0.9)	a* (p=0.67)	b* (p=0.74)
Pressed PEKK	75.5 (±0.57)	1.78 (±0.25)	8.13 (±0.96)
Milled PEKK	75.4 (±0.43)	1.62 (±0.38)	8.56 (±1.2)

5.6.1.2. Biaxial Flexural Strength (BFS)

The testing was performed using a universal testing machine (Loyds Instrument Model LRX) using the ball on ring configuration at a cross-head speed of 1mm/min using a 2500 N load cell and 100.6% sensitivity.

Ten samples (12mm x 1mm) were tested and the recorded fracture load was used to calculate the BFS according to the following equation (Piddock et al., 1986):

Equation 1

$$\sigma_{\max} = \frac{P}{h^2}[0.606\log_e(a/h) + 1.13]$$

Where P is the recorded fracture load (N), a is the radius of the supporting ring (mm) and h is the sample thickness (mm).

The results can be seen in Table 18 below and show very similar results with no significant difference between pressed and milled groups in the fracture load and BFS.

Table 18: Average fracture load and BFS (n=10) of pressed and milled PEKK discs (1.0 mm thick).

Samples	Fracture load (N) (p=.280)	BFS (MPa) (p=.279)
Pressed PEKK	113.9 (±14.5)	239.9 (±30.5)
Milled PEKK	122.4 (±17.9)	257.8 (±37.8)

5.6.1.3. Hardness

Four samples (12mmx 1.4mm) of each group, pressed and milled, were subjected to indentation using Vickers Hardness machine (Foundrax, Somerset, UK). Samples were indented with 5 Kg weight and 5 seconds dwell time to record 10 readings for each group.

The pressed group gave a similar average Vickers hardness of 33.5 kgf/mm2 (± 0.32) in comparison to the milled group 33.7 kgf/mm2 (± 0.2). No significant difference could be determined according to the statistical analysis (p= 0.171).

5.7. Summary

Preparation instructions were followed as per Pekkton® ivory's manual up to the pressing stage. Pressing programs were clarified with the use of operating instructions for AUSTROMAT® press-i-dent furnace. For the IVOCALR Programat® EP3000 furnace, the changeable parameters for pressing are: standby temperature, temperature increase rate, holding temperature, holding time and abort speed. The lower the abort speed rate, the longer the plunger presses before release.

A number of trials were performed using different plunger types, investment material, burnout and pressing temperatures. A significant change in the IVO PR3 regime compared to routine practice was to use the IVOCLAR EP3000 to cool down and stabilise the mould's temperature from wax burnout temperature before pressing instead of allowing it to cool on the bench or by using different third furnace to cool below 400°C before the pressing step. This was achieved by programming a firing program for 20 minutes under 365°C. Also using Empress 1 ring set was significant as it allowed using the disposable plungers provided from Cendres+Métaux to be used. The benefit was a uniform temperature for both the mould and plunger resulting in the best pressing results which is thought caused by:

- Cooling in the same furnace instead of being transferred between three furnaces with different temperatures.
- Using refractory plungers same as the mould's material.

This method was successfully repeated 10 times to produce discs used for the optical evaluation (see chapter 6). This protocol was developed before the CAD/CAM blanks were available and later pressed and milled PEKK samples were compared in relation to their optical and mechanical properties. It was found that there was no significant difference (significant level $p<0.05$) between pressed and milled samples in CIE L*a*b* colour values, biaxial flexural strength and hardness. This finding validates samples produced via steps described in the IVO PR5 pressing regime.

This pressing protocol allows the processing of PEKK using a standard ceramic pressing furnace for sample production. The advantage is that the purchase of new expensive equipment is not necessary to process the material via either pressing or milling. It was found to be a reliable method to produce the disc samples for this research with the available ceramic pressing furnace and it would be of interest of other researchers who would like to produce small numbers of samples for pilot studies. On the other hand, producing samples via milling out of a factory pressed PEKK blanks is a much easier method as its saves the time eliminating the need to: wax-up, sprue, invest, burn out, hot pressing, divesting and sprue cutting and finishing.

5.8. Conclusion

This study demonstrates that it was possible to hot press Pekkton® ivory using a standard ceramic pressing furnace. The method was successfully repeated many times to produce copings and discs used for this research. The comparison between pressed PEKK samples using a standard ceramic pressing furnace gave similar results to equivalent milled samples with no statistically significant difference in the optical and mechanical aspects.

Chapter 6

Optical Properties of PEKK Composite Veneered Structures*

* Work from this chapter was presented at:

- The 2015 IADR/AADR/CADR General Session & Exhibition, March 11-14, 2015, in Boston, Mass., USA. Poster titled: Evaluation of the Optical Properties of PEKK Based Restorations. Alsadon, O. A., Wood, D., Patrick, D., Copponnex, T., Pollington, S.
- The Pekkton® Circle Conference 2016, 16 September 2016, Biel-Bienne, Switzerland. Oral presentation titled: Composite Veneered Pekkton® Crowns: How do they compare?

6.1. Introduction

Aesthetics play an important role when restoring teeth and hence any restorative material should match the surrounding natural teeth. The substructure material always plays an important role in the final result of any bilayered restoration and porcelain fused to metal restorations are widely adopted method for restoring teeth but with not very good shade matching in comparison with ceramic substructures such as zirconia (Stevenson and Ibbetson, 2010). As a result the use of aesthetic, metal-free restorations is increasing as the all-ceramic approach and technologies are now well established in dentistry with a variety of materials indicated for different clinical situations (Sadowsky, 2006, Spear and Holloway, 2008).

Ceramic veneering materials have usually been advocated for indirect restorations but increasingly light cured resin-based composites are being used as veneering materials for ceramic, metal and polymer substructures due to the developments of bonding techniques, improved mechanical properties of composites and ease of fabrication (Jordan, 1993, Ferracane, 2011).

Veneering materials play an important aesthetic role in successfully restoring teeth, especially in the anterior region where the opacity of a substructure or a discoloured tooth may need to be masked.

Ceramic veneering materials have evolved to a stage where there is a range of tooth like shades available and these have been used for over 50 years as veneering materials for alloys (e.g. NiCr to create a PFM) and ceramic

substructures (e.g. zirconia to create a high strength ceramic substructure crown) (Kelly et al., 1996).

High performance polymers in dentistry for fixed applications tend to use composite resin as a veneering material, although they may be used as a monolithic material or as support for a ceramic crown.

Bonding composite to the polymer surface requires micromechanical retention by shot-blasting using alumina oxide particles and the application of a universal and/or resin bonding primer (Fuhrmann et al., 2014). These steps are well established in dental technology and are used with a variety of materials and procedures.

When comparing the optical properties of the substructure materials available, metal alloys are all opaque, however do differ in colour from warm gold through to dark grey hues of nickel chrome alloys.

Ceramic substructures demonstrate the most variation. The materials can be stained to an appropriate tooth colour and they are available in a range of translucencies from some types of zirconia which are opaque to glass infiltrated ceramics and lithium disilicates which show a high degree of light transmittance.

The polymers to date are opaque and only available in a limited range of colours. The polymer colour presents a challenge to the dental technician in the same way as a metal substructure in that the surface colour must be 'modified' prior to the aesthetic veneering materials being applied.

This chapter explores the effect of the substructure colour on the definitive restoration.

6.2. Aim

To evaluate the optical properties of PEKK substructures before and after veneering with light cured resin-based composite and compare them to equivalent substructure materials and veneers.

6.3. Objectives

- To determine the parameters of spectral reflectance and CIE L*a*b* colour coordinates of metal, ceramic and polymer veneered substructures.
- To calculate the opacity, translucency parameter and colour difference (ΔE).

6.4. Methods

The optical properties of the substructure materials (PEKK, Zirconia and NiCr) and veneering materials (ceramic and composite) were first assessed as single layered samples before testing as bilayered samples. The sample groups tested are shown in Table 19.

Veneering materials of the same shade (A2) were selected for the study. The samples were produced and finished to a thickness of 1.0mm for single layered groups, and 1.3mm for the laminate groups, according to clinical recommendation by Pekkton® ivory manual (0.8mm for substructure and 0.5mm for the veneer).

Each group consisted of three samples (n=3) 16mm in diameter, wide enough to cover the spectrophotometer's target mask opening of 3 mm. All specimens were polished under water using waterproof SiC abrasive paper P400 and P800 respectively in a rotating disc polisher (Metaserv Buehler, UK). Three readings from different areas where taken for each sample resulting in a total of 9 individual recordings for each group.

Table 19: Materials samples for optical properties evaluation.

Sample group (n=3)		Material	Brand	Description	Lot no.
Monolayer Groups	Veneers	Composite	VITA VM LC	Light cured composite: UDMA, TEGMA, Silica, primary particle (40- 50nm)	33211
		Ceramic	VITAVM9 veneering material	High-fusing, fine structure feldspathic ceramic for veneering zirconia substructure	32380
	Substructures	Zirconia	VITA In-Ceram® YZ	Zirconium dioxide (ZrO_2), yttrium oxide (Y_2O_3) 5%, hafnium oxide (HfO_2) < 3%, aluminium oxide (Al_2O_3) and silicon dioxide (SiO_2) <1% (weight percentage)	10921
		Metal	Talladium Tilite V, Talladium, Inc, USA	Non-precious Medical ceramic alloy containing Nickel, Chromium, and Molybdenum.	042011
		PEKK	Pekkton Ivory, Cendres+Métaux SA	High performance polymer consists of OXPEKK® IG (implant grade PEKK) and Titanium Dioxide for colouring and optimisation of mechanical properties.	175701
Laminates Groups		Zirconia & Ceramic	VITA In-Ceram® YZ & VITAVM9 veneering material	Zirconia substructure veneered with felspathic ceramic bonded following manufacturer guidelines.	10921 & 32380
		Zirconia & Composite	VITA In-Ceram® YZ & VITA VM LC	Zirconia substructure veneered with light cured composite resin bonded following manufacturing guidelines.	27651 & 33211
		Metal & Composite	Talladium Tilite V & VITA VM LC	Metal substructure veneered with light cured composite resin bonded following manufacturing guidelines.	042011 & 33211
		PEKK & Composite	Pekkton Ivory, Cendres+Métaux SA & VITA VM LC	PEKK substructure veneered with light cured composite resin bonded following manufacturing guidelines.	175701 & 33211

6.5. Sample preparation

6.5.1. Composite resin

A silicone mould (Dublisil 15, Dreve Dentamid GmbH, Germany) was produced (Figure 36) to assist in the fabrication of the composite resin samples (VITA VM LC Dentine paste, VITA Zahnfabrik H. Rauter GmbH & Co.KG, Germany). The composite surface was light cured using a calibrated halogen light curing unit (Coltolux75, Coltène Whaledent Group, Switzerland) for 60 seconds to harden the composite resin. The discs were removed from the mould and cured for a further 60 seconds from the other side. The samples were polished using waterproof silicon carbide abrasive paper (BuehlerMet II, Germany) sizes P400 and P600 respectively on a rotating polishing disc (Metaserv Buehler, UK).

Figure 36: Composite being shaped in a silicone mould.

6.5.2. Veneering Ceramic

Dentine shade ceramic powder (VITAVM9 veneering material, VITA Zahnfabrik H. Rauter GmbH & Co.KG, Germany) was mixed with modelling liquid and formed to a disc shape using a silicone mould. The ceramic slurry was condensed and dried to remove excess moisture using tissue. The ceramic disc was removed from the mould and placed on a firing tray.

A calibrated vacuum furnace (VITA VACUMAT 40T, VITA Zahnfabrik H. Rauter GmbH & Co.KG, Germany), was used to fire the samples at 910°C following manufacturers instruction. Final polishing was undertaken under water using carbide abrasive paper P400 and P600 respectively on a rotating polishing disc (Metaserv Buehler, UK).

6.5.3. Zirconia

CAD/CAM blocks (In-Ceram YZ 20/15, VITA Zahnfabrik H. Rauter GmbH & Co.KG, Germany) were used to prepare the zirconia samples. These blocks were sectioned using a diamond blade (Buehler diamond wafering blade, USA) in a precision saw (IsoMet® 1000 Precision Saw, Buehler, USA) to a thickness greater than the final desired thickness by 20% (Figure 37). This difference in size is to compensate the shrinkage that occurs during firing.

Light YZ colouring liquid was used to stain the zirconia specimens a shade close to that of 2M2 shade. The specimens were submerged in the liquid for 2 minutes (Figure 38) before firing using a vacuum furnace (VITA VACUMAT 40T, VITA Zahnfabrik H. Rauter GmbH & Co.KG, Germany) at 700°C for 5 minutes to eliminate excess liquid. The specimens were then sintered at

1530°C for two hours using a high temperature furnace (Ceramill therm, Amann Girrbach AG, Austria). Figure 39 shows the sample after colouring and sintering. The samples were polished under water using carbide abrasive paper P400 and P600 respectively in rotating polishing disc (Metaserv Buehler, UK). The thickness was checked using a digital calliper (PK-0505, Mitutoyo Corporation, Japan) the final result was 1.0mm and 0.8mm thick specimens for substructure and laminate groups respectively.

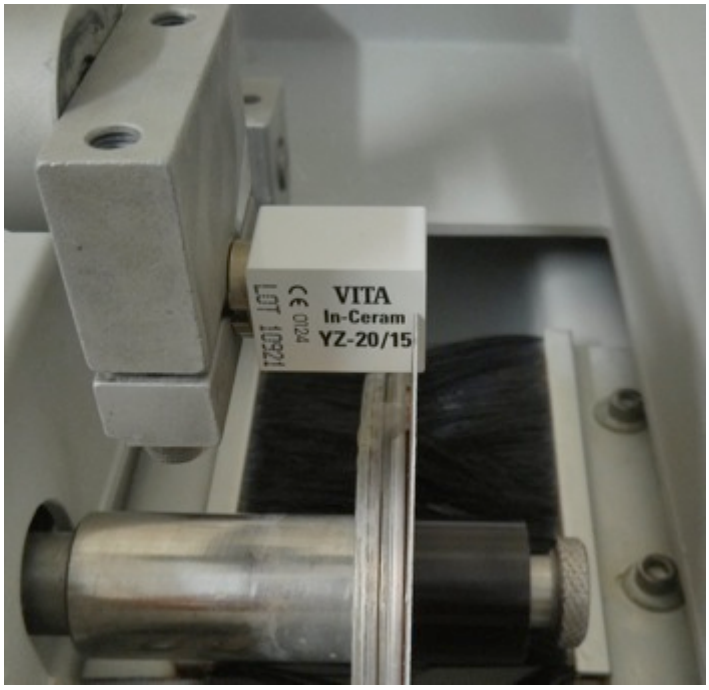


Figure 37: VITA In-Ceram YZ blank while sectioned using diamond disc.

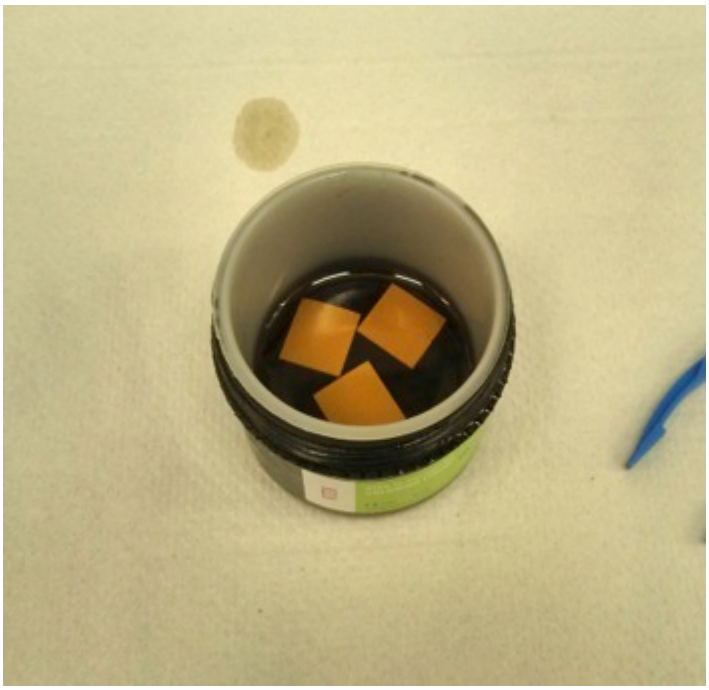


Figure 38: YZ samples submerged in colouring liquid for two minutes.

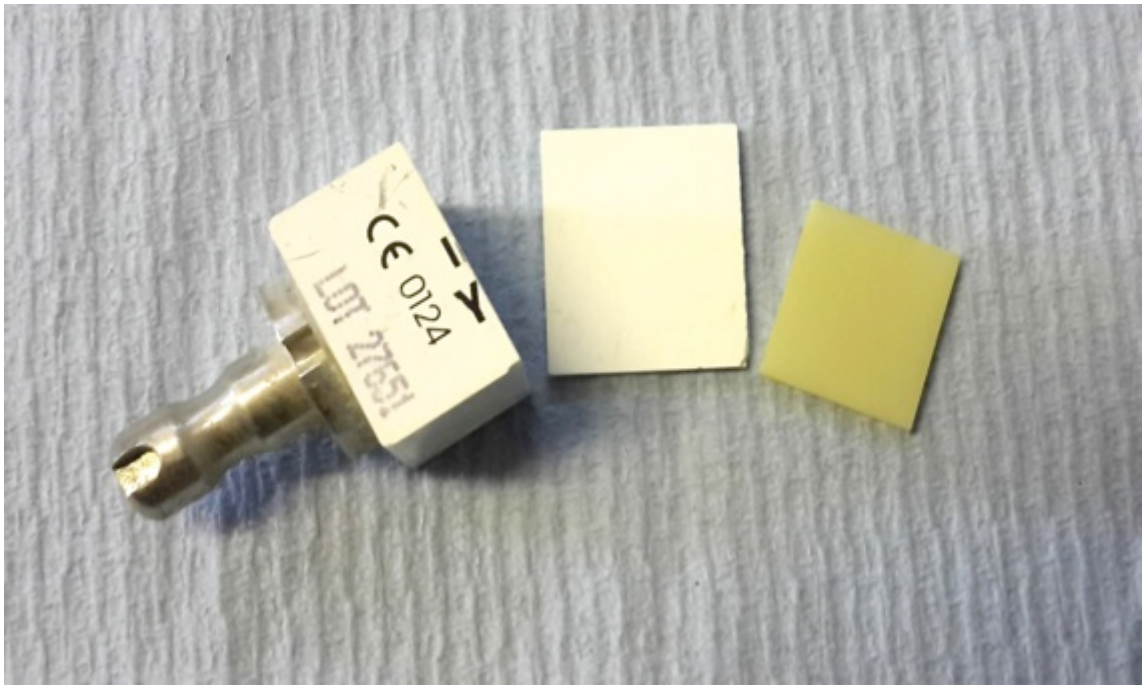


Figure 39: Zirconia final sample on the right.

6.5.4. PEKK

The high performance polymer material (Pekkton ivory, Cendres+Métaux SA) is provided as ingots to be hot-pressed, or discs to be machined. The user's manual recommends using Austromat press-i-dent DEKEMA furnaces for pressing. However, as part of this research a pressing regime was established for an Ivoclar EP3000 pressing furnace (details in previous chapter 5).

Discs of wax were shaped and sprued as shown in Figure 40. Investment material (IPS PressVEST Speed, Ivoclar Vivadent AG, Liechtenstein) was used to invest the patterns and preheating carried out by placing the set moulds in a burnout furnace (Vecstar LF3, Vecstar Limited, UK) at 850°C for 45 minutes. Pekkton ivory was pressed using the Ivoclar EP3000 and the ring was left to cool before shot-blasting the investment away from the pressed discs using Al_2O_3 110µm particles under 2 bar pressure. The samples were removed from the sprues using a cutting disc and finished using a diamond bur. The samples were polished under water using carbide abrasive paper P400 and P600 respectively in rotating polishing disc (Metaserv Buehler, UK).

A digital calliper (PK-0505, Mitutoyo Corporation, Japan) was used to measure the thickness and achieve 1.0 mm thick discs for the single layer sample groups, and 0.8 mm discs to be veneered with light cured composite resin as a laminate group samples. Figure 41 shows the final PEKK samples.

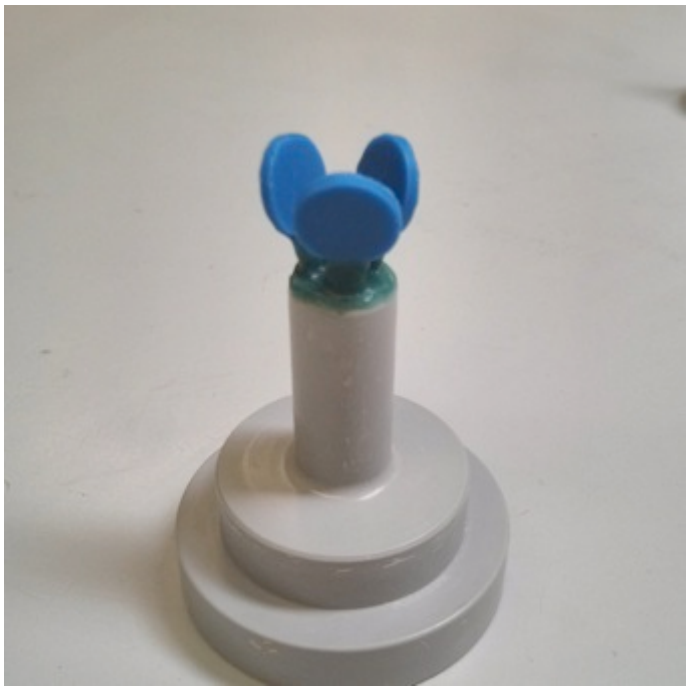


Figure 40: Discs of wax sprued to mould former prior to investing and pressing Pekkton ivory.

Figure 41: PEKK ingot (left) and pressed samples (right).

6.5.5. Metal

Disc shaped wax samples were invested using phosphate bonded investment material (SHERAFINA-RAPID, SHERA Werkstoff-Technologie GmbH & Co. KG, Germany) and the ring was left to set for 45 minutes before removing the base. The wax burn-out stage was carried out in a furnace for 45 minutes at 850°C before taking the ring to the casting machine and casting the alloy (Talladium Tilite V, Talladium, Inc, USA) at 1329°C.

Moulds were left to cool and the metal discs de-vested and shot-blasted using 110µm Alumina particles. Sprues were separated using rotary cutting discs and discs were finished and polished using carbide bur and carbide abrasive paper P400 and P600 under water respectively. The finished samples were 1.0mm thick discs for the single layer samples group and 0.8mm discs for composite veneered group. Figure 42 shows metal discs before finishing and veneering with composite.

Figure 42: Alloy for casting (left) and cast metal disc samples (right).

6.5.6. Composite veneered groups: YZ/LC, Metal/LC and PEKK/LC

PEKK, metal and zirconia bonding surfaces were prepared using the same methods prior to placing composite resin veneer. The bonding surface was shotblasted using Al_2O_3 110µm particles under 2 bar pressure before applying the bonding primer. Different primers were used according to the substructure materials' manufacturers recommendation as follows:

- PEKK: visio.link®, Bredent GmbH & Co. KG, Germany.
- Zirconia: Monobond® Plus, Ivoclar Vivadent AG, Liechtenstein.
- Metal (Kuraray Alloy primer®, KURARAY CO., LTD, Japan).

A thin coating of VITA VM LC opaque paste was applied evenly on the primed surface and light cured for 60 second using a halogen light cure unit (Coltolux75, Coltène Whaledent Group, Switzerland).

Composite resin dentine paste was applied to the opaque layer using a plastic spatula and VITA VM LC modelling liquid. The disc was placed in a silicone mould to facilitate shaping of the veneer and light cured for 60 seconds (Figure 43). The sample was removed from the mould and light cured again for a further 60 seconds to ensure full polymerisation of the composite resin. The composite resin veneer was then polished using waterproof carbide abrasive paper P400 and P600 respectively. The end result was a 1.3 mm thick sample of 0.8 mm substructure and outer 0.5 mm composite veneer.

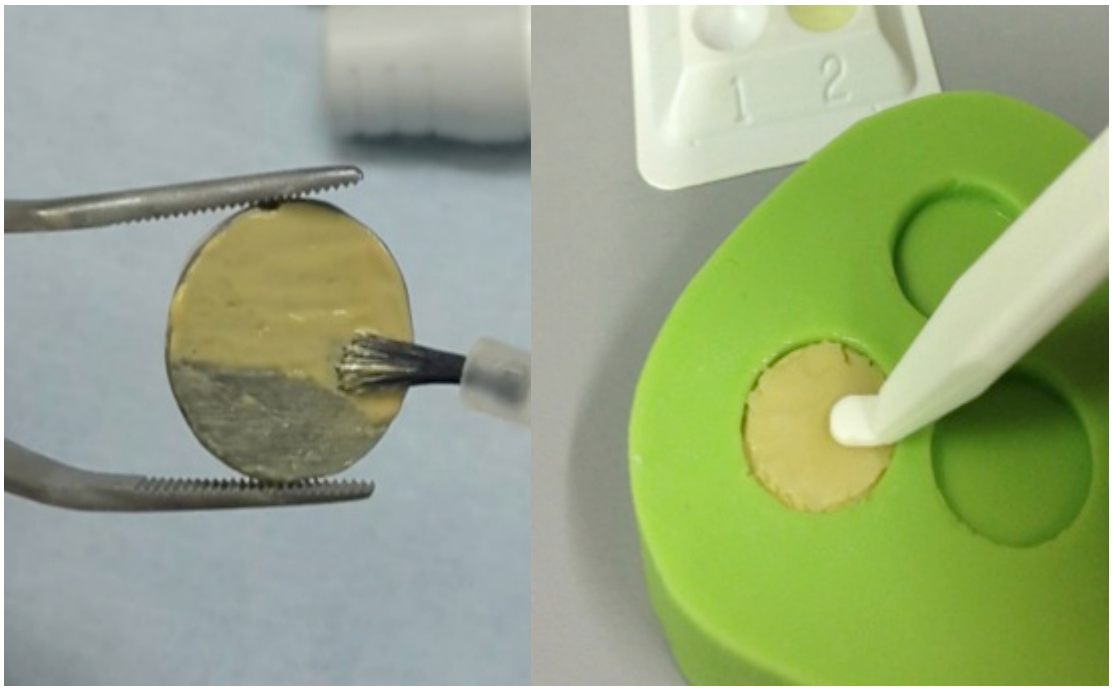


Figure 43: Building the composite veneer starting with the opaque layer using a brush (left) and dentine using a plastic spatula (right).

6.5.7. Ceramic veneered Zirconia group: YZ/VM9:

VM9 Effect Bonder powder was mixed with the Effect Bonder liquid (VITA Zahnfabrik H. Rauter GmbH & Co.KG, Germany) and evenly brushed onto the zirconia surface and fired according to manufacturing instructions using a vacuum furnace (VITA VACUMAT 40T, VITA Zahnfabrik H. Rauter GmbH & Co.KG, Germany). The dentine layer was applied using a silicone mould to shape the veneer. The dentine was mixed with the liquid and packed in the mould on top of zirconia samples and dried using soft tissue before removing the samples from the mould (Figure 44). Dentine firing was carried out following the manufacturer's instructions and the samples were left to cool. The ceramic veneer was polished using waterproof carbide abrasive paper P400 and P600 respectively rotating polishing disc (Metaserv Buehler, UK).

This reduced the final specimen thickness to 1.3 mm, measured using a digital calliper (PK-0505, Mitutoyo Corporation, Japan).

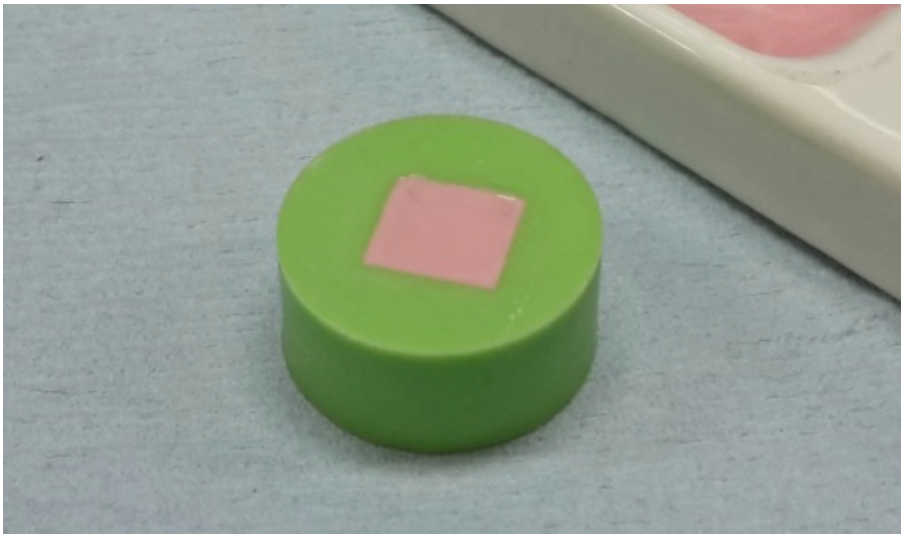


Figure 44: Dentine shade ceramic powder packed using a silicone mould.

6.6. Optical parameters measurements

A spectrophotometer (CM-2600d Konica Minolta Sensing, Inc., Japan) and colour data software (Spectra Magic NX, Konica Minolta Sensing, Inc., Japan) were used to record:

- The spectral reflectance of the samples between wavelengths 360 to 740nm at 10nm intervals. The data was used to calculate the following optical parameters:
- CIE L*a*b* colour value coordinates: L* represents lightness; a*: red-green coordinates and; b*: yellow-blue.

The data was used to calculate the following optical parameters:

- Opacity (%) was determined using the following equation (Shiraishi et al., 2011):

Equation 2

$$Opacity\ (\%) = \frac{R_b}{R_W} \times 100$$

Where R_b is the average reflectance when tested with a black background, and R_w is the average reflectance when tested with a white background. The average reflectance is dividing the total reflection at each wavelength to the number of wavelength points.

- Translucency Parameter (TP): Was determined following the equation below (Johnston et al., 1995):

Equation 3

$$TP = \left[\left(L_W^* - L_B^*\right)^2 + \left(a_W^* - a_B^*\right)^2 + \left(b_W^* - b_B^*\right)^2\right]^{1/2}$$

- The colour difference (ΔE*) between different groups was calculated using the following equation (Azzopardi et al., 2009):

Equation 4

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

Where ΔL*, Δa* and Δb* is the difference in the colour coordinates between two samples.

Three recordings were taken of each sample (n=3) in different positions resulting in a total of 9 recordings.

All measurements were carried out over a white background (L*= 99.9, a*= 0.1 and b*= -0.26) and a black background (L*= 22.7, a*= 0.2 and b*= -0.35) under D65 illuminate (day light) and 3mm target mask opening (Figure 45).

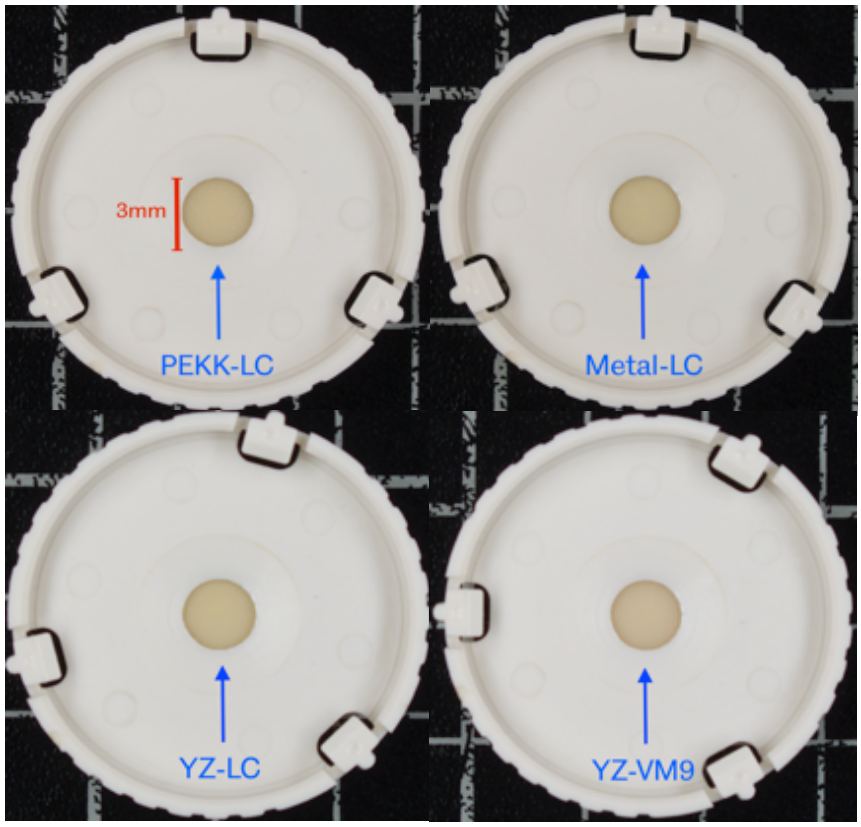


Figure 45: Laminate samples under the spectrophotometer's target mask.

6.6.1. Statistical analyses

Results were compared with one-way ANOVA and paired t-test using statistical data analysing software Minitab 15 for Widows XP (Minitab Ltd., UK). Groups with different superscript letters indicate significant differences were the P value is less than 0.05.

6.7. Results

6.7.1. Monolayer Groups

Figure 46 and Figure 47 show the spectral reflectance curves for 1.0mm thick samples of the substructure (PEKK, metal and YZ) and veneering materials (LC and VM9) on white and black backgrounds respectively.

On a white background, the metal group showed a small increase in reflectance at longer wavelengths across the visible spectrum, as does the PEKK material. The PEKK does exhibit grater absorbance at shorter wavelengths giving rise to the colour (beige) rather than the grey hue of the alloy.

YZ, LC and VM9 groups reflect almost the same amount of light in the long wavelength range after a sharp increase at around 400nm. This represents a greater yellow-orange-red reflection for the YZ, LC and VM9 groups.

Reflectance on black background can be seen in Figure 47 where the PEKK and metal groups showing the same reflectance across the visible spectrum wavelengths as recorded when on a white background. This is a result of the 'masking power' or opacity of the material.

The YZ, LC and VM9 groups reflected the same amount of light on white and black backgrounds under 400nm, however above this a decrease of approximately 30% is demonstrated with the decrease at 700nm of LC showing almost 50% decrease with reflectance on a white background being 75% in comparison to 40% on a black background. This difference in the

reflectance when tested with white and black backgrounds indicates that these samples show a high degree of translucency with the background colour or absorbance having a large effect on the light reflectance of the veneering material.

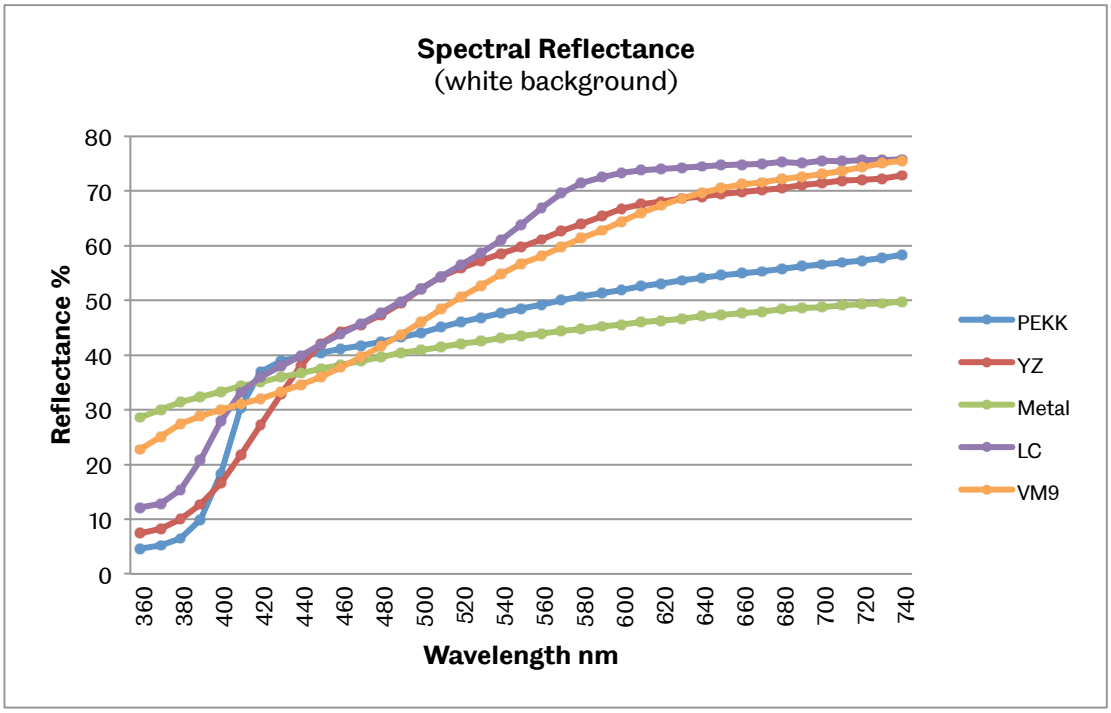


Figure 46: Spectral Reflectance data curve of the substructure and veneering samples (1.0mm) under white background and D65 illuminant.

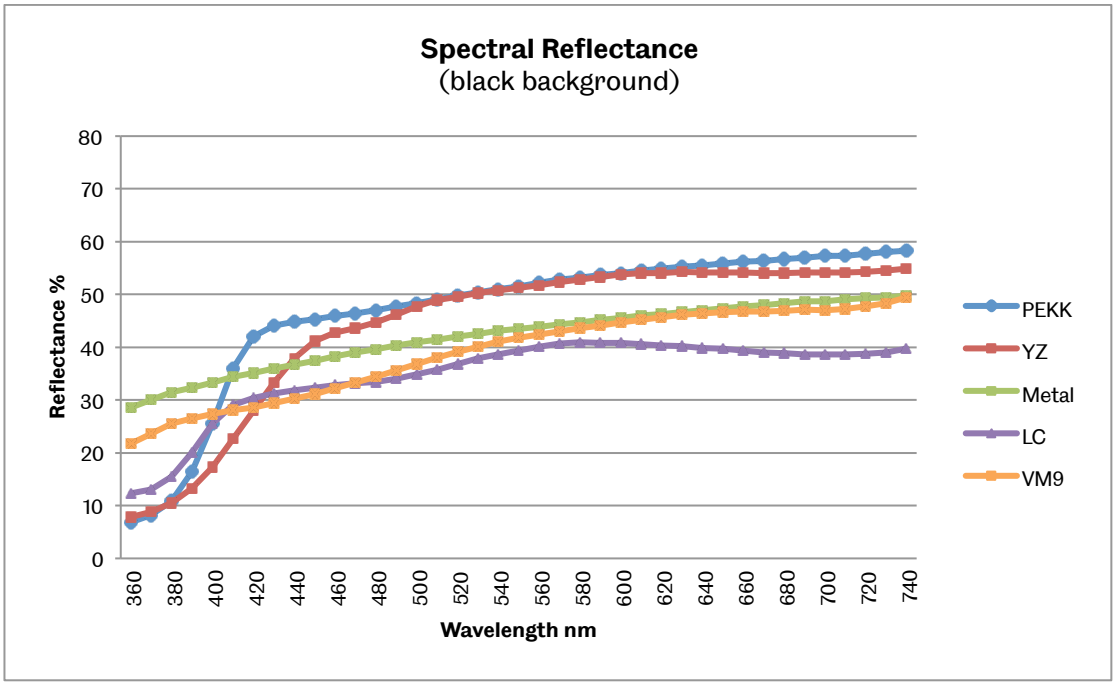


Figure 47: Spectral Reflectance data curve of the substructure and veneering samples (1.0 mm) under black background and D65 illuminant.

The opacity was calculated using the spectral reflectance data and the L*a*b* colour values for the translucency parameter (Figure 48).

The PEKK and metal groups showed 100% opacity and 0 TP, hence same spectral reflectance curve regardless of the colour of the background.

The zirconia demonstrated opacity of 84% whereas the ceramic group VM9 has a greater degree of light transmittance with opacity of 73.3%. The composite opacity was calculated as 61% as a result of the difference in the recorded reflectance curve under white and black backgrounds.

The Translucency parameter demonstrates an inverse relationship to these. The values are higher for less opaque samples having a TP of 9, 13 and 20 for YZ, VM9 and LC groups respectively.

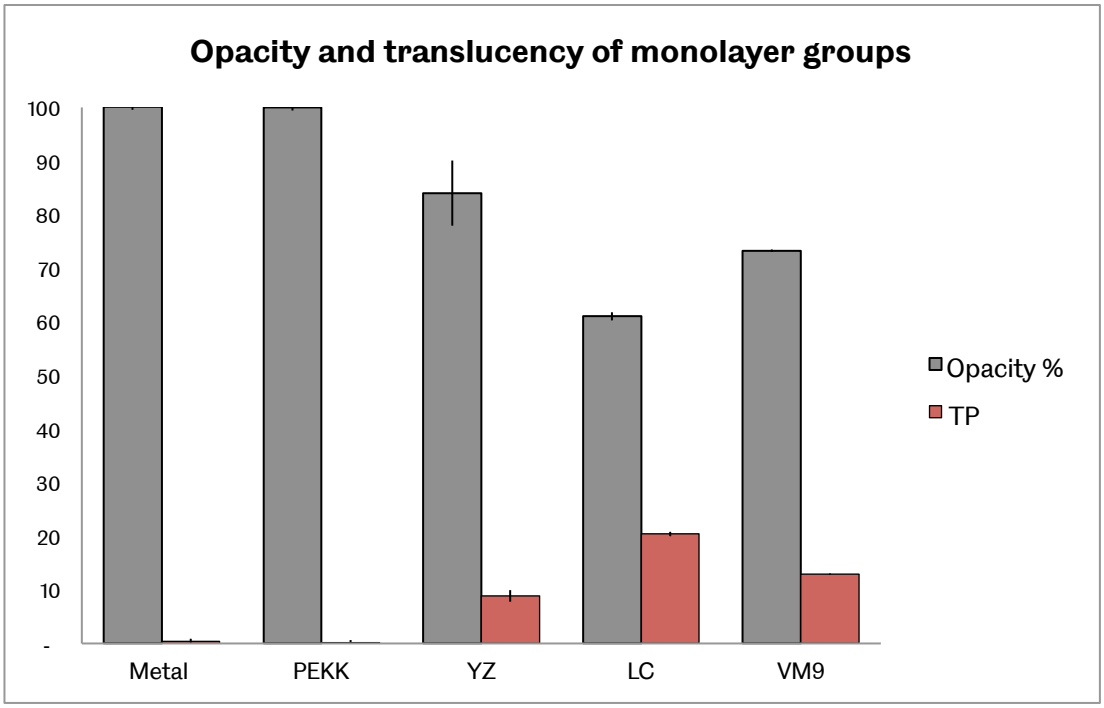


Figure 48: Opacity and translucency parameter for the 1.0mm monolayer groups (substructures and veneers).

Colour coordinates L*a*b* of substructure and veneering samples (1.0mm) under white and black background are detailed in Table 20.

PEKK and metal groups showed the same colour values when recorded over white and black backgrounds. Again this is a result of the opacity of the material and the colour coordinates being calculated from the reflectance data.

The YZ group shows similar L* and a* values to PEKK group with black background. With white background, YZ, LC and VM9 show much higher a* and b* values than seen with black background indicating colour shifting more to yellow and red shades in accordance with the spectral reflectance.

Table 20: CIE L*a*b* values of the substructure and veneering samples of 1.0mm thickness on black and white backgrounds. Groups with different superscript letters indicate significant differences (P<0.05) and groups with same superscript letters indicate no significant difference (P>0.05).

Material	L*		a*		b*	
	Black	**White**	**Black**	**White**	**Black**	**White**
Metal	72.5^{a} (±0.8)	72.2^{a} (±0.92)	0.8^{bc} (±0.06)	0.8^{a} (±0.06)	6.7^{a} (±0.25)	6.7^{a} (±0.32)
PEKK	75.5^{b} (±0.17)	75.5^{b} (±0.57)	1.76^{d} (±0.26)	1.78^{b} (±0.25)	8.07^{b} (±1.06)	8.13^{a} (±0.96)
YZ	76.51^{b} (±1.51)	81.5^{cd} (±2.51)	-1.4^{a} (±0.62)	1.12^{ab} (±1.1)	12.86^{c} (±0.95)	20.17^{b} (±2.96)
LC	68.38^{c} (±0.15)	83.55^{d} (±0.31)	0.47^{b} (±0.05)	4.03^{c} (±0.09)	8.27^{b} (±0.26)	21.49^{b} (±0.14)
VM9	70.27^{d} (±0.35)	79.43^{c} (±0.25)	1.18^{c} (±0.12)	4.15^{c} (±0.18)	12.51^{c} (±0.17)	21.19^{b} (±0.2)

6.7.2. Laminate Groups

Spectral reflectance of laminate groups when tested on white and black backgrounds are shown in Figure 49 and Figure 50 respectively.

All zirconia based groups showed a decrease in light reflectance when placed on the black background. The difference was primarily in the long wavelength range with a decrease in reflectance of approximately 10-20%.

On the black background, all three composite veneered groups demonstrated the same light reflectance across the wavelength range from 360nm-740nm with two increasing slopes in 380nm and 480nm wavelengths.

On a white background, the groups with an opaque substructure material (PEKK, Metal) stayed the same where as the YZ group showed a difference in reflectance at the longer wavelengths.

All the composite veneered laminate groups exhibited similar spectral reflectance between wavelengths 400 and 600nm with the YZ+LC reflecting approximately 5% more at higher wavelengths on the white backgrounds. This could be related to the translucency of the zirconia substructure.

In comparison, the ceramic veneered zirconia YZ+VM9 showed a reflectance between 400nm-600nm as the composite laminates groups but increased by about 10% at higher wavelengths. Indicating higher shift towards yellow-red shades between about 580nm-740nm wavelengths.

The reflectance curve of the YZ+VM9 group was in accordance with composite veneered groups between 400nm-600nm wavelengths with a

slight increase thereafter by about 5% at higher wavelengths. This slight difference in reflectance with white and black backgrounds indicates limited translucency that could relate to the thickness of samples.

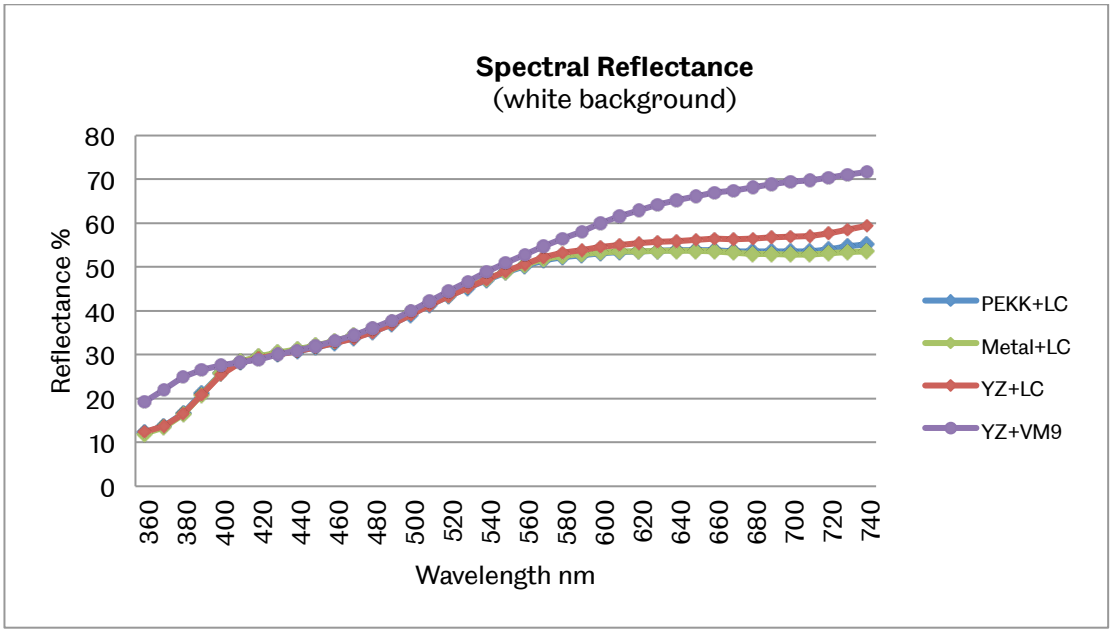


Figure 49: Spectral Reflectance data curve of the laminate samples (1.3mm) under white background and D65 illuminant.

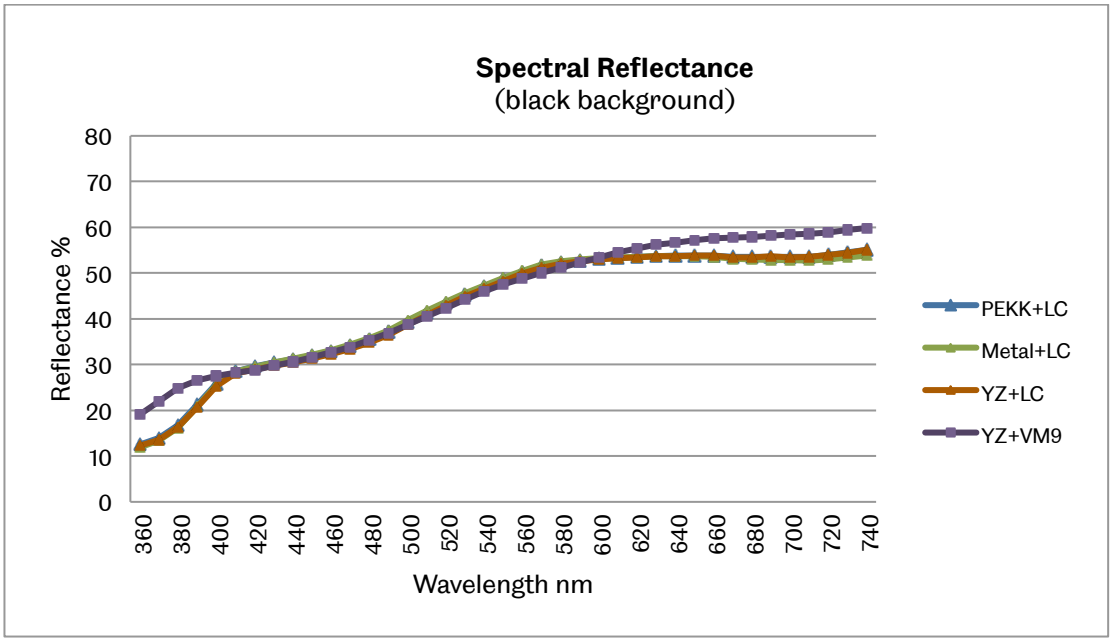


Figure 50: Spectral Reflectance data curve of the laminate samples (1.3mm) under black background and D65 illuminant.

The opacity and TP of the laminate groups are shown in Figure 51. The opacity and TP results are in accordance with the spectral reflectance data with the composite veneered groups Metal+LC and PEKK+LC completely opaque (100% and 0 TP).

The YZ+LC showed very similar results with opacity of 97% and 1 TP value, however a small amount of light does get transmitted through the zirconia and the composite opaque does not completely mask the zirconia substructure and hence allowing some translucency through the structure. The YZ+VM9 showed the most translucency among laminate groups with opacity of 90.5% and 5 TP value.

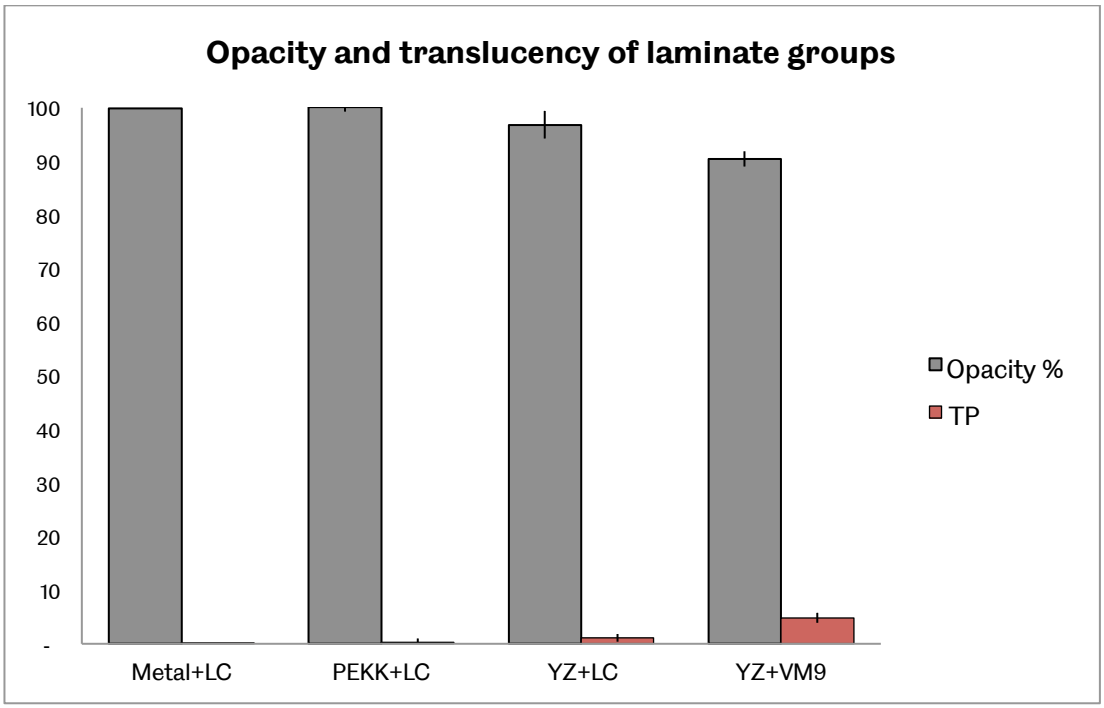


Figure 51: Opacity and translucency parameter of the 1.3mm laminates groups.

Table 21 shows the colour coordinates for the laminate groups (1.3mm) veneered with A2 shade composite (LC) and porcelain (VM9).

All the composite veneered groups PEKK+LC, Metal+LC and YZ+LC, showed a very similar L*a*b* values with no significant difference.

The PEKK and metal based groups showed the same recorded values under white and black backgrounds in accordance with the reflectance and opacity data.

These data are also reflected on the values of zirconia-based laminates with slight shift in values towards red-yellow shades under white backgrounds.

Table 21: CIE L*a*b* values of the laminate samples of 1.3mm thickness on black and white backgrounds. Groups with different superscript letters indicate significant differences (P<0.05) and groups with same superscript letters indicate no significant difference (P>0.05).

Material	L*		a*		b*	
	Black	White	Black	White	Black	White
Metal+LC	74.49^{a} (±0.27)	74.5^{a} (±0.22)	1.9^{a} (±0.22)	1.93^{a} (±0.18)	18.2^{a} (±0.46)	18.2^{a} (±0.45)
PEKK+LC	74.33^{a} (±0.15)	74.31^{a} (±0.11)	2.13^{a} (±0.26)	2.16$^{a, b}$ (±0.3)	18.17^{a} (±0.56)	18.47^{a} (±0.71)
YZ+LC	74.1^{a} (±0.27)	74.67^{a} (±0.35)	2.4^{a} (±0.14)	3.17^{b} (±0.72)	18.65^{a} (±0.65)	19.21^{a} (±0.69)
YZ+VM9	73.99^{a} (±0.14)	76.4^{b} (±0.51)	3.85^{b} (±0.27)	6.15^{b} (±0.23)	18.12^{a} (±0.4)	21.64^{b} (±0.77)

6.7.3. Colour difference (ΔE*)

Equation 4 was used to calculate the colour difference (ΔE*) between any two different groups on white and black backgrounds. The colour difference between any two groups can be seen in Table 22.

As the colour is very different to natural eye between PEKK, metal and zirconia, and therefore the ΔE* value between them is very high.

The veneering materials (A2 shade) LC and VM9 gave a ΔE* of 4.1 and 4.7 on white and black backgrounds respectively. This is expected from what can be seen in the spectral reflectance and L*a*b* data. Furthermore links to difference between them when bonded to the same zirconia substructure, YZ+LC and YZ+VM9, that showed a ΔE* value of 4.2 on white background and 1.5 on black background.

The least ΔE* difference was between the composite veneered groups PEKK+LC, Metal+LC and YZ+LC with lowest recorded difference of 0.4 and 0.28 on white and black background respectively between PEKK+LC and Metal+LC groups.

Table 22: Colour difference between all tested groups in this study.

Groups	Backing	Metal	PEKK	YZ	LC	VM9	YZ-VM9	YZ-LC	PEKK-LC	Metal-LC
Metal	White		23.40	33.19	35.78	32.12	30.18	26.98	26.19	26.19
	Black		23.38	25.67	16.45	19.7	25.89	26.13	26.04	26.18
PEKK	White	23.40		13.48	15.77	13.85	14.24	11.21	10.43	10.13
	Black	23.38		5.83	7.23	6.88	10.37	10.69	10.17	10.18
YZ	White	33.19	13.48		3.80	3.81	7.31	7.20	7.46	7.32
	Black	25.67	5.83		9.52	6.76	7.85	7.33	6.74	6.59
LC	White	35.78	15.77	3.80		4.13	7.46	9.21	9.90	9.86
	Black	16.45	7.23	9.52		4.70	11.83	12.01	11.67	11.75
VM9	White	32.12	13.85	3.81	4.13		3.66	5.25	6.13	6.18
	Black	19.7	6.88	6.76	4.70		7.24	7.34	7.03	7.12
YZ-VM9	White	30.18	14.24	7.31	7.46	3.66		4.22	5.51	5.77
	Black	25.89	10.37	7.85	11.83	7.24		1.55	1.75	2.01
YZ-LC	White	26.98	11.21	7.20	9.21	5.25	4.22		1.30	1.61
	Black	26.13	10.69	7.33	12.01	7.34	1.55		0.60	0.78
PEKK-LC	White	26.19	10.43	7.46	9.90	6.13	5.51	1.30		0.40
	Black	26.04	10.17	6.74	11.67	7.03	1.75	0.60		0.28
Metal-LC	White	26.19	10.13	7.32	9.86	6.18	5.77	1.61	0.40	
	Black	26.18	10.18	6.59	11.75	7.12	2.01	0.78	0.28	

6.8. Discussion

In this chapter, the aim was to evaluate the optical properties of this new substructure material against zirconia and metal substructures when veneered with the same material. Also to compare the polymer/composite system to zirconia/ceramic systems with the same colour shade.

The colour and translucency of composites resins can vary depending on the degree of polymerisation (Lee et al., 2004, Kim and Lee, 2007, Celik et al., 2011) veneer thickness and the translucency and colour of the underlying supporting material (Koishi et al., 2001, Khashayar et al., 2014).

Therefore, the dimensions and polymerisation steps for the composite resins layers were standardised for all samples prepared. A halogen light curing unit was chosen to ensure better curing results and colour consistency as it has been proven to deliver the best possible emission range (Janda et al., 2004).

For this study, the first evaluation focused on single layer groups of the substructure and veneering materials. The substructure materials PEKK, zirconia and metal are very different in colour when observed to the eye (Figure 39, Figure 41 and Figure 42). When quantifying this difference using the spectrophotometer, the PEKK and metal groups were demonstrating the same reflectance along the visible spectrum on both white and black backgrounds. This demonstrates that the material is optically opaque at the dimensions used.

PEKK samples showed similar values in all coordinates when measured on both white and black backgrounds and gave values of 75.5 for L*, 1.7 for a* and 8 for b* values. The same observation was also recorded with the metal samples.

This finding is in accordance with their spectral reflectance over black and white backgrounds. This is to be expected from opaque materials and explains the same colour values.

Coloured zirconia, to match A2 veneer shade, was used in an attempt to achieve the best colour as possible for the zirconia samples and later for the layered samples. The coloured zirconia was similar in the spectral reflectance to the PEKK and metal groups when placed on the black background but was closer to the pattern of the veneering materials when tested on the white background.

This means that the zirconia demonstrates some translucency, which is reflected on the CIE L*a*b* with higher values recorded when measured on a white background L*= 81.5, a*= 1.12 and b*= 20.17, than when tested with the black background L*= 76.51, a*= -1.4 and b*= 12.86.

The substructure materials, PEKK and metal, were completely opaque 100% with a translucency parameter (TP) of 0. The coloured zirconia substructure was a bit more translucent at about 84% with a TP of 9.

This is explained by the black background absorbing any light that is transmitted through the sample to the black material, whereas when placed

on a white background, the light transmitted gets reflected back through the sample to the detector/observer.

The single layered 1.0 mm thick PEKK gave an extremely low TP value of 0. When compared to the translucency of human dentine, the translucency of PEKK is far from being close to it and in a study by Yu et al. (2009a) have stated that the translucency parameter of 1.0 mm thick human dentine sample was 16.4, using testing configurations (spectrophotometer, target mask size and illuminant) similar to that used in this evaluation. A better and closer result to human dentine was found when testing the coloured zirconia as a substructure material that gave a TP value of 9 when tested exclusively. Similarly, a study by Kim and Kim (2014) have tested the translucency of A2 shaded zirconia samples and the affect of colouring liquid application on their translucency, and the TP value off all tested samples was at about 10 with the conclusion that the number of application did not have any affect on the overall translucency. In contrast, different zirconia shades have shown to have a significant effect on the restoration's translucency as concluded in a study by Spyropoulou et al. (2011).

From the findings of this study, it is thought that the shading might have an effect on the translucency of zirconia as having the highest standard deviation among all tested groups in the opacity (± 6.1) and translucency parameter (± 1.1), which is in agreement with that study of Spyropoulou et al. (2011).

When making a subjective assessment of the materials optical properties, the translucent veneering materials look similar in the hand but different when

placed on white and black backgrounds. This was confirmed when tested and the spectral reflectance was higher when measured solely on a white background in comparison the black background.

The composite group of A2 shade showed values of L*= 83.5, a*= 4.0 and b*= 21.5 on a white backing and L*= 68.4, a*= 0.5 and b*= 8.3 on a black background. The change in coordinates represent a shift in position in the colour space, decrease in L* representing a decrease in value or lightness, and similar decreases in a* and b* which represent a reduction in colour saturation. This light is being absorbed by the black background resulting in a less vibrant appearance to the material.

A similar observation was seen with ceramic (VM9) samples of the same shade on a white background resulted in colour coordinates of L*= 79.4, a*= 4.2 and b*= 21.2 and L*= 70.3, a*= 1.2 and b*= 12.5 on a black background.

The composite and ceramic samples showed different colour values to each other under both white and black backgrounds although these two materials, which are both veneering materials, shade A2 and are from the same company. This finding is in accordance with other studies were different restoration materials of the same shade gave significantly different CIE L*a*b* colour values when tested under the same configurations (Kim and Lee, 2009, Ardu et al., 2011, Gueth et al., 2013, Bagis and Turgut, 2013, Stawarczyk et al., 2016).

The L*a*b* values of VITA A2 shade of different materials are different in other studies (Lee et al., 2001, Lee et al., 2007, Shokry et al., 2006), but direct

comparison is difficult as the testing configuration, sample finishing and thickness differ between different studies.

As for the opacity measurement, as expected from the findings of the L*a*b* values and the spectral reflectance under black and white backgrounds, both evaluated veneering materials showed relative translucency with opacity of %61 and TP of 20, and %73.3 and TP of 13 for the LC and VM9 groups respectively.

The significant part of the study was the composite laminates that were made following minimum fabrication recommendations (for Pekkton® ivory), substructure samples were 0.8 mm thickness and veneered with 0.7 mm thick veneers.

The bonding between substructure and veneers were accomplished following manufacturer guidelines and in accordance with dental laboratory procedures. All substructures were brushed with composite resin opaque layer, to enhance bonding, and light cured before building the composite resin veneer (dentine). This layer masked the underlying substructure and hence the colour values for all three composite veneered bi-layered groups (PEKK+LC, Metal+LC and YZ+LC) where the same with no significant difference between the PEKK+LC group and other composite veneered groups (Table 21) and indeed they appear the same to the eye when held in the hand. The same thing was found with the spectral reflectance showing very similar pattern along the visible spectrum regardless of the underlying substructure material under black and white backgrounds.

All the composite veneered laminate groups exhibited similar spectral reflectance between wavelengths 400 and 600nm with the YZ+LC reflecting approximately 5% more at higher wavelengths on the white backgrounds. Under black backgrounds they all follow the same pattern, which is in accordance with L*a*b*.

The zirconia substructure was also masked in the ceramic veneer group with the opaque effect bonder before building the outer porcelain veneer. The reflectance of the zirconia ceramic group (YZ+VM9) was close to that of composite veneered groups but was higher after around 600 nm. The higher wavelengths are those of yellow, orange and red suggesting that the reflection is a result of the VM9 material being denser.

This difference in colours between restorations produced with a composite or ceramic veneer when bonded to zirconia substructure is likely to be due to the colour difference between the veneers as mentioned before between the LC and VM9 groups.

Linking to the colour values and spectral reflectance, the opacity of PEKK+LC and Metal+LC groups were the highest value of 100% and 0 TP against other zirconia laminate groups. The zirconia veneered with composite YZ+LC group showed high opacity values of 97% and 1 TP, and 90.5% and 5 TP when veneered with porcelain YZ+VM9. The slight translucency of the YZ+LC group, in comparison to other composite veneered groups, could be explained that the opaque layer did not fully cover the zirconia surface and hence appeared less opaque.

Different alloys are used as substructures for fixed prosthodontics such as high gold, Nickel chromium NiCr, Cobalt chromium CoCr, gold Au and pladium Pd alloys. A review by Stevenson and Ibbetson (2010) found that many studies revealed difference in the L* and b* values meaning difference in the lightness and yellowness-blueness between them. In general, they found that most of the studies revealed higher L* and b* values of gold alloys against other alloys such as NiCr and Pd alloys. On the contrary to that, a study by Stavridakis et al. (2000), smaller L* and b* values were found with gold alloys against other Pd alloys. Other studies showed contradictory values between different dental alloys, such as the study by Ozcellik et al. (2008), that showed significant difference in the a* and b* values between gold and NiCr and CoCr alloys.

The contradiction between different studies could be related to different reasons such as different testing configuration, different sample finishing and thickness of the samples and thickness ratio between layers. Furthermore, the number of firing cycles of the porcelain has an influence on the overall appearance of the metal (Yilmaz et al., 2009), zirconia (Cellik et al., 2008) and alumina (Sahin et al., 2010) based samples.

A possible explanation of the differences is the fact that alloys when heated produce oxides that can be absorbed by the ceramic veneer and therefore affect the colour of the restoration (Stevenson and Ibbetson, 2010).

Hence, direct comparison to other studies should be considered with caution in the case of studies with similar and clear testing configuration and regime.

Using the colour difference (ΔE) to compare two groups (Table 22) showed the least difference was between the composite veneered bi-layered groups. PEKK+LC groups showed a ΔE of 0.4 (white background) and 0.28 (black background) against the Metal+LC group and a ΔE of 1.3 (white background) and 0.6 (black background) against the YZ+LC group.

The zirconia substructure groups, composite veneered YZ+LC and ceramic veneered YZ+VM9, of the same shade veneer showed a ΔE value of 4.2 (white background) and 1.5 (black background).

The PEKK composite group and zirconia ceramic groups gave ΔE values of 5.5 and 1.7 on white and black backgrounds respectively.

When comparing the veneering materials exclusively, LC and VM9 gave a ΔE of 4.1 and 4.7 on white and black backgrounds respectively. There is no definitive agreement about what is the acceptable limit of colour difference in restorative dentistry according to some studies in the field. It was stated by Ruyter et al. (1987) that a colour difference ΔE less than 3.3 can be considered as acceptable. This is also supported by Um and Ruyter (1991) where they agreed that a ΔE of 1.0 difference could be recognised and it is acceptable up to 3.3 difference. Another study by Alghazali et al. (2012) determined a ΔE of 1.9 and 4.2 as values for perceptibility and acceptability respectively. Furthermore, higher ΔE difference values were concluded in other studies as perceptibility and acceptability ΔE difference threshold (Douglas et al., 2007, Johnston and Kao, 1989).

In this study, the lower numbers of ΔE of 1.0 as noticeable difference and up to ΔE of 3.3 as acceptable difference will be regarded as the threshold in considering differences between two groups. This can mean that having PEKK, metal or zirconia to support the composite resin veneer will have unperceivable or acceptable difference between each other.

When comparing the composite veneered groups to the ceramic veneered group, ΔE values where high. This may be predicted having shown the colour difference between the composite resin and ceramic veneers. The materials of the same shade were significantly different and gave a ΔE difference exceeding 4 under both black and white backgrounds.

The total thickness of the laminate restorations, especially substructure thickness, significantly affects the overall translucency of the restoration (Kursoglu et al., 2015, Heffernan et al., 2002). Overall, zirconia alone, or monolithic zirconia, restorations is nowhere close to be considered as an esthetic substitute for enamel and dentine as found in a study by Sulaiman et al. (2015) where they evaluated different brands of zirconia and under different thicknesses. As a zirconia substructure, a study by Pecho et al. (2012) have suggested that the zirconia could be a suitable substitute of human dentine as a translucent restorative material when coloured and veneered with a suitable material, after concluding that no significant differences was found between zirconia and human dentine.

A similar study was published recently by Stawarczyk et al. (2016) where they evaluated the optical properties of different substructure materials: PEEK,

zirconia, CoCrMo alloy and titanium oxide along with different veneers: VITA Mark 2, IPS e.max CAD, LAVA Ultimate and VITA Enamic. They have concluded that having PEEK as a substructure material was comparable with using the other well known substructure material as well as that the different veneering material of the same shade were actually different in the L*a*b* colour values. A major limitation in their study was not bonding the veneer and substructure materials in any dental laboratory or clinically known procedure i.e. melting fusion, etching, priming etc. and was simply placed on top of each other. Another limitation is the relatively thick substructure sample used in the research of 1.5 mm, which can affect the colour evaluation outcome.

Showing that using PEKK is no different in its optical properties than other well-known materials as a substructure material, it would be interesting to know the colour-stability after being inside the mouth for months and years.

Other polymers such as resin composite restorations have been in the spotlight for their discoloration after being in service due to different causes such as aging (Rattacaso et al., 2011, Da Col dos Santos Pinto et al., 2013, Gouveia et al., 2016, Celik et al., 2011, Buchalla et al., 2002, Diamantopoulou et al., 2013, Ardu et al., 2011). This could be related to the materials composition and filler particle size allowing the water to penetrate the matrix or filler-matrix interface (Vichi et al., 2004). On the other hand, high performance polymers such as PEEK have been known to be as a colour-stable restorative material (Bechir et al., 2016). A study by (Heimer et al., 2016) showed that PEEK was significantly (p<0.001) better colour stable polymer when tested

after stored in different media for a week than composite and PMMA materials.

6.9. Conclusions

With the limitation of this research, it may be stated that:

- Having different substructure material did not cause any significant difference in in the L*a*b* colour values when veneered with the same resin composite veneer.
- Having zirconia substructure gave a little more translucency with composite veneer and even more with porcelain veneer in comparison with composite veneered PEKK and metal laminates.
- Different results were found between light cured composite resin and porcelain of the same shade when evaluated both solely and bonded to underlying substructure.

This study suggests that having different substructure materials has no clinical impact on the aesthetics of the final restoration when using the same indirect light cured composite veneer. Furthermore, different materials cannot be presumed to produce equivalent shade even if they were described by the manufacturer as being in the same shade.

Chapter 7

Structural Integrity of PEKK Bi-layered Molar Crowns*

* Work from this chapter was presented at:

- The BSODR Conference 2015, 14-16 September 2015, in Cardiff, Wales. Poster titled: Structural Integrity of Poly-Ether-Ketone-Ketone (PEKK) Based Bi-layered Molar Crowns. Alsadon, O. A., Wood, D., Patrick, D., Copponnex, T., Pollington, S
- The Pekkton® Circle Conference 2016, 16 September 2016, Biel-Bienne, Switzerland. Oral presentation titled: Composite Veneered Pekkton® Crowns: How do they compare?

7.1. Introduction

In dentistry, most of the restorative materials manufacturers provide data sheets with different values of mechanical and strength properties, for example, compressive strength and flexural strength. Such data is obtained by testing standard samples shapes, different to that of the intended purpose of the material, i.e. dental prostheses. The fact that the material will be used to produce prosthesis and will therefore go through a production process (e.g. grinding, shotblasting and etching), is asymmetrical in shape, and made out of more than one material before being bonded to a tooth, is likely to have an impact on the strength of the prosthesis compared with standard, evenly shaped samples strength (Casson et al., 2001). Such conditions lead to the suggestion to employ other types of testing rather than relying purely on standard strength tests (Kelly, 1995).

One such procedure to evaluate the structural integrity of crowns made out of different materials is to subject them to occlusal load to measure their resistance to fracture and the results are measured in Newtons.

A polyetherketoneketone (PEKK) based polymer has been recently introduced to dentistry as a restorative material for a variety of applications including fixed structures veneered with light cured composite resin. This application is comparable to other well established substructure materials such as metal and zirconia both of which are frequently veneered with feldspathic porcelain and can also be veneered with light cured composite.

This research will focus on the PEKK/composite bi-layered crowns in comparison to metal and zirconia veneered with the same light cured composite.

Different configurations of the structural integrity test have been cited (Casson et al., 2001, Zhi-Yue and Yu-Xing, 2003, Yildirim et al., 2003, Hayashi et al., 2006, Beuer et al., 2008, Al-Makramani et al., 2009, Jalalian et al., 2011, Yucel et al., 2012) with variables including: indenter shape and size, magnitude of the load and the relative position of the indenter and underlying abutment material and design. For this study a first mandibular molar was chosen to test high performance crowns, as this is the region where restorations are likely to be exposed to the maximum chewing forces inside the mouth.

7.2. Aim

To evaluate the occlusal fracture resistance of mandibular molar crowns made from a PolyEtherKetoneKetone (PEKK) based polymer (Pekkton® ivory) when veneered with light-cured composite.

7.3. Objectives

- To evaluate the fracture resistance of PEKK based crowns when subjected to occlusal static load in comparison to equivalent zirconia-composite and metal-composite bi-layered crowns
- To assess the effect of different substructure materials on the structural integrity and mode of fracture of these bi-layered crowns when veneered with the same material.

7.4. Methods

The materials used for this chapter are detailed in Table 23 below.

Table 23: Detailed materials used in crowns samples fabrication.

Sample n=20		Material	Brand	Lot no.
Abutments	Die and base	Polyurethane	AlphaDie MF, Schültz-Dental GmbH, Germany	2013007844 2014003042
	Periodontal ligament	Light-bodied impression material	President light body, Coltene Whaledent, Switzerland	G25522
Crowns	Substructures	Zirconia	In-Ceram YZ®, VITA Zahnfabrik GmbH, DE	37850
		Metal	Talladium Tilite V, Talladium, Inc, USA	042011
		PEKK Polymer	Pekkton Ivory, Cendres+Métaux SA	Experiment blocks for CAD/CAM milling (provided from the company)
	Veneer	Composite	Vita VM LC®, VITA Zahnfabrik GmbH, DE	LOT37810 LOT47971 LOT33211
Primers		Zirconia	Monobond® Plus, Ivoclar Vivadent AG, Liechtenstein.	LOT37850
		Metal	Kuraray Alloy primer® , KURARAY CO., LTD, Japan.	042011
		PEKK	visio.link®, Bredent GmbH & Co. KG, Germany.	141432
Cement		Resin cement	Multilink Automix, Ivoclar Vivadent AG, Liechtenstein	T40253 U44073

7.4.1. Abutment and base

An anatomical lower first molar crown (Nissin Dental Products Inc., Japan) was duplicated using silicon material (Dublisil 15, Dreve Dentamid GmbH, Germany) and reproduced using Class IV die stone (Dentona esthetic-base® gold, Dentona AG, Germany). The anatomical stone molar was prepared following standard shoulder procedure and following tooth morphology and a 12° taper to reduce the occlusal dimensions by 1.5mm and circumferentially by 1.0mm (Figure 52).

From the literature, few attempts have been made to find the best repeatable and standardised method for creating an abutment with periodontal ligament (PDL) simulation. The most suitable technique was to cover the molar roots manually with wax starting 2mm below the cementoenamel junction (CEJ) and placing it inverted in the two-part silicon mould for the base to be poured (Figure 53 and Figure 54). After the base sets, the wax was removed with the assist of hot water and steam and the routs and socket were cleaned with water and dried before filling the created mould with light bodied impression material (President light body, Coltene Whaledent, Switzerland) and fixing the tooth back in the base. This step was to simulate the PDL in the fabricated samples creating a thin layer of about 0.2mm (± 0.05).

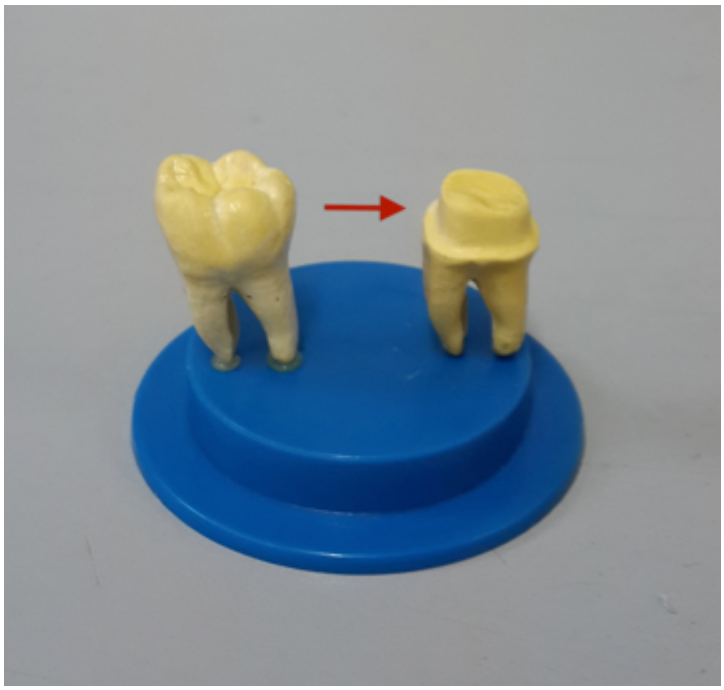


Figure 52: Duplicated mandibular first molar (left) and after preparation (right).

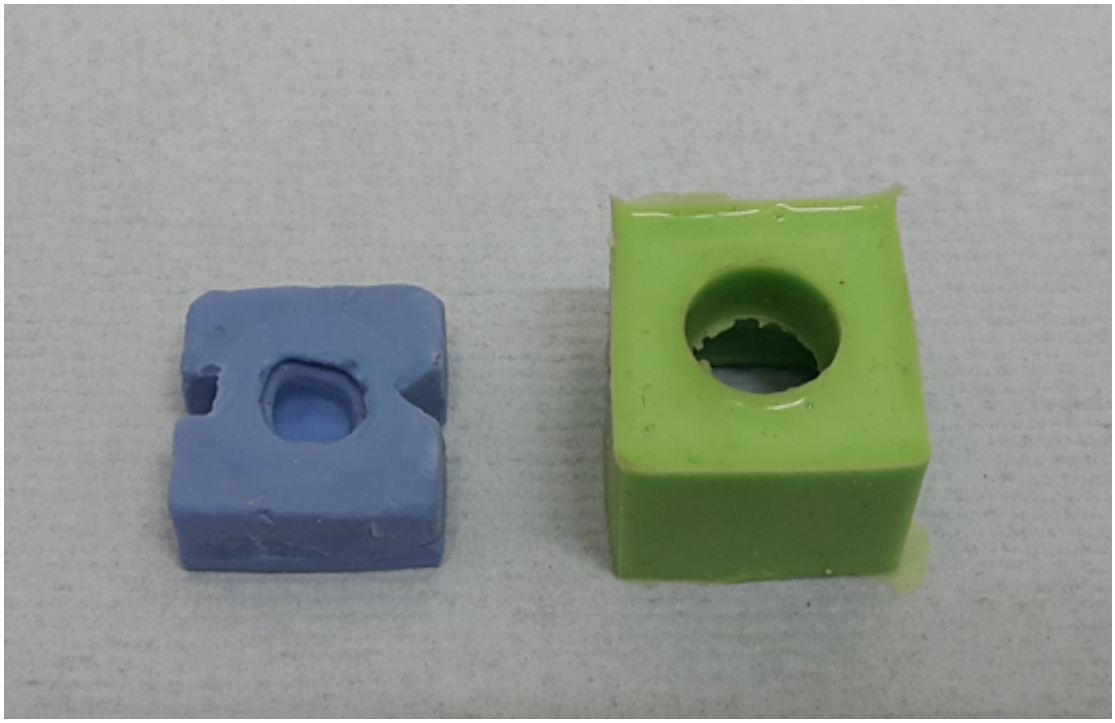


Figure 53: Two-part mould to hold die and create bone socket like base.

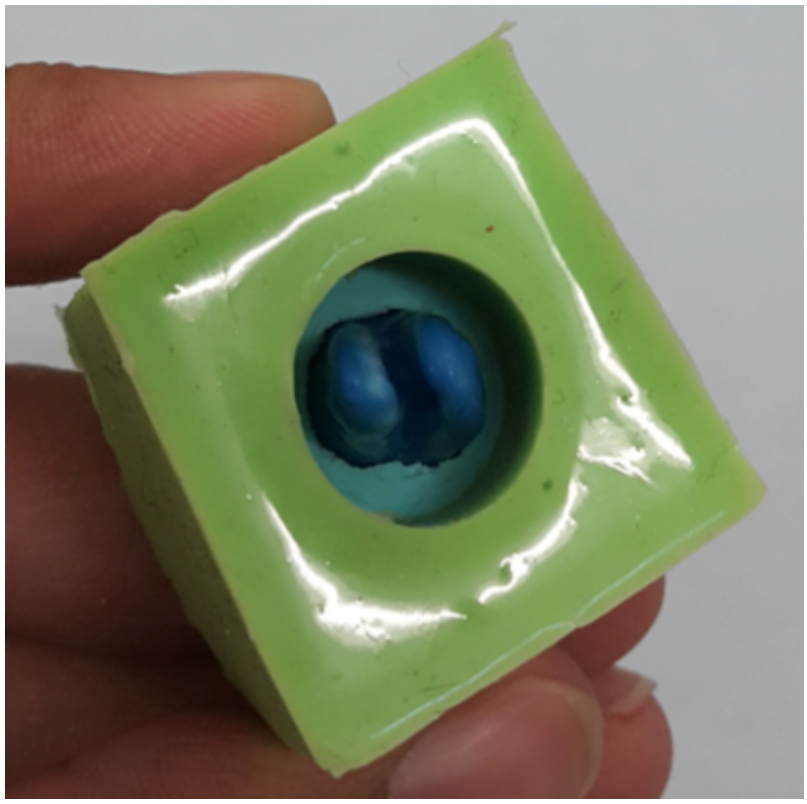


Figure 54: View of die placed in the two-part mould with the root covered with wax to create the space for the light bodied impression material to simulate the periodontal ligament.

7.4.2. Crown substructure design

The prepared master die was digitalised using a 3D scanner (Identica Blue, Medit Corporation, Korea). After obtaining the digital die model, computer design software (exocad GmbH, Germany) was used to design the crown substructure following the guidelines of the material manufacturer. The substructure thickness was 0.8mm in the occlusal surface and 0.7mm in the circular surface (± 0.02mm). The final design was saved as an STL formatted file ready for milling.

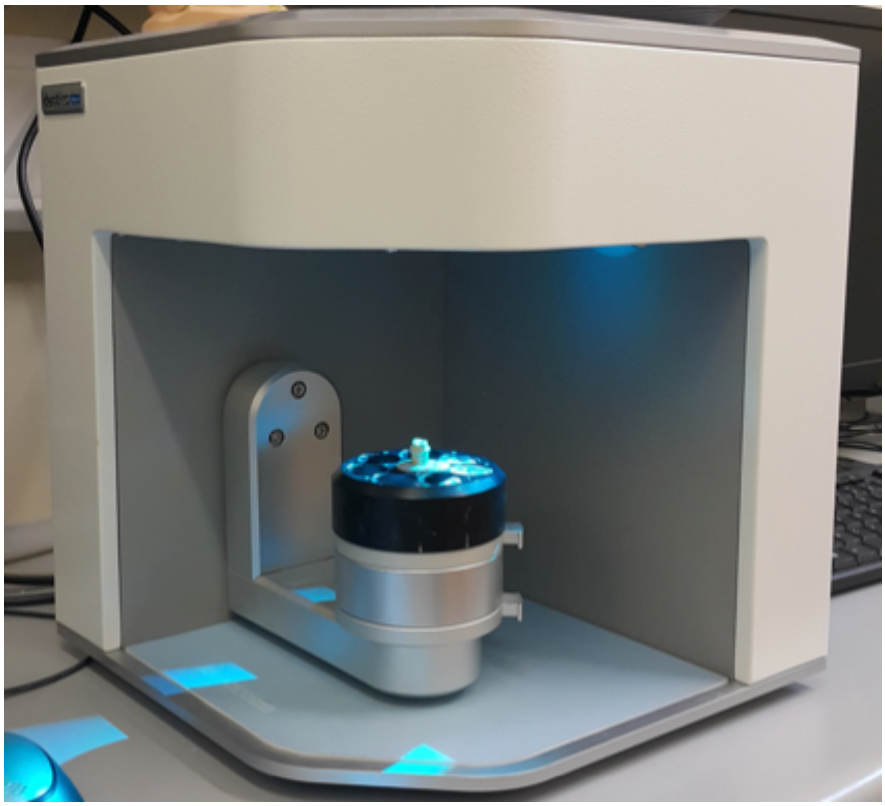


Figure 55: 3D scanner used to scan the master prepared die.

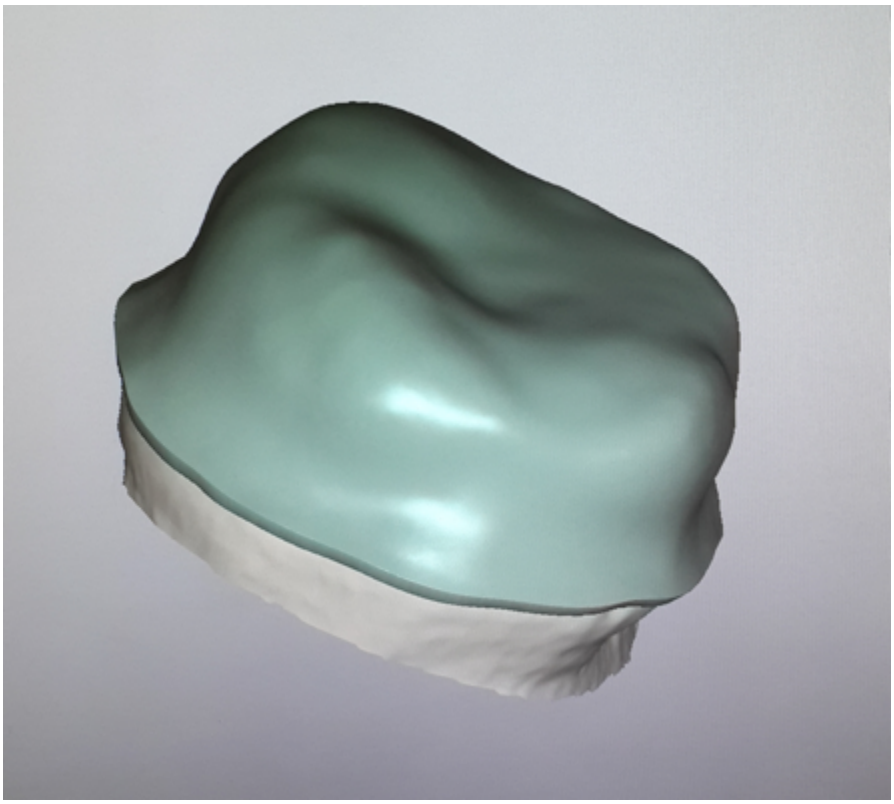


Figure 56: Designed substructure ready to be sent to the milling machine.

7.4.3. Substructure production and surface preparation

All substructures were milled via a CAD/CAM milling machine (Roland DWX50, Roland DGA Corp. USA). The detailed procedures used for fabricating different substructures are:

7.4.3.1. PEKK

Pekkton® ivory disc shaped blanks were used to produce the PEKK crown copings via milling. The remaining parts from the connectors were finished using a diamond bur in a micromotor handpiece (Figure 57). The outer surface was then shot-blasted using 110µm Alumina particles under 2 bar pressure until even in texture. The samples were then cleaned with water and dried before veneering.

Figure 57: PEKK substructure before shot blasting with Al_2O_3 particles.

7.4.3.2. Zirconia

Yttruim partially stabilised zirconia blanks were used to produce zirconia copings via CAD/CAM milling. They were separated from the blank using a diamond bur, which was also used to re-contour the surface around the connecters. The oversized copings were sintered at 1530°C in a furnace (Ceramill® therm, Amann Girrbach AG, Austria) which then shrunk by approximately 20% to the desired size (Figure 58). The outer surface was then shot-blasted using 50µm Alumina particles under 2 bar pressure until an even finish was achieved then cleaned with water and dried prior to veneering.

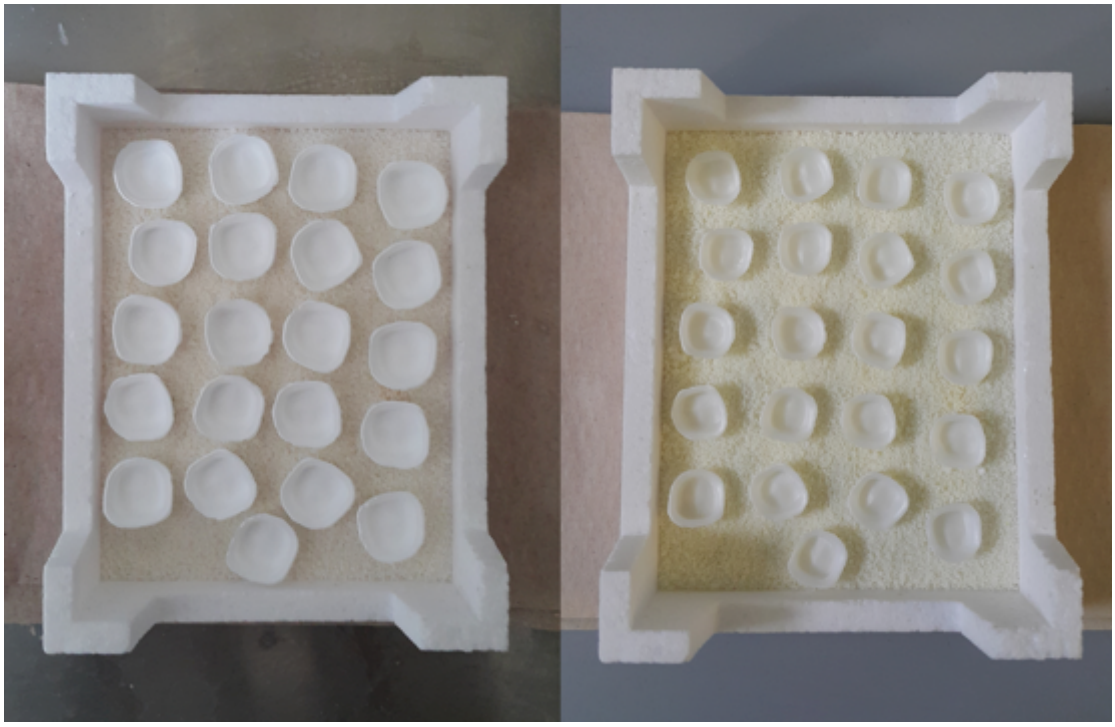


Figure 58: Milled zirconia substructures before sintering (left) and after (right).

7.4.3.3. Metal

Wax copings were milled from a wax blank. Each coping was attached with a sprue and placed in investment ring set before being invested using phosphate-bonded investment material (SHERAFINA-RAPID, SHERA Werkstoff-Technologie GmbH & Co. KG, Germany). After mixing the investment following the manufacturer guidelines and pouring into the ring, it was left to set for 45 minutes before removing the base. The wax burn-out stage was carried out in a furnace for 45 minutes at 850°C before taking the ring to the casting machine and casting the alloy at 1329°C. Castings were left to cool, de-vested and the metal substructures were shot-blasted using 110µm Alumina particles. Sprues were separated using rotary cutting discs and substructures were finished by shot-blasting using 110µm Alumina particles and rinsing with water and drying prior to being veneered (Figure 59).

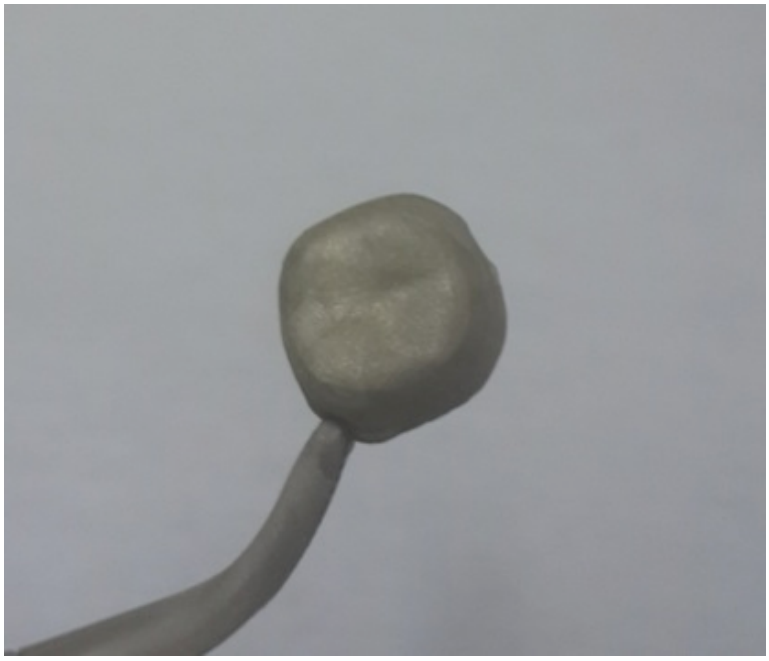


Figure 59: Metal substructure before composite veneering step.

7.4.4. Composite veneering

Each type of substructure was primed prior to veneering according to the manufacturers instructions. This step was to enhance bonding between substructure and veneer and the used primers are described in Table 23.

Following priming, opaque paste was applied as a thin layer using a brush before light curing. A silicone index was created using the master model to ensure that a consistent veneer shape and thickness was achieved for all samples (Provil novo, Heraeus Kulzer GmbH, Germany). The outer veneer produced from composite dentine was applied and shaped around the substructure using a plastic spatula and with the assistance of the silicone index. The composite veneer was then light cured on all five sides (occlusal, buccal, lingual, mesial and distal) each for 60 seconds to ensure full polymerisation of the composite veneer. The crowns were finished using carbide and diamond burs and a final thickness check was performed using a measuring gauge calliper on all sides. Final polishing was performed using buff rotary and polishing compound (KMG, CANDULOR AG, Switzerland) and crowns were rinsed with water and dried (Figure 60).

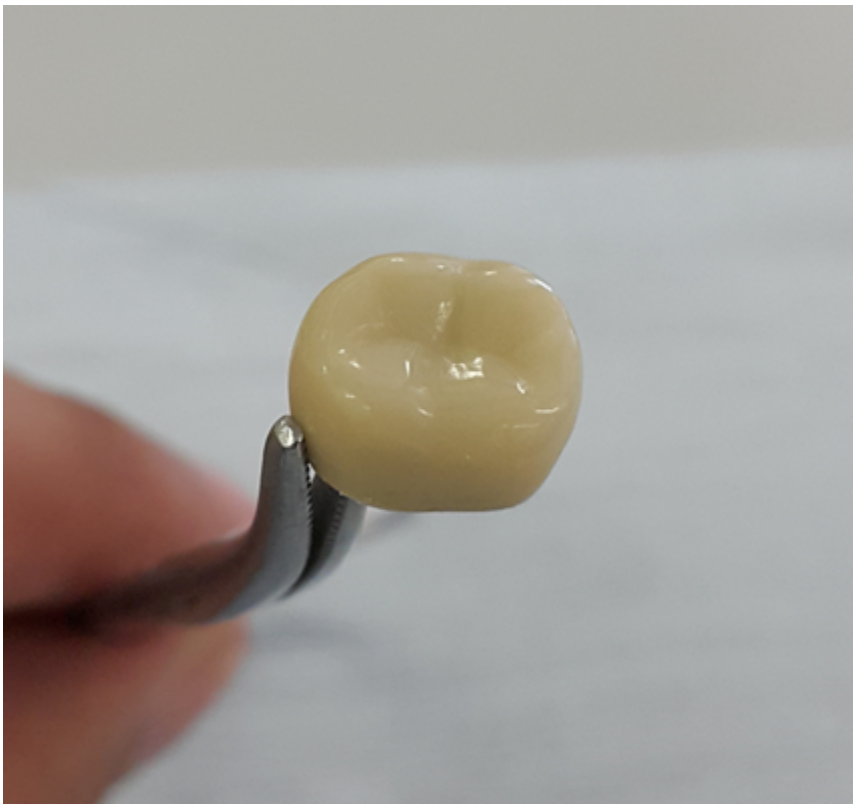


Figure 60: Crown after veneering with composite ready for cementing and testing.

Figure 61: View from fitting side of different crowns types: PEKK (left), metal (middle) and zirconia (right), before cementing step.

7.4.5. Cementing crowns

All crowns were shot-blasted on the fitting surface and rinsed with water and dried. The crowns were then cemented using resin cement (Multilink Automix, Ivoclar Vivadent AG, Liechtenstein) following the manufacturer guidelines. All crowns were subjected to 40 N load for 3 minutes through a silicone cushioned metal rod using a universal testing machine and the resin cement was light cured during this stage (Figure 62). This was to mimic the hand pressure when cementing a crown clinically and to standardise the cementing process.

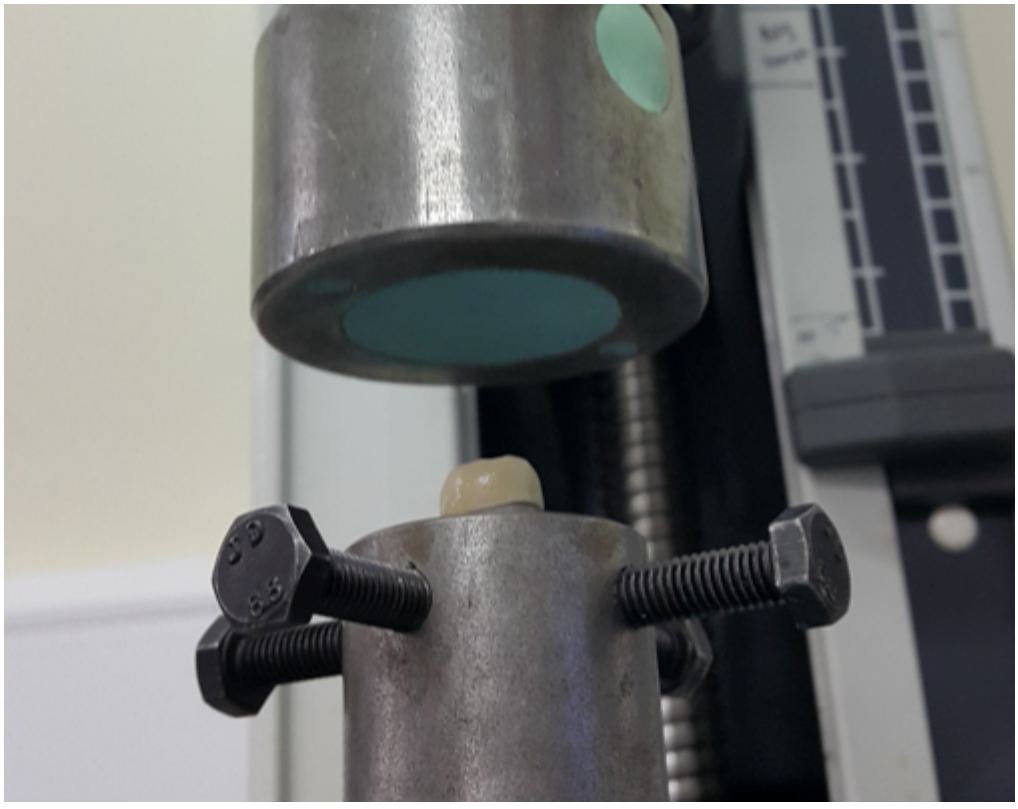


Figure 62: Crowns cementing pressing procedure using silicon cushioned rod under 40 N for 3 mintues.

7.4.6. Fracture resistance test

Each sample set was divided into two groups (central fossa or buccal cusp: n=10) to allow the effect of different occlusal loading to be compared. A universal testing machine (Lloyds Instrument Model LRX, Lloyd Instruments Ltd, UK) was used to apply a static load through a 4mm diameter ball steel indenter at a crosshead speed of 1mm/min with a latex sheet between crown and indenter. The force was measured in Newtons (N) and mode of fracture was also recorded and categorised according to Burke's classification (Table 24).

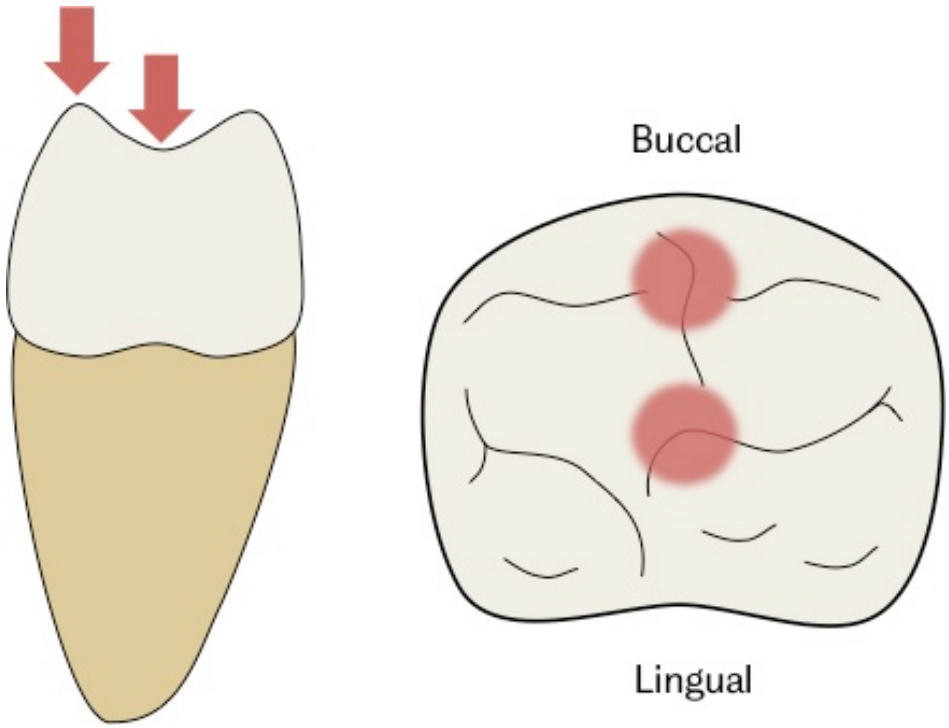


Figure 63: Indenter contact points in the buccal and central sides for all tested groups.

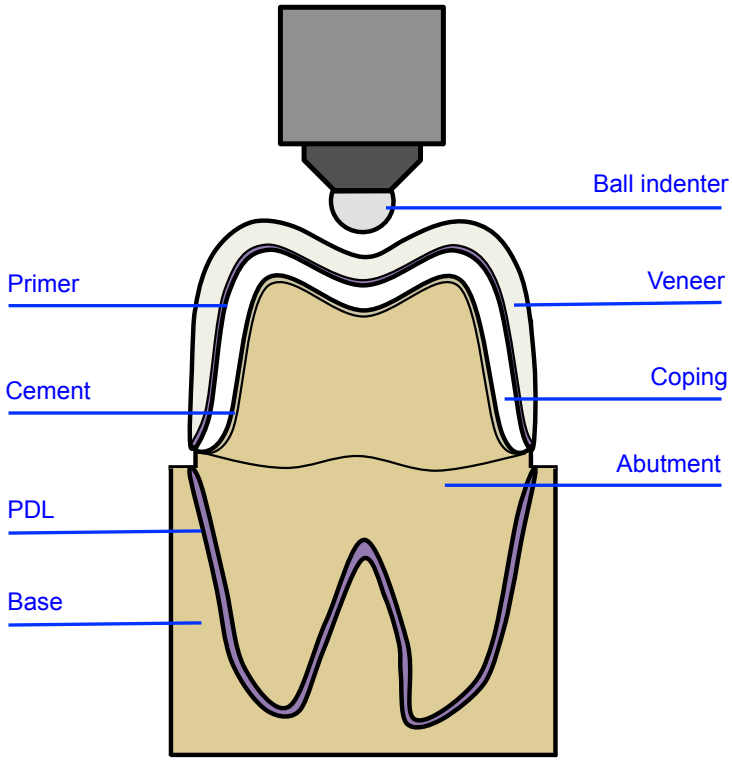


Figure 64: Illustration of the tested samples showing all different parts involved.

Table 24: Fracture mode codes and description following Burke's classification (Burke, 1999).

Code	Description
1	Minimal fracture or crack
2	Less than half of crown lost
3	Half of crown displaced or lost
4	More than half of crown lost
5	Severe fracture of tooth and/or crown

7.4.7. Statistical analysis

IBM SPSS Statistics 22 software was used to compare Fracture Strength results using one-way ANOVA and Games-Howell tests to determine any significant difference between groups. Significance difference for the recorded mode of fracture between groups was determined using Kruskal-Wallis and Mann-Whitney tests.

7.5. Results

The fracture resistance results for all the tested groups can be seen in Figure 65 and the detailed results can be in Table 35 and Table 36 in appendix 13.1.1. The mode of fracture based on Burke's classification can be seen in Table 25, Figure 66 and Figure 67. Each group was divided to two sub groups to allow comparison of having load applied at different points on the occlusal surface.

Central fossae groups 1) PEKK/LC, 2) Metal/LC and 3) YZ/LC were tested with the indenter placed in the middle of the fossa and the load at fracture was recorded. PEKK and zirconia groups fractures were clear and recorded unlike the metal group where the machine reached its maximum load capacity (around 2100 N) before aborting the test without any visible fracture. The PEKK group showed an average failure at about 1900 N and the zirconia group showed a significantly lower failure at about 1700 N. Both groups showed fracture through the substructure and veneer as one structure without visible veneer delamination.

Buccal cusp groups 4) PEKK/LC, 5) Metal/LC and 6) YZ/LC had the load subjected on the buccal cusp incline and all three groups demonstrated failures. Group 4) PEKK/LC showed an average failure of 1416 N with all fractures observed through both substructure and veneer as one structure without any visible delamination unlike the other two groups. Group 5) Metal/LC showed an average fracture load at 1384 N with fractures recorded as a delamination of the composite veneer (Figure 69). Group 6) YZ/LC showed a significantly lower average fracture load of 600 N with the fracture

occurring in the composite veneer and recorded as code 2 fracture within the veneer.

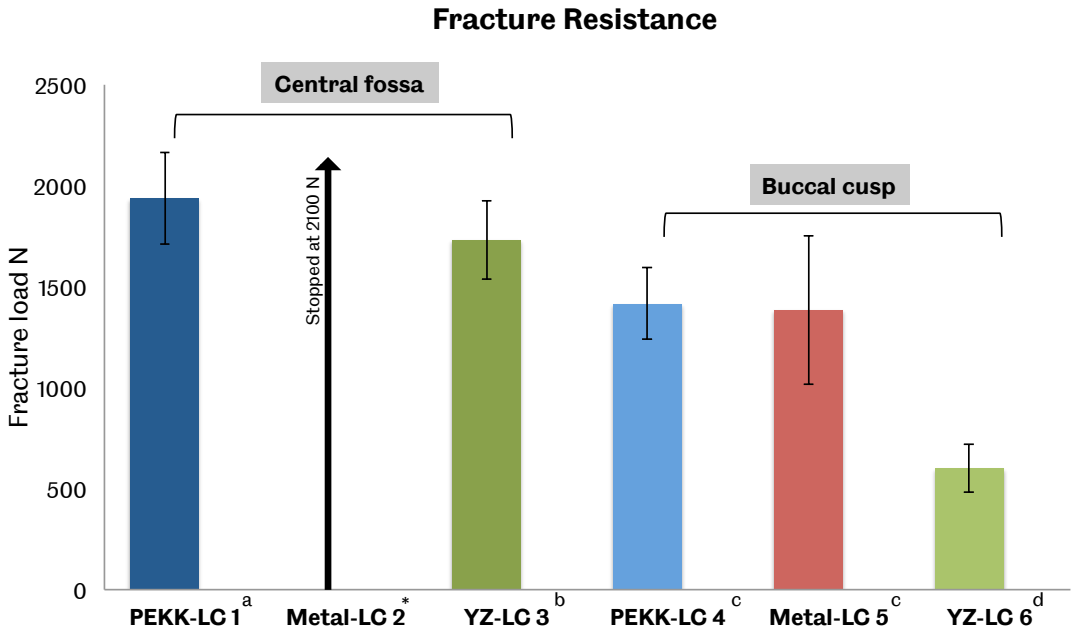


Figure 65: Fracture resistance results in Newtons for all groups. *These samples withstood the maximum limit of the universal tester of 2100 N without detecting any signs of fracture. Different superscript letters indicate significant differences (P<0.05) and groups with same superscript letters indicate no significant difference (P>0.05).

Table 25: Mode of fracture for all tested crowns following Burke's classification (1 minimal fracture and 5 severe fracture). The letter "v" indicates fracture within the veneer only. Different superscript letters indicate significant differences (P<0.05) and groups with same superscript letters indicate no significant difference (P>0.05).

Groups		Fracture Code				
		1	**2**	**3**	**4**	**5**
Central fossa	PEKK-LC 1[a]	4	0	1	1	4
	Metal-LC 2[b]	10v	0	0	0	0
	YZ-LC 3[a]	0	0	1	3	6
Buccal cusp	PEKK-LC 4[a]	0	1	3	2	4
	Metal-LC 5[b]	0	8v	1v	1v	0
	YZ-LC 6[b]	0	10v	0	0	0

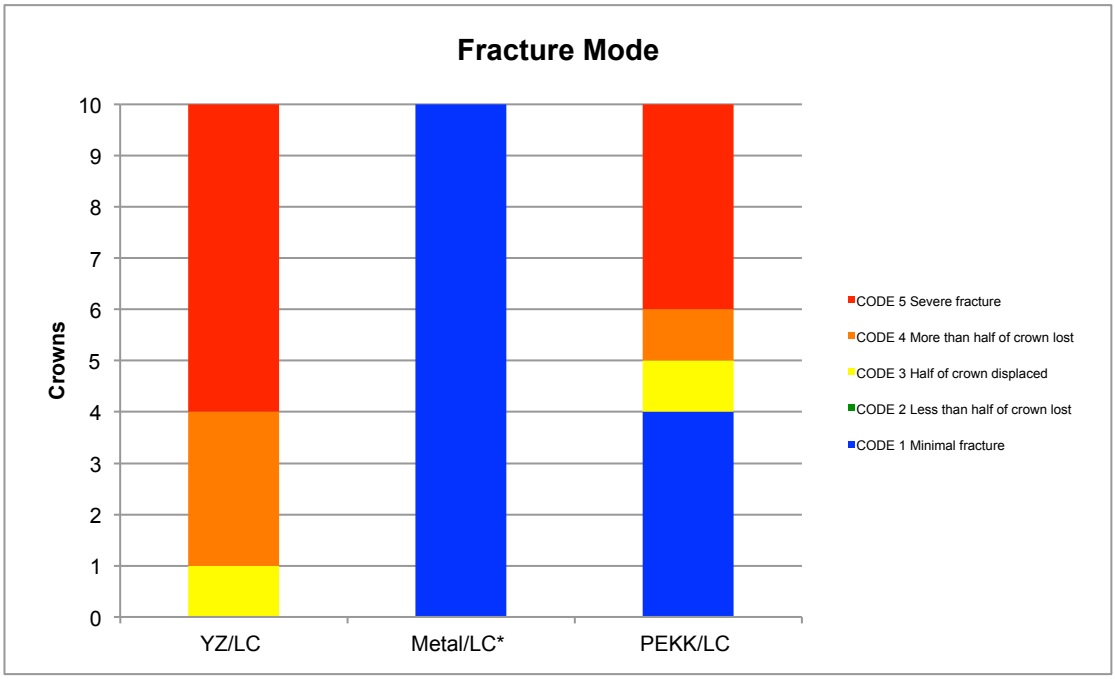


Figure 66: Mode of fracture for the central fossa group. * indicates that all recorded fractures in this group were within the composite veneer only.

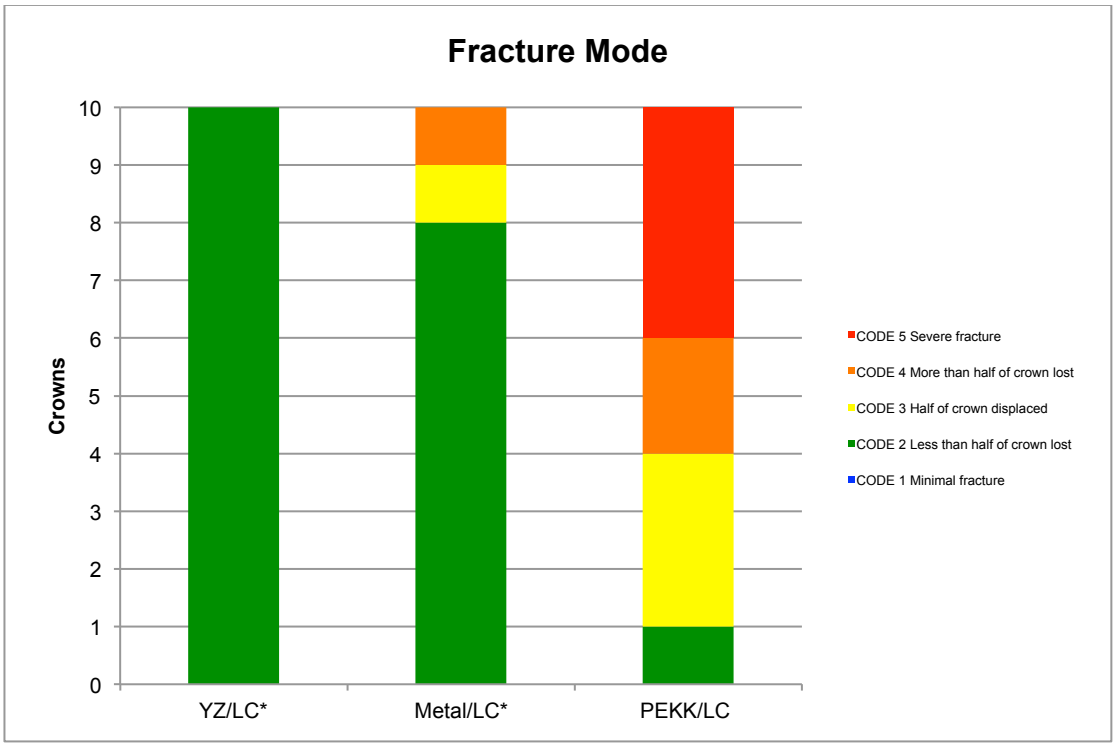


Figure 67: Mode of fracture for the buccal cusp group. * indicates that all recorded fractures in this group were within the composite veneer only.

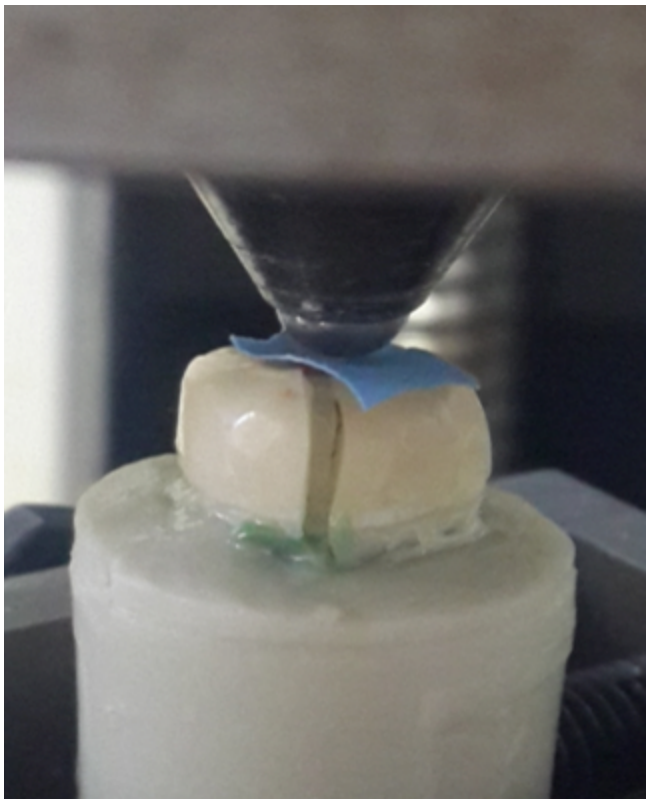


Figure 68: Group 3 YZ/LC severe fracture code 5.

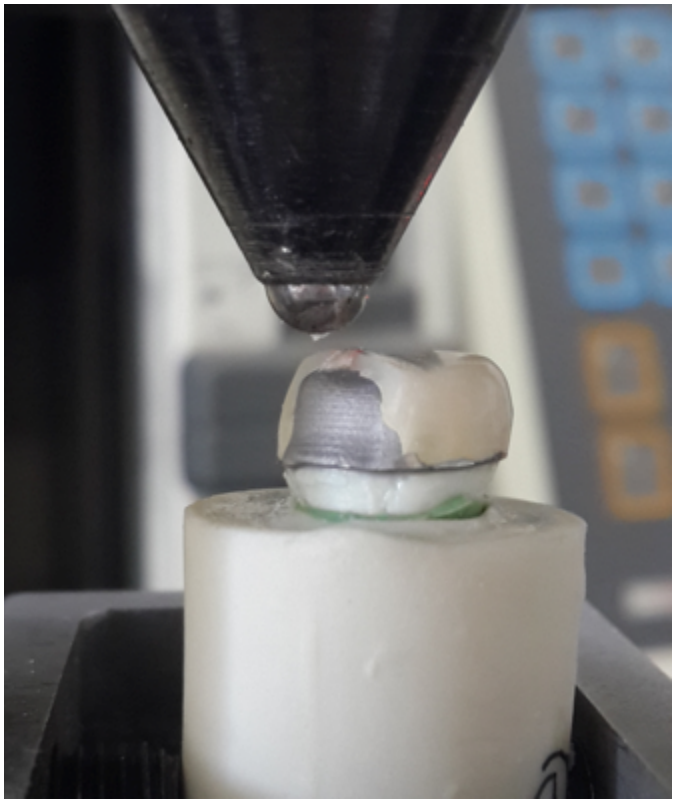


Figure 69: Metal-LC crown with code 2 veneer fracture.

Figure 70: PEKK-LC crown with severe fracture code 5.

7.6. Discussion:

This in vitro evaluation takes into account the complex shape, component layers, bonding of materials, bonding to tooth and material production on the overall structural integrity by the means of its resistance to fracture, the maximum load it can withstand before fracture. Such test configurations and fabrication processes differ between studies, for example using a ball or a bar to apply load or the type of the underlying abutment (Casson et al., 2001, Yucel et al., 2012). It has been stated that the thickness and design of the substructure and veneer, design, and cement and type of abutment may affect the fracture resistance of crowns along with mechanical properties of the substructure and veneer materials (Scherrer and de Rijk, 1992, Sundh and Sjogren, 2004). This gives rise to the variation in results between different dental restoration investigations and hence the difficulty in directly comparing results between different studies (Al-Makramani et al., 2009).

The limitation of the load to failure tests have been discussed as being not applicable to real life situations (Isgro et al., 2011). This is primarily due to the test failing to reproduce crown failure as observed clinically, i.e. the different mode of fracture observed. Similarly the use of high load used in the test exceeds maximum recorded bite forces (Kelly, 1999). Such forces vary considerably depending on gender and age, but overall the molar region has a higher force (Waltimo and Kononen, 1993).

Other limitations include intra oral adjustment, temperature, saliva, chemical environment, direction of load applied and variation of load applied,

antagonist material mechanical properties (modulus of elasticity in particular), and mechanical properties of the supporting structures.

Nevertheless, the test is extremely useful in undertaking pre-clinical trials of novel materials or new designs or processing routes that are being investigated for future use. Using the material processed into the definitive crown shape and bonded to the appropriate substructure, unlike the uniform samples in standard mechanical testing, is suggested as reason enough rather than relying purely on standard strength tests (Kelly, 1995).

Standardising of samples for this test was achieved as much as possible given that the substructure was milled using CAD/CAM and the light cured composite was hand-built with the assistance of a silicone impression of the master crown. All specimens were fabricated to a clinically expected full contour crown in diameter, shaped and cemented to the die. The results obtained from an in-vitro laboratory based test cannot be directly applied to the oral environment since there are differences in magnitude and direction of load and surrounding environment. Nevertheless, attention was given to creating samples as close to the oral cavity as possible such as mimicking the periodontal ligament using the light bodied impression material (Soares et al., 2005), using abutment and base with elastic moduli close to dentine and bone (Rosentritt et al., 2000), and using a rubber sheet under the indenter to even the stress on the crown (Tsitrou et al., 2010).

A resin cement (Multilink Automix, Ivoclar Vivadent AG, Liechtenstein) was chosen to cement all crowns since it is indicated by all manufacturers and the

same cementing steps could be used for all PEKK, metal and zirconia groups. Furthermore, Multilink Automix with Pekkton Ivory gave good bonding results as revealed in a study by (Fuhrmann et al., 2014).

A first mandibular molar was chosen as an abutment for the tested crowns due to being in the region where the highest biting forces are recorded in the mouth (Ferrario et al., 2004).

The contact points for the mandibular first molar is focused along the central fossa and the buccal cusps (Nelson et al., 2010). Therefore, the tested groups were divided into two sub groups depending on the location of the load to allow comparison. Having different loading points showed large differences in fracture load resistance between the two loading points (fossa and buccal) in the same crown design for all tested groups. When comparing the groups in general, PEKK and Metal groups followed the same pattern having significantly higher fracture loads than zirconia groups in both central fossa and buccal cusp groups. A ceramic veneered zirconia crown would have made a suitable control group for this evaluation as it is now considered a widely used method for fabricating crowns (Raigrodski, 2004, Denry and Kelly, 2008). In a previous research study, zirconia composite veneered maxillary first molar crowns were subjected to fracture resistance test against feldspathic porcelain veneered zirconia crowns and the results showed no significant difference between them (Alsadon et al., 2017). This is also in accordance with other research comparing fracture resistance of zirconia prostheses when veneered with porcelain and composite (Taguchi et al., 2014, Komine et al., 2014, Kamio et al., 2015) and monolithic zirconia

crowns (Sorrentino et al., 2016). A similar study by Honda et al. (2016) showed that there was no significant difference between composite veneered zirconia, ceramic veneered zirconia and metal porcelain veneered restorations in their resistance to fracture.

The fracture of the PEKK groups showed no delamination of the veneer in both buccal and central fossa groups and all fractures occurred through the PEKK substructure and the composite veneer. The mode of fracture ranged from code 1 (minimal fracture or crack) to code 5 (severe fracture) in the fossa group with no significant difference when compared with the zirconia group.

When the load was applied to the buccal cusp, the PEKK samples demonstrated a fracture mode which ranged from code 2 to code 5 with no delamination and was significantly different than the zirconia group, where all the fractures were within the veneer as code 2. Similarly the metal group showed the fracture was clear delamination mostly as code 2. This implies an improved bond between the PEKK substructure and the composite veneer in comparison to the zirconia and metal substructures, as all fracture modes in different indenter positions were through PEKK and composite as one structure.

A possible explanation of the high fracture resistance of PEKK crowns could be that it has a low elastic modules of 5.1 GPa which gives it a better flexibility when compared to the metal (190 GPa) and zirconia (210 GPa) which will match that of the veneering composite (4.5 GPa) and abutment with an

elastic modulus close to the dentine, which gives the whole structure matching flexibility, eliminating stress concentration zones that could lead to failure.

These samples can be directly compared to results gained from a research study in which the author have been collaborated with to ensure the same testing regime with the same abutment and preparation to create monolithic crowns. In this study, crowns of the same thickness of three different materials: hybrid ceramic (Vita Enamic, VITA, Germany), nano ceramic reinforced polymer (LAVA Ultimate, 3M ESPE, USA) and lithium disilicate ceramic (IPS e.max Press, Ivoclar Vivadent AG, Liechtenstein) were used. In this test, the indenter was paced in the central fossa and the results were 1126 N ±108, 1476 N ±142 and 1496 N ±165 respectively.

When comparing the PEKK/LC group with these groups, it shows that the PEKK composite veneered crowns showed significantly higher fracture resistance than the definitive monolithic crowns of resin-ceramic blocks and pressed ceramics (Figure 71).

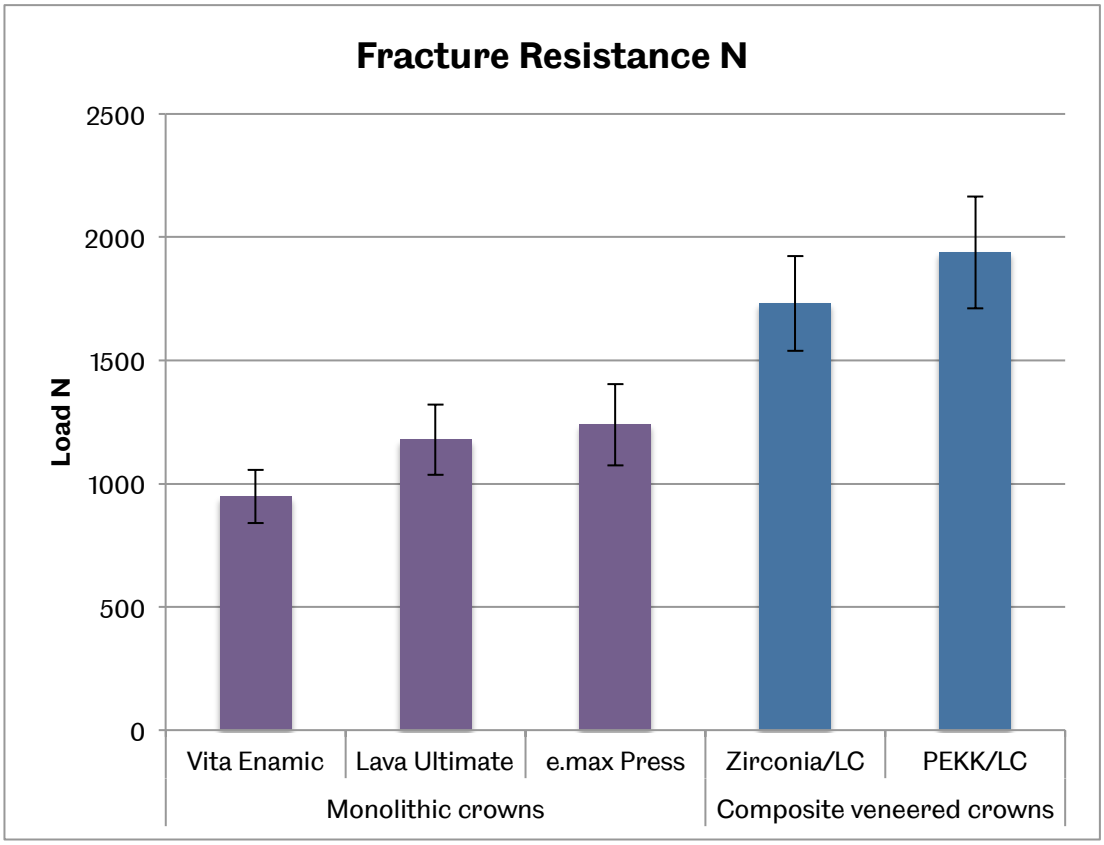


Figure 71: Fracture resistance of monolithic crowns against composite veneered crowns evaluated in this study (n=10).

With the limitations of this test, results of this evaluation indicate that PEKK based crowns showed favourable structural integrity in resisting fracture than zirconia based crowns and to some extent similar to metal based crowns. This static load testing was able to show a clear difference between different crown groups having one variable as the underlying supporting substructure.

A direct conclusion from this load to failure tests to clinical application is not possible, however the data shows that the failure is in the same order of magnitude for the novel restoration and hence further investigation is indicated.

The effect of fatigue under simultaneous cyclic loading and thermocycling or circulated temperature controlled water should be considered as a tool to predict long-term success in an environment closer to that of the oral cavity. Such tests can be performed using “chewing simulators” and the fatigue results can be analysed to give an indicator of the long term performance of the prostheses and is an area that needs to be explored.

7.7. Conclusions:

Within the limitation of this work, the following conclusions could be drawn from the work undertaken in this chapter:

- The fracture resistance of PEKK based crowns showed significantly higher strength than zirconia based crowns and comparable results to metal-based crowns with no significant differences were found.
- All PEKK groups recorded fractures were through the substructure and veneer in both central fossa and buccal cusp loadings with no delamination as seen with metal and zirconia groups in buccal cusp loading.
- The zirconia and metal based crowns showed a greater degree of delamination in comparison to PEKK based ones indicating superior bond between the substructure and veneer.

Chapter 8

Durability of PEKK Bi-layered Molar Crowns*

* Work from this chapter was presented at the Pekkton® Circle Conference 2016, 16 September 2016, Biel-Bienne, Switzerland. Oral presentation titled: Composite Veneered Pekkton® Crowns: How do they compare?

8.1. Introduction:

In addition to trauma failures, dental prostheses can fail inside the mouth after years of functioning and can fracture while simply biting on soft food (McCabe and Walls, 2008). A possible way to assess restorative materials and prostheses longevity is to subject them to conditions close to the oral environment and evaluate their performance. Here, the restoration is subjected to repeat stresses at low magnitude that may cause cracks to form, and in time grow, until complete failure occurs. This phenomenon is described as fatigue failure (Wiskott et al., 1995, Powers et al., 2006). Different approaches to evaluate fatigue failures have been used in restorative dentistry as described previously in chapter 2.6.2.

Once a restorative material has been tested mechanically, then tested in terms of the integrity of prostheses designs involving different materials, it is logical to subject these materials to conditions that simulate those that would be expected inside the oral cavity. Dependent upon the results, a randomised controlled clinical trial, which is considered the gold standard, may then be indicated.

Different approaches and fatigue machines are used to investigate this area. One approach is to subject samples to cyclic loading until fatigue failure occurs under thermocycled or temperature controlled water. Different methods in achieving this have been described previously in chapter 2.6.2. All methods share some common features: wet environment, stresses and time

cause sample failure and this occurs at loads lower than their known maximum strength.

8.2. Aim:

To evaluate the durability of mandibular molar crowns made from a polyetherketoneketone (PEKK) based polymer (Pekkton®ivory) when veneered with light-cured composite through testing their resistance to fatigue failure.

8.3. Objectives:

- To compare the fatigue limit of PEKK based crowns subjected to cyclic loading using a five station fatigue chewing machine under circulated 37°C water to equivalent zirconia-composite and metal-composite bi-layered crowns.
- To compare the fatigue life of PEKK based crowns subjected to cyclic loading using a five station fatigue chewing machine under circulated 37°C water to equivalent zirconia-composite and metal-composite bi-layered crowns.
- To assess the effect of different substructure materials on the durability and mode of fracture of these bi-layered crowns when veneered with the same light cured composite.

8.4. Methods:

8.4.1. Fatigue chewing machine:

A custom made five-station fatigue machine was used to assess fatigue limit and fatigue life (Figure 72).

The machine was built by researchers at The University of Liverpool and has been validated in published studies (Padipatvuthikul and Mair, 2008, Padipatvuthikul and Mair, 2009, Mair et al., 2011). The machine is powered with an electric motor (CMG electric motor, Australia) and the power is transferred through two cams to five eccentric rotating cams that contact the lever through an adjustable rotating wheel. Each lever individually delivers load to crowns through a silicone cushioned metal 4.25 mm ball indenter (Figure 73).

Along with the mass of the lever itself, additional disc weights are used to control the required load for each station. Each station is connected with a digital counter to record the number of cycles. After sample failure the counter switches off keeping a record of the number of cycles at sample fracture while the machine keeps working and other arms still counting. This is done by having an adjustable switch that can be placed directly under each lever so that the lever touches the switch as the lever slightly drops after sample fracture.

At the water container where the samples will be positioned, a water circulator (Techne Circulator C-85A, Techne, UK) is connected to keep the

water circulated at 37°C during the test. The machine is fitted with two emergency stop buttons in addition to the switch-off button in the main control unit. The main control unit also has the ON switch and controls the machine rotating speed, which for this test was set at 90 cycles per minute.

Figure 72: Five station fatigue chewing machine.

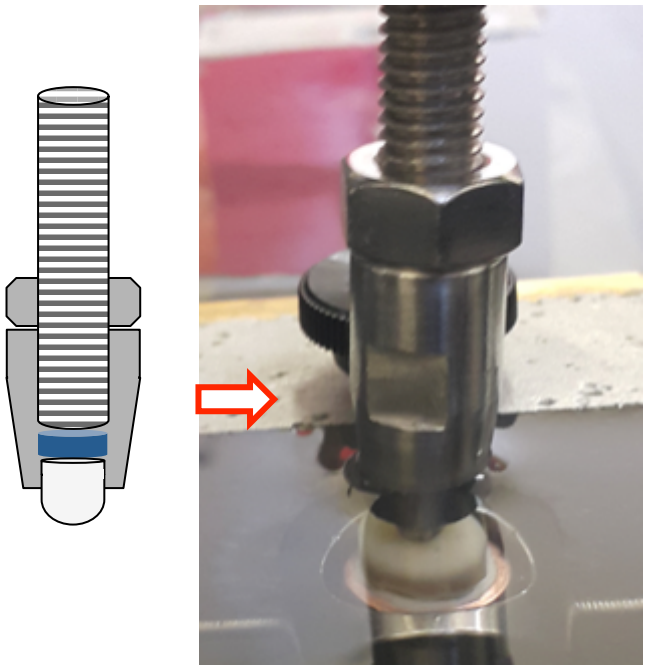


Figure 73: Silicon cushioned (in blue) indenter.

8.4.1.1. Load calibrating:

The fatigue machine uses weight discs to control the load to be applied on samples. Different weights discs ranging from 0.5 Kg to 2.5 Kg are placed on the loading rod on each lever (Figure 74). To calibrate the load applied on samples, an electric sensor (TR150 load cell indicator, Novatech Measurements Limited, UK) was used to measure the load applied through the indenter in Newtons (Figure 75). A custom block with a sensor cell attached to it was placed at the sample holder where the crowns samples are to be placed. A detailed table of the loads can be seen in Table 37 in the appendix.

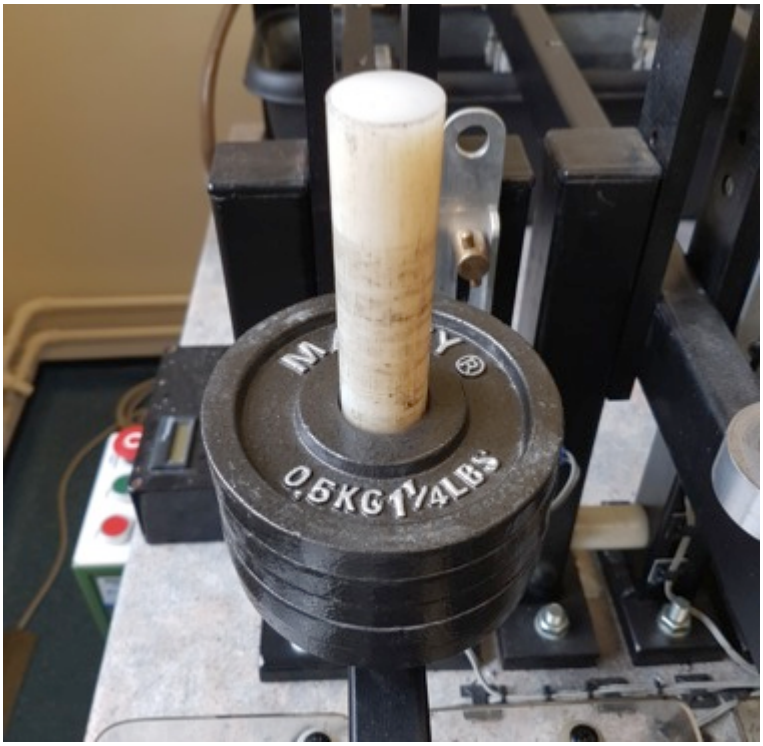


Figure 74: Metal weight discs placed on the lever.

Figure 75: Load indicator and sensitive cell placed at the sample mount under the indenter.

8.4.2. Fatigue samples

The abutment and PDL production for this chapter was produced in the same manner described previously in the structural integrity chapter (chapter 7.4.1). The base was also produced in the same manner with the addition of a 15mm diameter copper ring to add an extra support when fixing the sample in the fatigue chewing machine under the water (Figure 76).

Crown samples for this test were fabricated following the same steps described in detail previously in chapter 7.4. The material used and their lot numbers are detailed in Table 26.

The crowns were cemented to the abutments using resin cement (Multilink Automix, Ivoclar Vivadent AG, Liechtenstein) and were under 40 N pressure for 3 minutes using universal testing machine and light cured during the loading. Samples were left to set for at least 24 hours before storing in distilled water for another 24 hours.

Samples were then fixed in their sample mount and tightened using three screws before fixing the steel sample mount in the machine.

Articulating paper was used to position the sample in the correct position under the metal indenter before fixing the mount in place using two screws (Figure 77).

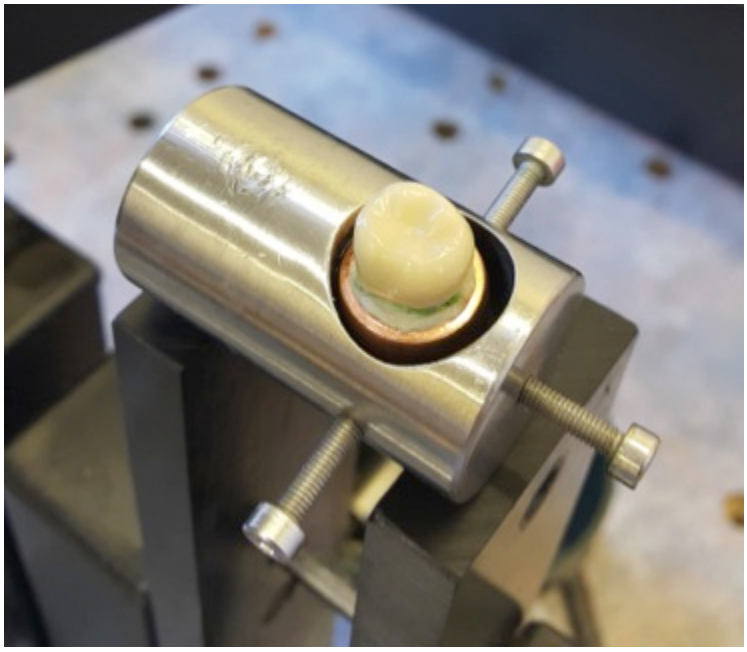


Figure 76: Crown sample fixed in the sample holder for the fatigue chewing machine. The copper ring added support to the sample.

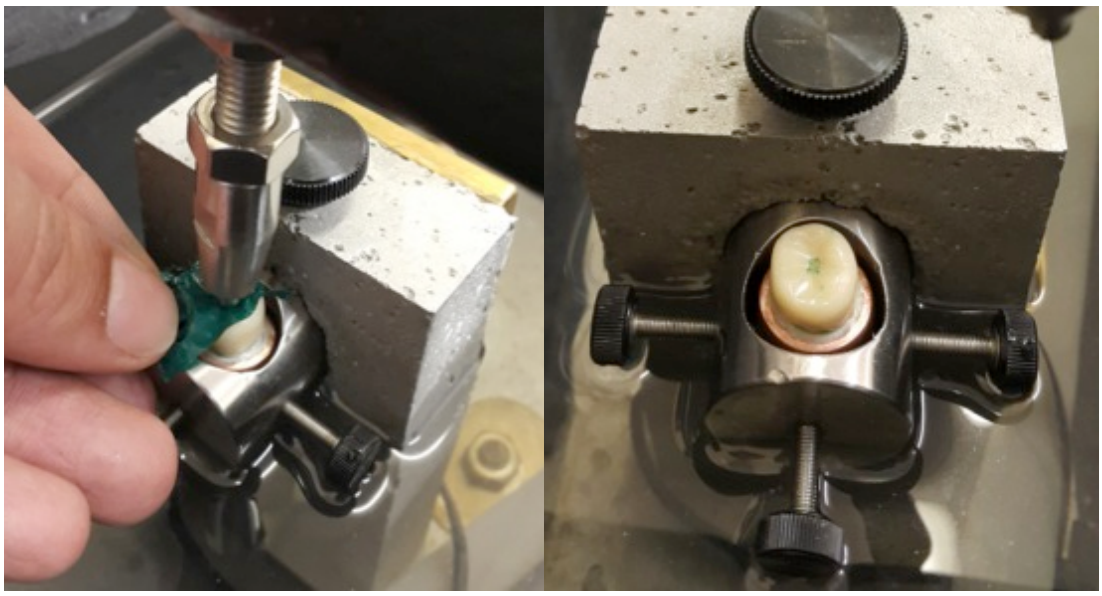


Figure 77: Positioning samples in the fatigue chewing machine.

Table 26: Materials used in sample fabrication for the fatigue chewing machine.

Material	Brand	Lot no.
Polyurethane	AlphaDie MF, Schültz-Dental GmbH, Germany	2013007844 2014003042
Light-bodied impression material	President light body, Coltene Whaledent, Switzerland	G25522
Zirconia	In-Ceram YZ®, VITA Zahnfabrik GmbH, DE	37850
Metal	Talladium Tilite V, Talladium, Inc, USA	042011
PEKK Polymer	Pekkton Ivory, Cendres+Métaux SA	Experiment blocks for CAD/CAM milling (provided from the company)
Composite	Vita VM LC®, VITA Zahnfabrik GmbH, DE	LOT44421 LOT39351 LOT11440
Zirconia primer	Monobond® Plus, Ivoclar Vivadent AG, Liechtenstein.	LOT37850
Metal primer	Kuraray Alloy primer® , KURARAY CO., LTD, Japan.	042011
PEKK primer	visio.link®, Bredent GmbH & Co. KG, Germany.	141432
Resin cement	Multilink Automix, Ivoclar Vivadent AG, Liechtenstein	T40253 U44073

8.4.3. Fatigue limit

The fatigue limit was evaluated using the staircase method (described in chapter 2.6.2.1).

An initial load was chosen for the first sample and it was cycled under water for 5000 cycles. If the sample survived, a new sample was then inserted and the load raised by one step (0.5 Kg) and cycled for 5000 cycles. If the sample fails, the load for the next sample should be lowered by one step (0.5 Kg). This should be repeated until at least five samples following the same sequence is achieved.

Following completion of the test, a diagram was generated using the used loads and samples that would show the fatigue limit pattern. The fatigue limit was calculated as the average load that 50% survived.

To calculate this, up to 5 samples should show an up and down pattern with regard to the ascending and descending samples and hence the test was done in a set of five samples at a time to achieve this pattern (Wiskott et al., 2007). In addition, sample size ranging from 15 to 25 samples was regarded as sufficient for accurate fatigue limit and the fatigue limit and the standard deviation was calculated using the following equations (Dieter, 1961, Garoushi et al., 2007):

Equation 5

$$Fatigue\ Limit = X_0 + d\left(\frac{\sum in_i}{\sum n_i} \pm 0.5\right)$$

Equation 6

$$Standard\ Deviation = 1.62d\left(\frac{\sum n_i \sum i^2 n_i - (\sum i n_i)^2}{(\sum n_i)^2} + 0.029\right)$$

where (X_0) is the lowest load level considered in this evaluation, (d) is the fixed load increments, (i) is the stress level where the lowest stress level is considered as i=0 and then i=1 and so forth and (n_i) is the number of failures or survival at a certain stress level. In the first equation, if the analysis is based on failures the positive sign is used, and when based on survivals the negative is used.

8.4.4. Fatigue life

The fatigue life was evaluated by subjecting the crowns to a 1 Kg load less than the fatigue limit for each group. The machine was set to run for 1,250,000 cycles and 5 samples of the same group were placed in the machine to start the test at the same time. The machine was paused every 100,000 cycles to check the samples before continuing the test.

Upon crown fracture, the counter on the arm with the fracture stops counting and the number of cycles the crown withstood before failure was recorded. The test was continued for the remaining crown samples in other stations until either all crowns failed or reached 1,250,000. The exercise was then repeated with a further five samples.

8.4.5. Statistical analysis:

The results obtained from the fatigue life experiment were analysed using the Weibull analysis method.

This analysis was performed using computer software (Reliability and maintenance analyst, USA). The values gained from this analysis method are the shape parameter (β) and life parameter (α) and from them a graphical plot can be generated. The β value can be interpreted in relation to reliability to: high $\beta>1$, regular $\beta=1$ and low $\beta<1$. The α indicates the average number of cycles at which samples fail, and both β and α determine the line location and slope in the plot.

Furthermore, IBM SPSS Statistics 22 software was used to determine any significance differences in the recorded mode of fracture between groups. This was performed using Kruskul-Wallis and Mann-Whitney tests.

8.5. Results

8.5.1. Fatigue limit results:

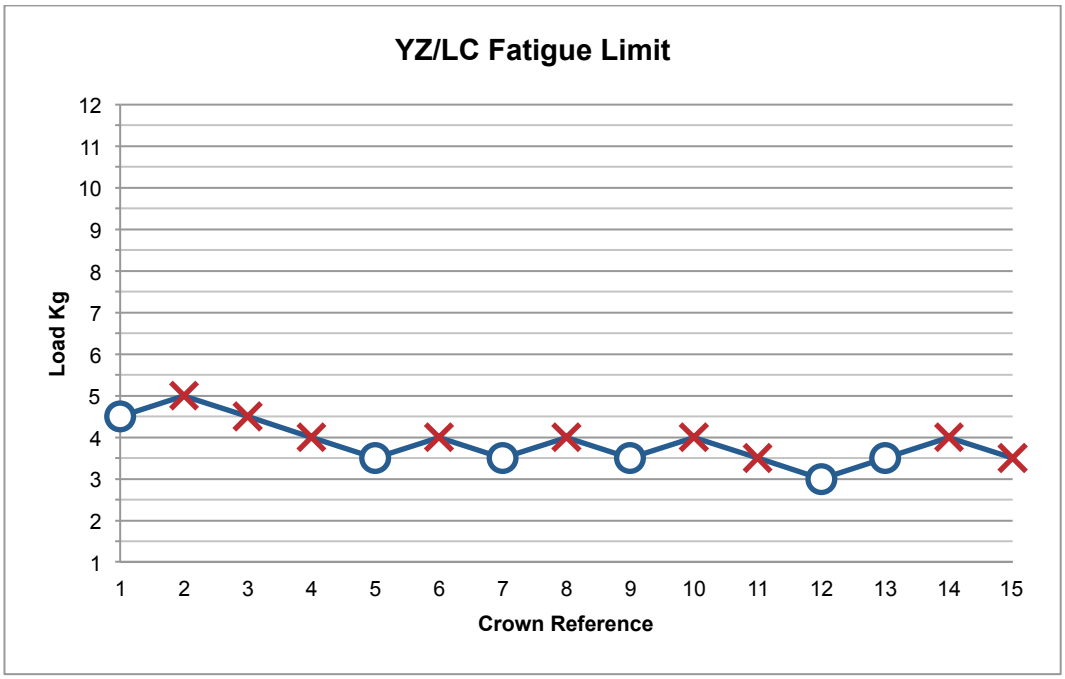


Figure 78: YZ/LC group fatigue limit using staircase method.

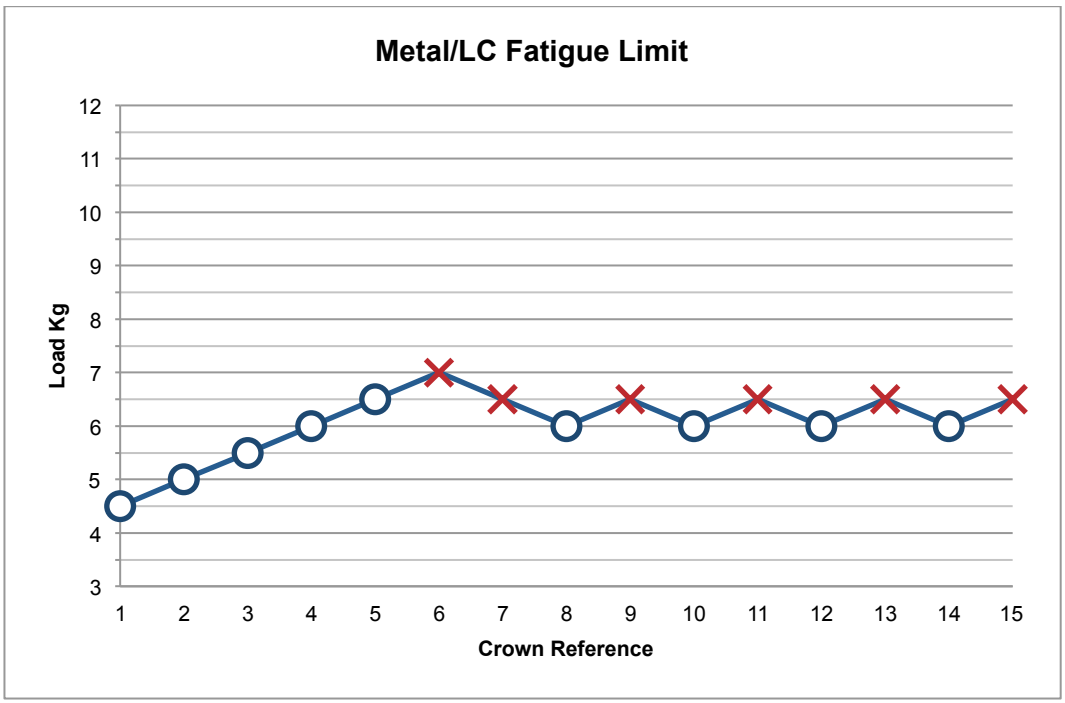


Figure 79: Metal/LC group fatigue limit using staircase method.

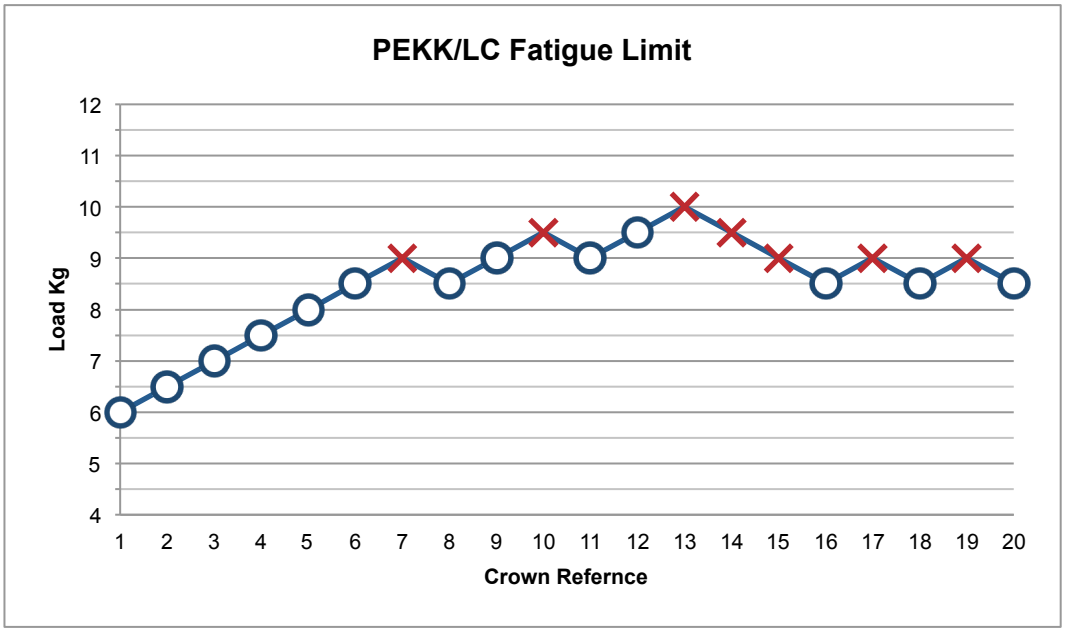


Figure 80: PEKK/LC group fatigue limit using staircase method.

Table 27: YZ/LC crowns analysed data for the fatigue limit equation.

Load N	$i_{(stress\ level)}$	$n_{i\ (failure)}$	$i.n_i$	$I^{2.}n_i$
388 (3 Kg)	0	0	0	0
422 (3.5 Kg)	1	2	2	2
457 (4 Kg)	2	5	10	20
489 (4.5 Kg)	3	1	3	9
522 (5 Kg)	4	1	4	16
Total		Σn_i= 9	$\Sigma i.n_i$= 19	$\Sigma i^2.n_i$= 46

Table 28: Metal/LC crowns analysed data for the Fatigue Limit equation.

Load N	$i_{(stress\ level)}$	$n_{i\ (failure)}$	$i.n_i$	$I^{2.}n_i$
586 (6 Kg)	0	0	0	0
619 (6.5 Kg)	1	5	5	5
652 (7 Kg)	2	1	2	4
Total		Σn_i= 6	$\Sigma i.n_i$= 7	$\Sigma i^2.n_i$= 9

Table 29: PEKK/LC crowns analysed data for the Fatigue Limit equation.

Load N	$i_{(stress\ level)}$	$n_{i\ (failure)}$	$i.n_i$	$I^{2.}n_i$
754 (8.5 Kg)	0	0	0	0
792 (9 Kg)	1	4	4	4
812 (9.5 Kg)	2	2	4	8
845 (10 Kg)	3	1	3	9
Total		Σn_i= 7	$\Sigma i.n_i$= 11	$\Sigma i^2.n_i$= 21

Table 30: Calculated fatigue limit results.

Group	Fatigue Limit N
YZ/LC	442.8 (±42.1)
Metal/LC	608.7 (±7.6)
PEKK/LC	790.4 (±29.2)

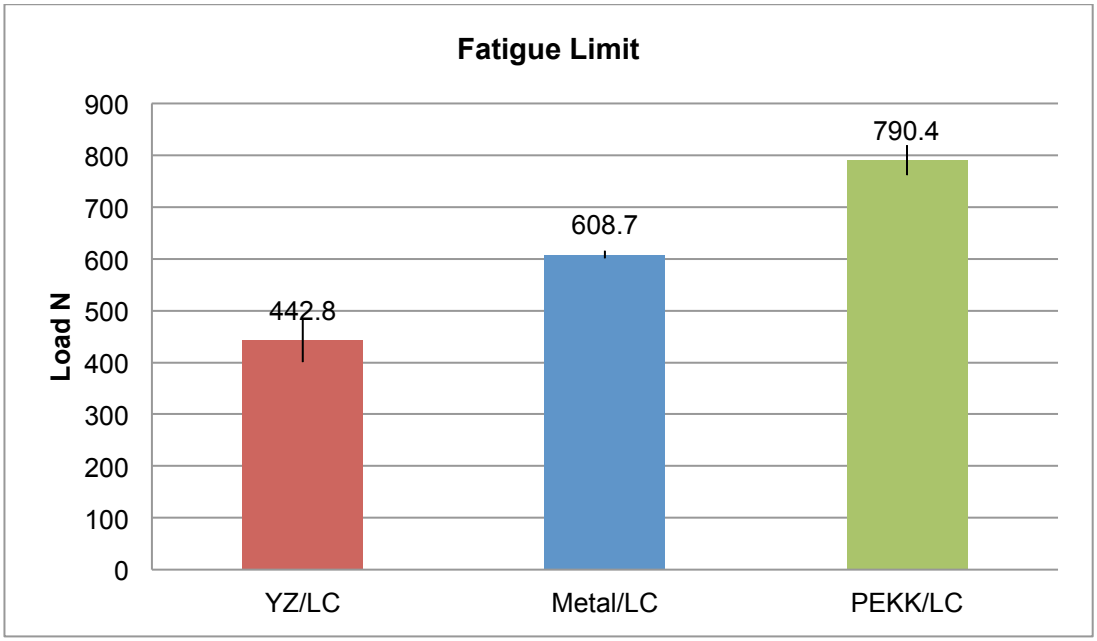


Figure 81: Calculated Fatigue limit for all tested groups.

8.5.2. Fatigue life:

Table 31: Fatigue life results using Weibull parameters for all groups and loads.

Group	Load	β (Failure rate indication)	α (Characteristic life scale)
YZ/LC	353 N (2.5 Kg)	0.6618	2736000
PEKK/LC	682 N (7.5 Kg)	0.6522	296900
Metal/LC	522 N (5 Kg)	0.6209	202400
YZ/LC	522 N (5 Kg)	0.273	25130
PEKK/LC	522 N (5 Kg)	1.291	3110000

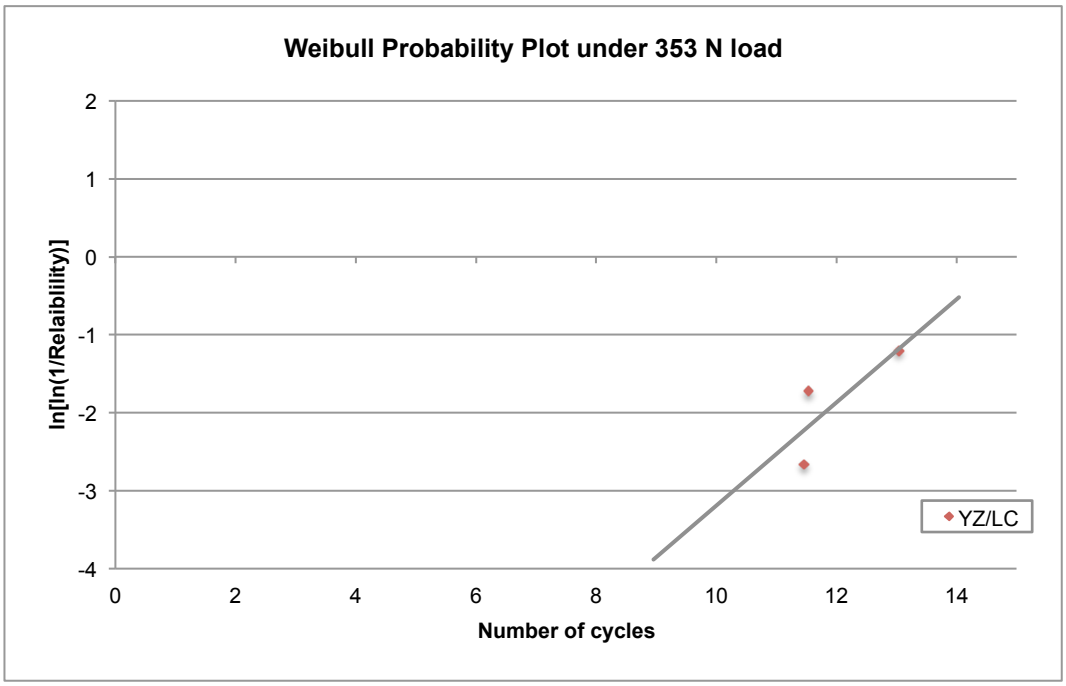


Figure 82: Weibull probability plot for the YZ/LC group under 353N (2.5 Kg) load.

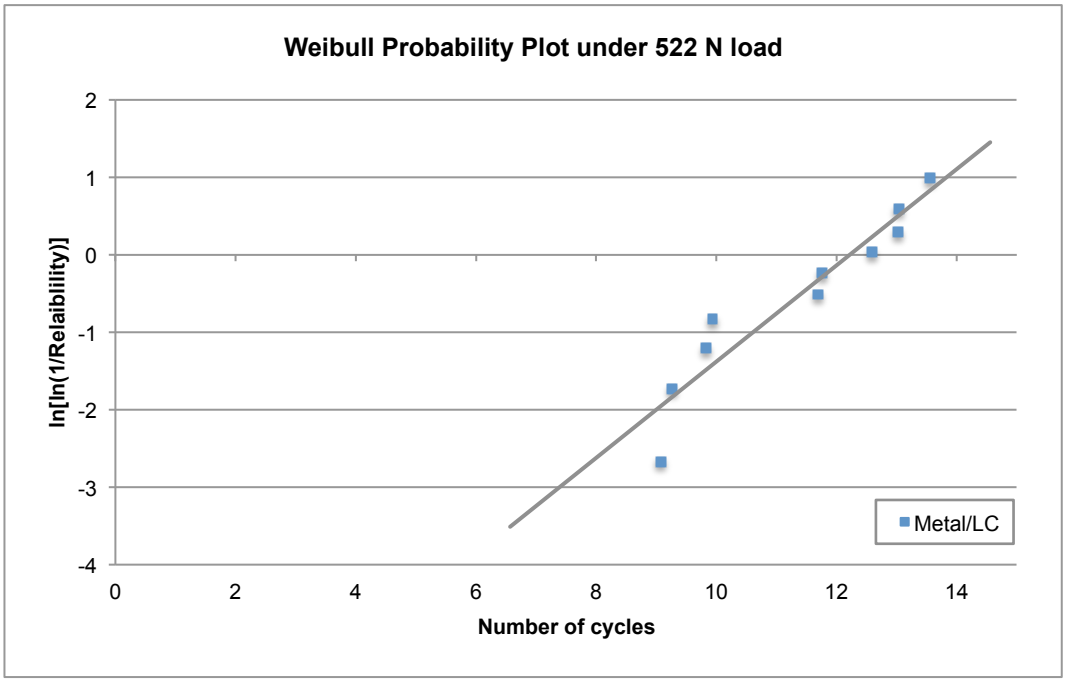


Figure 83: Weibull probability plot for the Metal/LC group under 522 N (5 Kg) load.

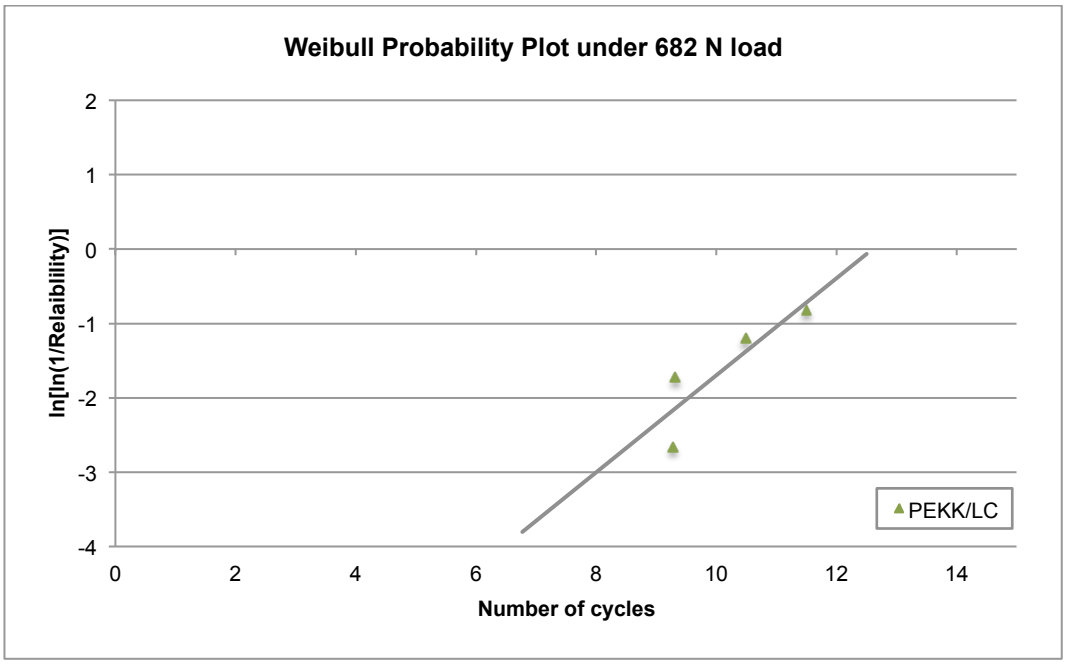


Figure 84: Weibull probability plot for the PEKK/LC group under 682 N (7.5 Kg) load.

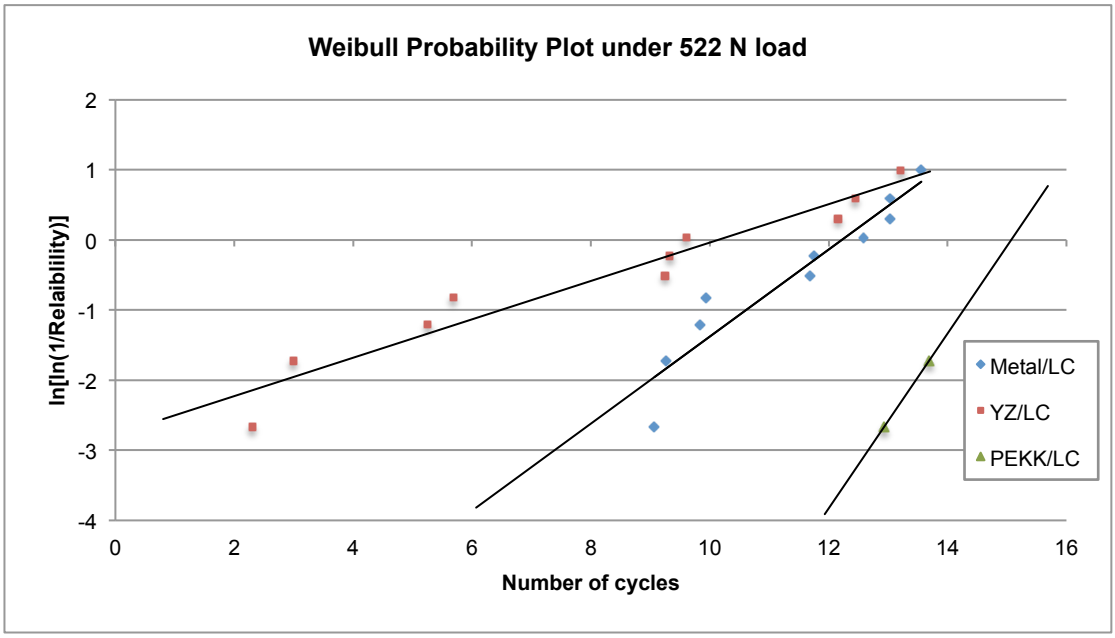


Figure 85: Weibull probability plot for all groups under 522 N (5Kg) load.

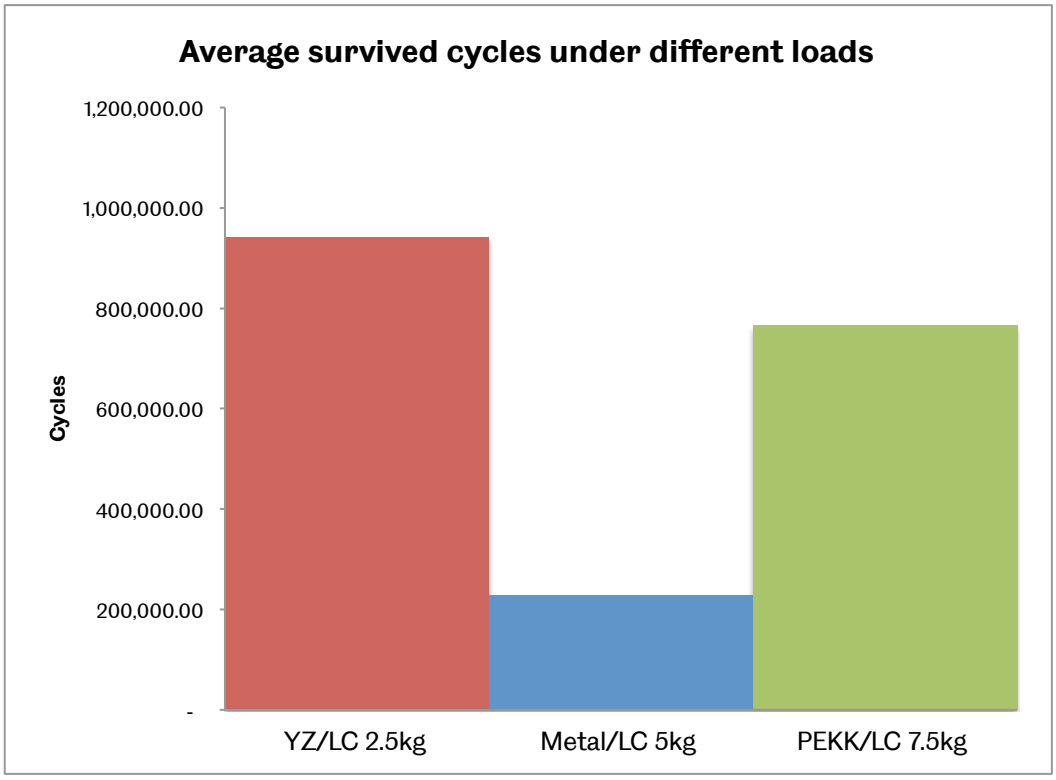


Figure 86: Average survived cycles of all groups each under assigned load close to its fatigue limit load.

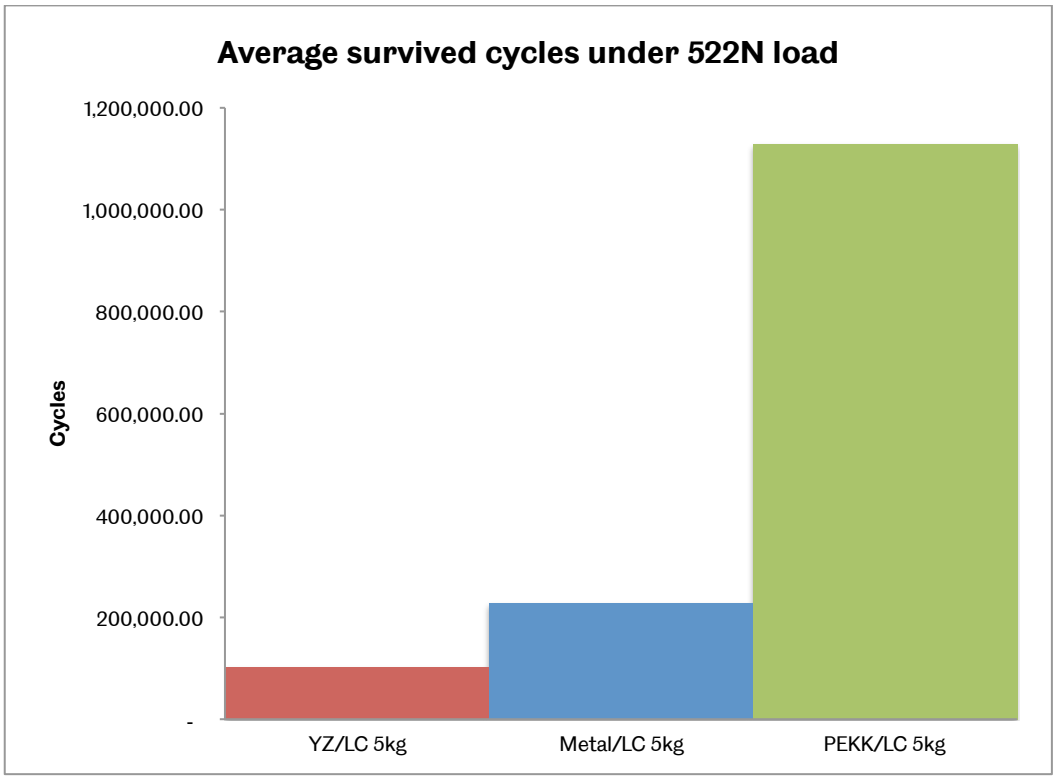


Figure 87: average survived cycles of all groups under same load of 522 N (5Kg).

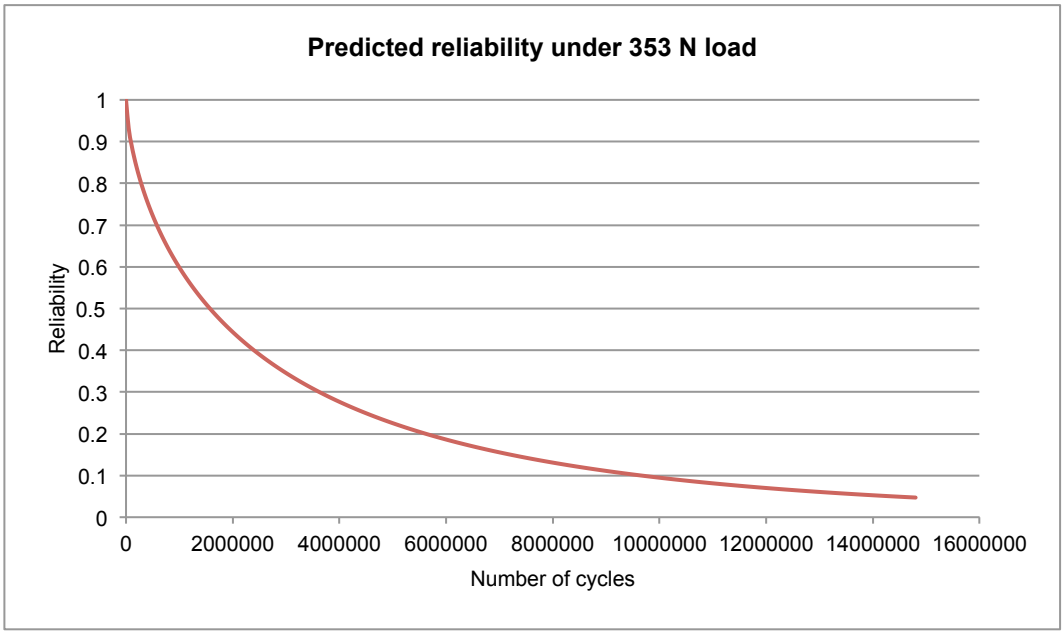


Figure 88: Predicted reliability of YZ/LC group under 353 N load using Weibull maximum likelihood graph.

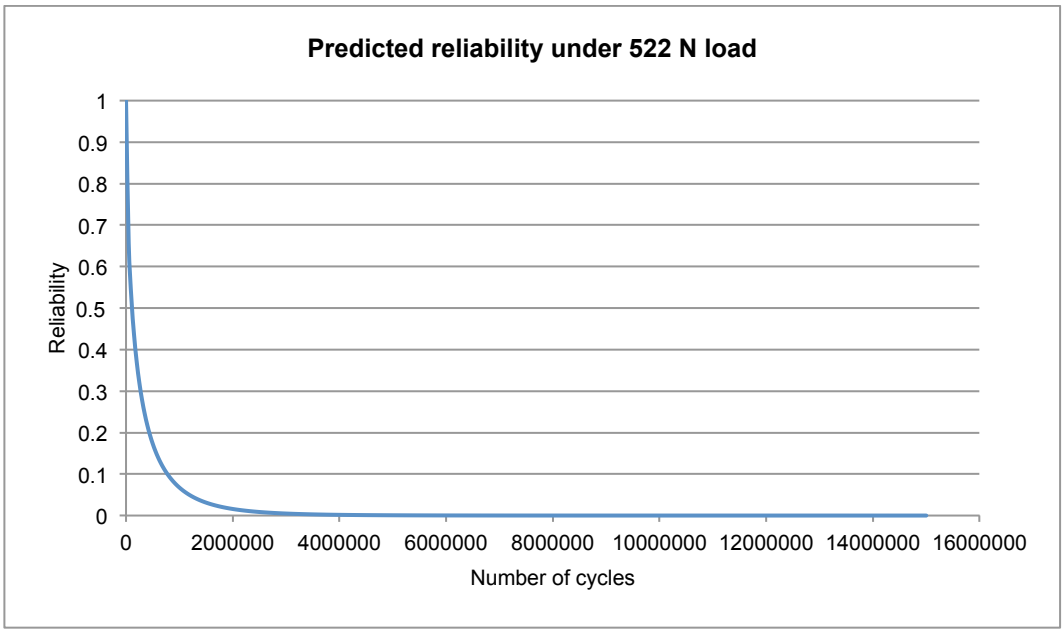


Figure 89: Predicted reliability of Metal/LC group under 522 N load using Weibull maximum likelihood graph.

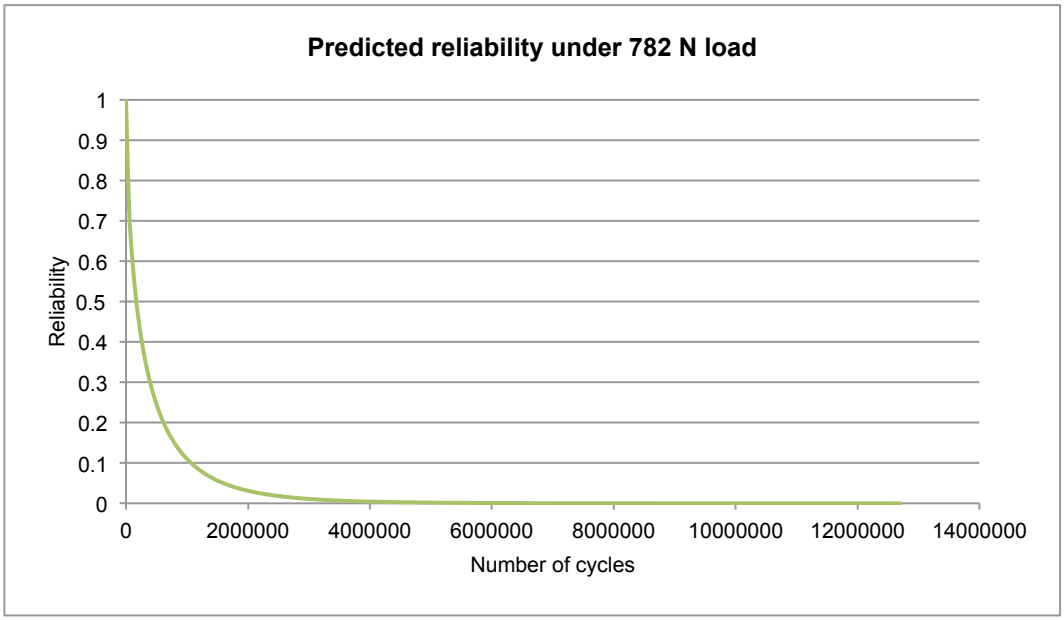


Figure 90: Predicted reliability of PEKK/LC group under 682 N load using Weibull maximum likelihood graph.

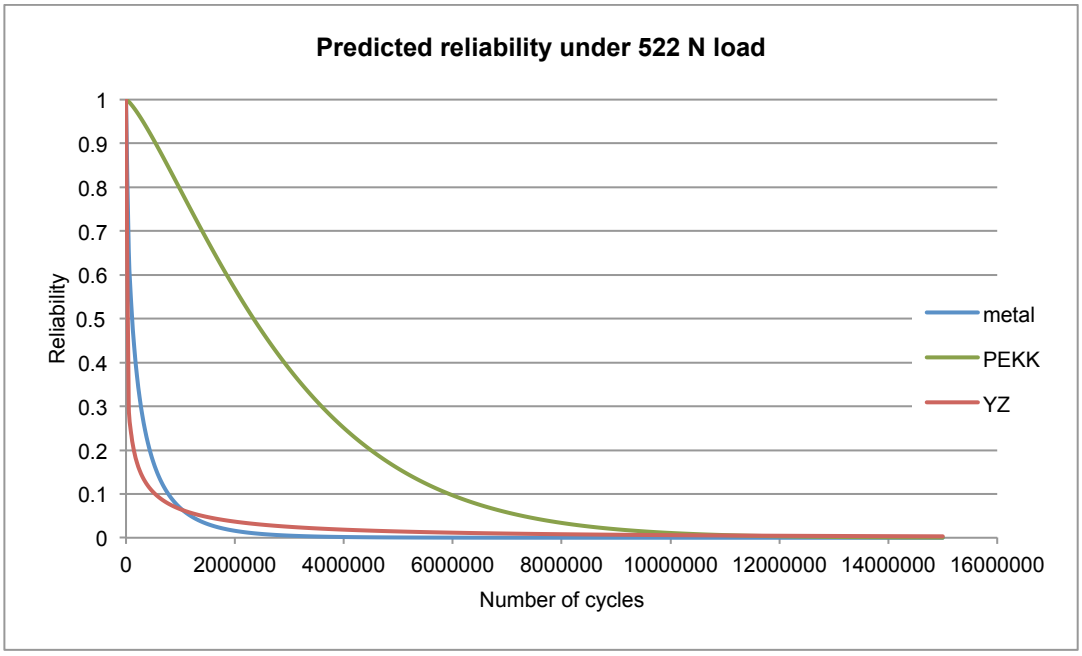


Figure 91: Predicted reliability of all groups under the same load of 522 N using Weibull maximum likelihood graph.

Table 32: Mode of fracture for fatigue life test under each group's fatigue limit load following Burke's classification (1 minimal fracture and 5 severe fracture). The letter "v" indicates fracture within the veneer only. Different superscript letters indicate significant differences (P<0.05) and groups with same superscript letters indicate no significant difference (P>0.05).

Group	Load	Fracture Code				
		1	**2**	**3**	**4**	**5**
YZ/LC[a]	353 N (2.5 Kg)	7(v)	0	1(v)	0	2(v)
Metal/LC[a]	522 N (5 Kg)	2(v)	2(v)	4(v)	2(v)	0
PEKK/LC[a]	682 N (7.5 Kg)	5(v)	4(v)	0	0	1(v)

Table 33: Mode of fracture for fatigue life test under 522 N load following Burke's classification (1 minimal fracture and 5 severe fracture). The letter "v" indicates fracture within the veneer only. Different superscript letters indicate significant differences (P<0.05) and groups with same superscript letters indicate no significant difference (P>0.05).

Group	Load	Fracture Code				
		1	**2**	**3**	**4**	**5**
YZ/LC[a]	522 N (5 Kg)	0	0	3(v)	1	5+1(v)
Metal/LC[b]	522 N (5 Kg)	2(v)	2(v)	4(v)	2(v)	0
PEKK/LC[c]	522 N (5 Kg)	8(v)	2(v)	0	0	0

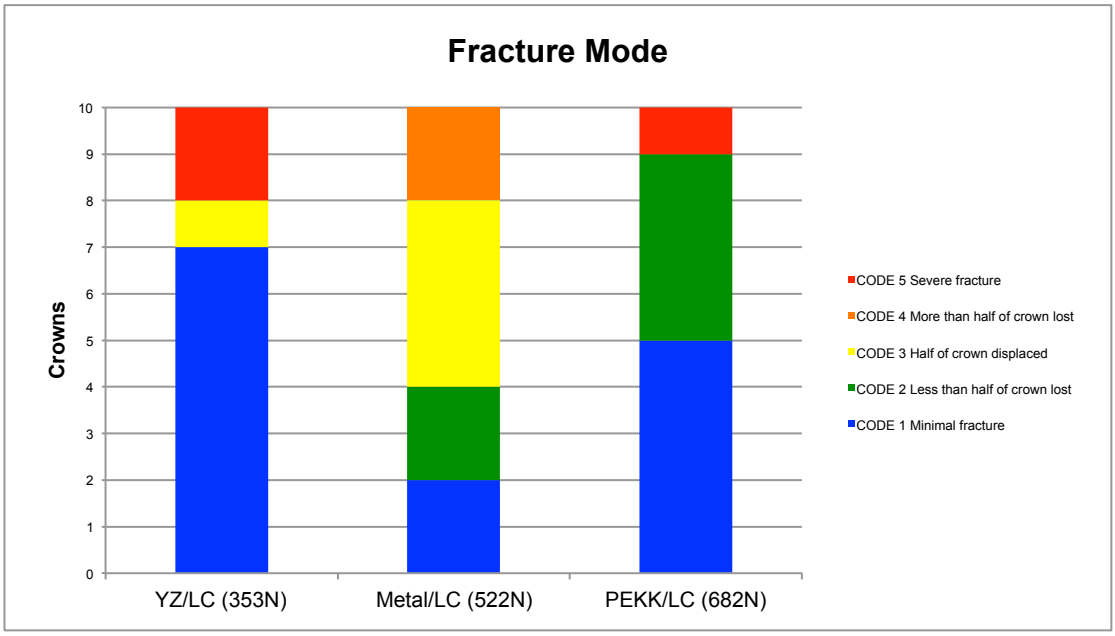


Figure 92: Fracture mode under each group's fatigue limit. All recoded fractures were within the composite veneer only.

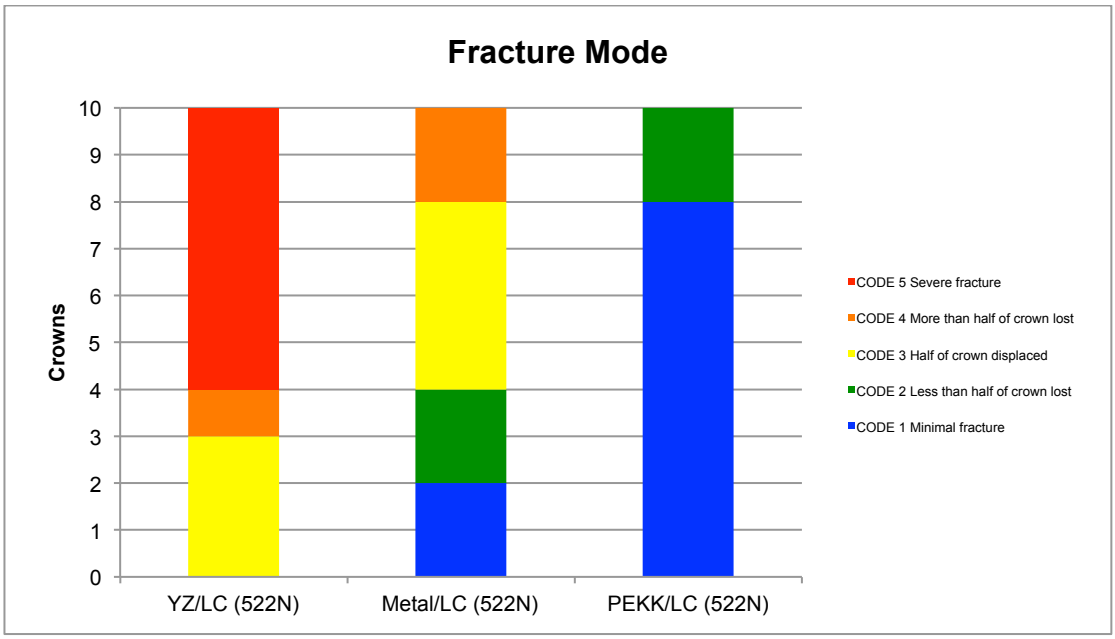


Figure 93: Fracture mode under 522 N. All recoded fractures were within the composite veneer only except in the zirconia group were 6 crowns showed fracture through the veneer and substructure.

Figure 94: Code 3 fracture from the YZ/LC group under 353 N load.

Figure 95: Code 5 fracture from the YZ/LC group under 353 N load.

Figure 96: Code 2 fracture from the Metal/LC group under 522 N load.

Figure 97: Code 4 fracture from the Metal/LC group under 522 N load.

Figure 98: Code 2 fracture from the PEKK/LC group under 682 N load.

Figure 99: Code 1 fracture from the PEKK/LC group under 682 N load.

Figure 100: Code 5 fracture from the YZ/LC group under 522 N load.

Figure 101: Code 3 fracture from the YZ/LC group under 522 N load.

Figure 102: Code 2 fracture from the PEKK/LC group under 522 N load.

Figure 103: Code 1 fracture from the PEKK/LC group under 522 N load.

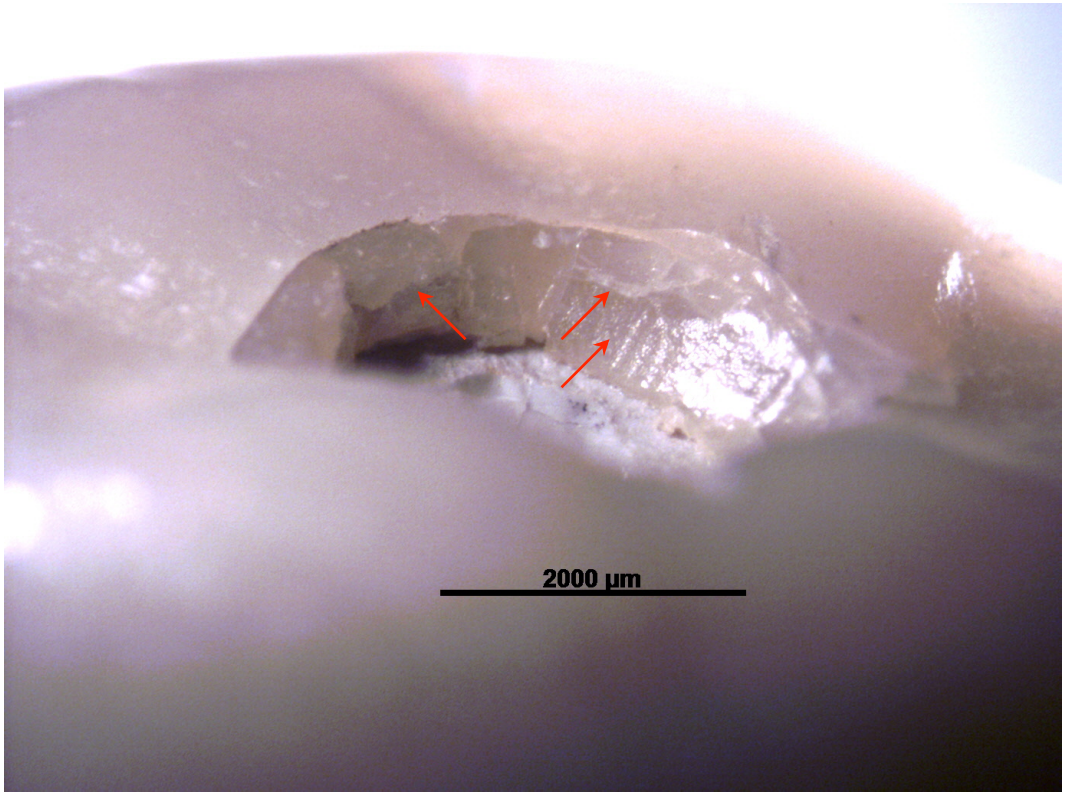


Figure 104: Code 1 fracture of PEKK/LC crown under 10x magnification. Red arrows show different fracture layers.

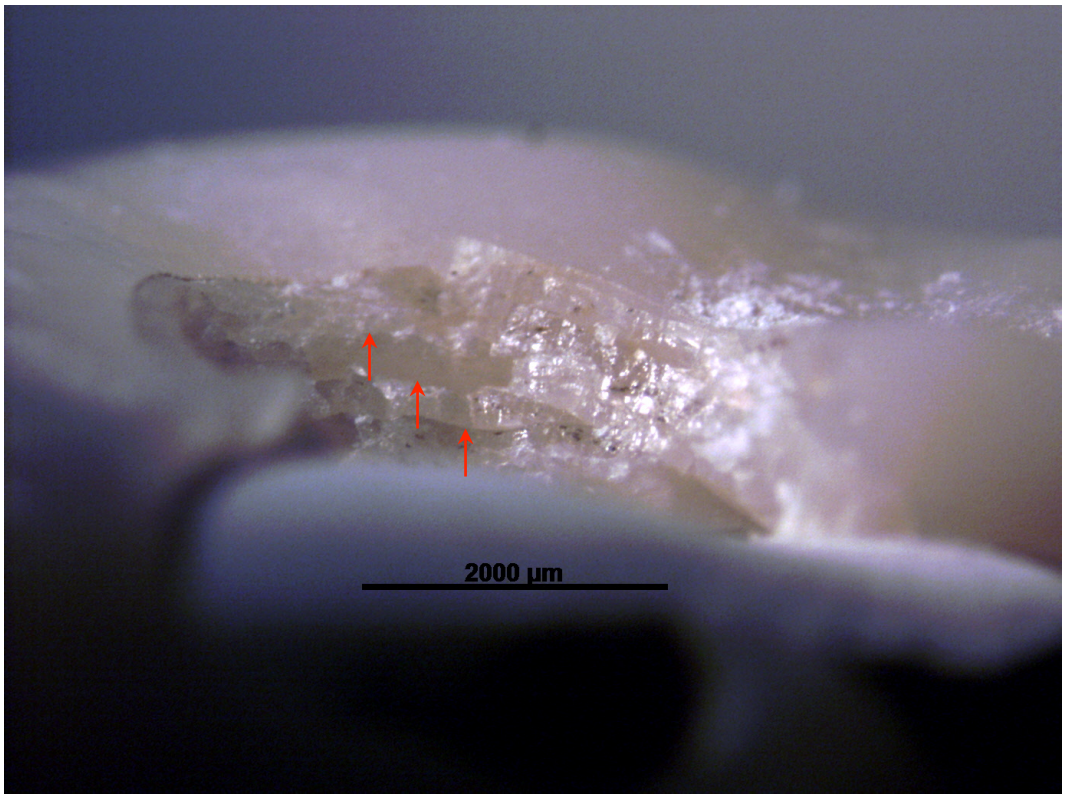


Figure 105: Code 2 fracture of PEKK/LC crown under 10x magnification. Red arrows show different fracture layers.

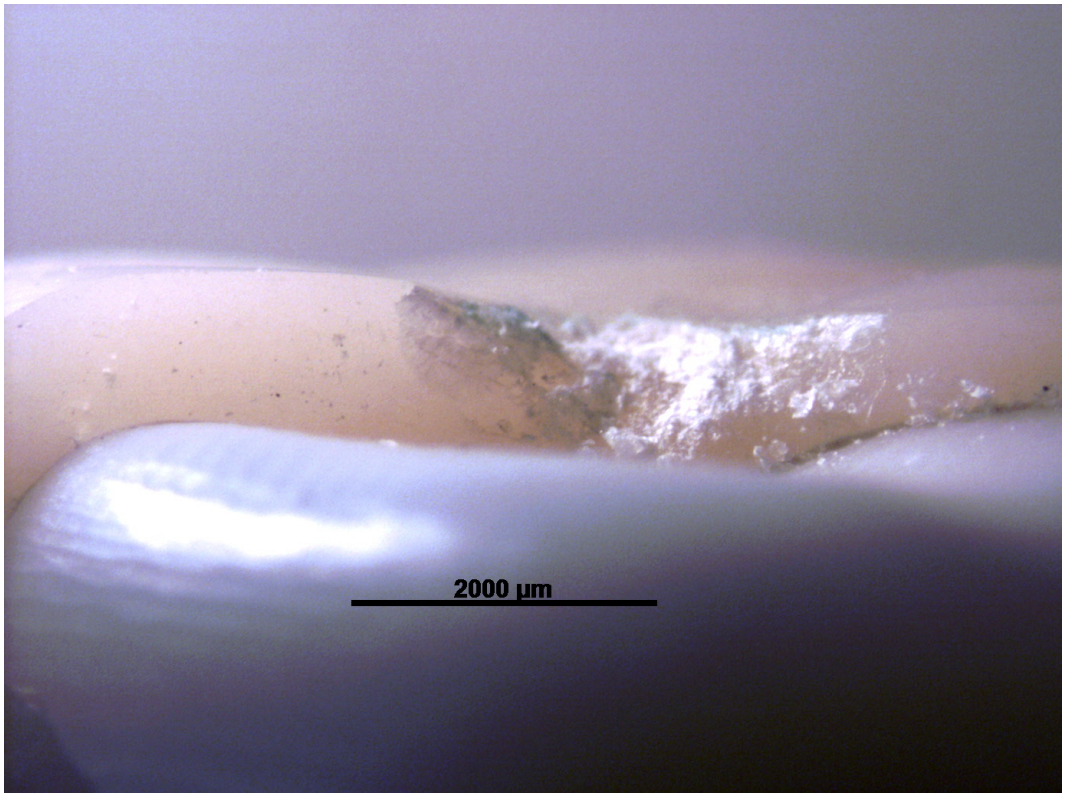


Figure 106: Code 3 fracture of YZ/LC crown under 10x magnification.

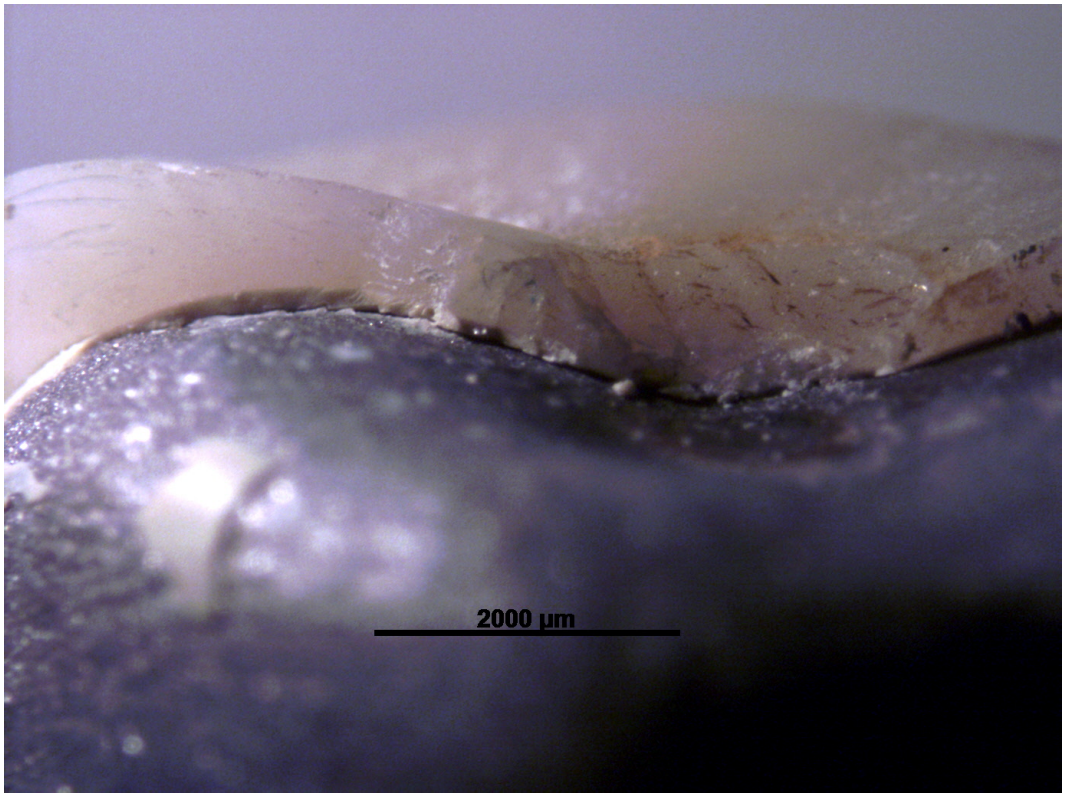


Figure 107: Code 3 fracture of Metal/LC crown under 10x magnification.

8.6. Discussion:

The machine used in this study was a custom built and has been used before in a number of studies (Padipatvuthikul and Mair, 2008, Padipatvuthikul and Mair, 2009, Mair et al., 2011). Limitations were noticed after using the machine for the type of samples and test performed in this study. Being all mechanical with no digital sensors monitoring the samples performance is considered a limitation especially when comparing to other machines in other studies that support such feature.

Since the veneering materials on all the tested groups were light cured composite, the fracture associated with these veneers as code 1 was considered as a survived sample due to two reasons:

1) The nature of the veneer and it being gradually penetrated with the steel indenter without catastrophic failure (as seen in most PEKK samples), the machine could not detected a fracture and hence could not distinguish when to count the failure time.

2) Such minor damage within the composite veneer is considered a reparable fracture inside the oral cavity and hence the crown would still be in service.

This testing method and protocol of evaluating the fatigue limit and fatigue life is time consuming in so much as it may take weeks or months to complete depending on the number of groups. However, it is the recommended

method as this provides more realistic results in comparison to other methods such as the accelerated testing methods (Lin et al., 2001).

Inside the mouth, the highest biting force is recorded in the molar region and the stresses generated on the crown from these masticatory forces cause failures that are generated from either the occlusal contact points on the outer surface or in some cases from the inner surface of the crown causing major fractures (Kim et al., 2008). To begin the fatigue limit experiment, fifteen molar crowns were assigned for each group to start the test using the staircase method.

For the YZ/LC and Metal/LC groups, 15 crowns were enough to get a fracture pattern to distinguish a fatigue limit load. The YZ/LC group showed a pattern following a load limit of 3.5 Kg load that correlates to 422 N (Figure 78). The Metal/LC group showed a fracture pattern around a load limit of 6 Kg that correlates to 586 N (Figure 79).

The PEKK/LC group used twenty crowns to distinguish the fatigue limit that was at 8.5 Kg, which correlates to 754 N (Figure 80). Using equation 8, the fatigue limit and the standard deviation were calculated and the results for PEKK/LC, Metal/LC and YZ/LC were 790.4 N (±29.2), 608.7 N (±7.6) and 442.8 N (±42.1) respectively (Table 31 and Figure 81).

It was predicted from the previous chapter that the zirconia group would show lower strength than the other PEKK and Metal groups. But unlike the previous load-to-failure test, the PEKK samples showed higher results than the metal. This is in accordance with the finding of a study by Keilig (2014)

were PEKK composite veneered molar crowns cemented to three different abutment materials (PMMA, CoCr and extracted human teeth) and subjected to cycling loading under 37°C water showed a fatigue limit higher than 600 N with limits of 750 N for both PMMA and CoCr, and 600 N for the natural tooth supported crowns.

The first evaluation of fatigue life experiment was carried out with loads close to the fatigue limit, in this case 1 Kg lower load than the fatigue limit. This resulted in loads of 2.5, 5 and 7.5 Kg to YZ/LC, Metal/LC and PEKK/LC groups respectively.

Due to the big variation between the loads, extra batches of samples were added to allow direct comparison between groups under the same load. For this, 5Kg (522 N) was chosen as it lies in the middle between zirconia and PEKK fatigue limits. Another reason to support choosing this load was that studies report that around 500 N is considered maximum average load in normal conditions in the mouth (Bakke et al., 1989, Tortopidis et al., 1998).

The samples were left to cycle until fracture or to reach the target of 1,250,000 cycles which approximates to be the equivalent of service life inside the oral cavity of 5 years, 250,000 cycles could be interpreted to being inside the mouth for a year (Sakaguchi et al., 1986).

Many studies recommended setting cycles equivalent to 5 years, some used 1,200,000 cycles (Nie et al., 2012, Naumann et al., 2006, Naumann et al., 2005, Kohal et al., 2006), others used 1,250,000 cycles (Shembish et al., 2016, Kern et al., 1993) and 1,000,000 for others (Rekow and Thompson, 2007).

A useful analysing tool was performed on the fatigue life result and the Weibull probability plots could give an indication of how reliable the samples are under the test condition and hence predict their performance. The plot can be interpreted depending on the formed lines as an upright line which shows a high reliability (high β value) and on the opposite downslope lines indicates unreliability (low β value). Also the higher survival rate the further to the right the line will be located (higher α value) and vice versa.

For the YZ/LC group, the fatigue life experiment was set under 2.5 Kg (353 N) and 7 crowns out of 10 survived the test and reached 1,250,000 cycles where the test was stopped with an average survived cycle number of 940,456 cycles. The Weibull probability plot of the YZ/LC group under 353 N load shows a line revealing a reliability of sample under this chosen load with the β value of 0.66 and a α value of 2736000 (Figure 82).

In the Metal/LC group under 5 Kg (522 N), none of the samples survived the target of 1,250,000 cycles and the Weibull probability plot showed an average reliability with a β value of 0.62 and a α value of 202400 (Figure 83). The average number of survived cycle may be visualised in Figure 86 and Figure 87 and the Weibull predicted reliability graphs of all groups are visualised in Figure 88, Figure 89, Figure 90 and Figure 91. All these graphs findings are in accordance with the findings of the Weibull probability plots mentioned before. The performance of the groups in the predicted reliability graphs could be expected from such an aggressive testing conditions, as the used loads are considered very high for any normal chewing forces inside the mouth. A study by Schindler et al. (1998) tested the chewing forces in the

molar region while eating different food and the results ranged between 55.6 N (± 10.0) to 529.5 N (± 11.4). It is not possible to make a direct comparison of these results with the zirconia porcelain veneered restorations from other studies due to different test configurations. Very few studies were found comparing zirconia substructures when veneered with composite to other restorations, but a study by Komine et al. (2014) had zirconia based crowns, veneered with both composite and porcelain, subject to thermocycling loading for 1,200,000 cycles before testing their fracture resistance. Three groups of composite veneered zirconia crowns, with different bonding configurations, showed no significant difference to the zirconia porcelain veneered control group. On the other hand, a study by Oderich et al. (2012) showed a higher survival rates of zirconia composite veneered premolar crowns than other same designed zirconia crowns when veneered with porcelain. This could be due to the composite layer acting as a better occlusal force shock absorber than the ceramic ones (Conserva et al., 2009).

These findings can be taken into consideration knowing that the metal and PEKK groups in this research showed better results than the zirconia based crowns. In addition, it was observed that the thermocycling loading did not cause any significant difference between composite and porcelain veneered zirconia groups, which is the same finding in other tests that did not subject samples to thermocycling loading (Taguchi et al., 2014, Kamio et al., 2015, Sorrentino et al., 2016, Alsadon et al., 2017).

For metal-based crowns, a study by Boff et al. (2014) concluded that metal composite veneered restorations showed lower fatigue resistance against

the zirconia composite veneered ones. A possible reason that this finding is different from the results of this research is that the bonding method used showed better results and hence survived higher cyclic loading under the circulated water for longer time than the zirconia samples.

With the PEKK/LC group under 7.5 Kg (682 N), 6 crowns survived the set target and, as with the previous groups, the Weibull probability plot showed an inclined line in the survival plot with a β value of 0.65. All three groups tested with loads close to their fatigue limit showed a β value of about 0.6, which indicates same survival response of each material to its fatigue limit regardless of the variation of the loads when compared between different materials. To be evaluated under the same load regardless of their fatigue limit, two extra groups, YZ/LC and PEKK/LC were added and tested under 522 N to be compared with the already tested Metal/LC. The results were somewhat expected as the 522 N was above the zirconia group fatigue limit and lower than PEKK's fatigue limit. None of the YZ/LC survived the test and fractured in the early stages of the test. The Weibull probability plot (Figure 85) shows the least inclined line that reveals an unreliability of samples under this load with a β value of 0.273.

PEKK/LC under the same load showed very high reliability with 8 crowns surviving the 1,250,000 cycles target and with a β value of 1.29. The same pattern could be observed in Figure 87 showing fatigue life of all groups under 522 N load where the PEKK/LC show higher survival rate than Metal/LC and YZ/LC respectively. The average number of survived cycles could be visualised in Figure 86 and Figure 87 and Weibull predicted

reliability graphs of all groups are visualised in Figure 88, Figure 89, Figure 90 and Figure 91. All these graphs findings are in accordance with the findings the Weibull probability plots mentioned before.

The crown fractures at the fatigue life test were analysed according to Burke's classification which is divided into 5 codes of fracture types ranging from code 1 as minor fracture to 5 as major crown failure (Table 33). The first batch of tested groups under each groups fatigue limit showed a crown failure within the composite veneer alone without any fracture in the underlying substructure for all the zirconia, metal and PEKK groups. The majority of YZ/LC group (7 crowns) under 353 N (2.5 Kg) were recorded as code 1 fracture as there was a visible indent in the composite veneer just under the position of the steel indenter, one crown was recoded as code 3 (Figure 94) and two crowns showed a severe fracture of the composite veneer code 5.

The Metal/LC under 522 N (5 Kg) load showed different fracture types within the composite veneer ranging between code 1 and 4 as can be seen in Figure 96 and Figure 97. PEKK/LC group under 682 N (7.5 Kg) showed the majority of fracture in code 1 and 2 in 5 and 4 crowns respectively with only 1 severe fracture in the composite veneer. These finding were in accordance with other research where bilayared crowns, mainly zirconia substructures, showed fracture within the veneer (porcelain and/or composite) and none within the substructure (Oderich et al., 2012, Guess et al., 2010).

As expected, when comparing the fracture codes of all groups under the same loads of 522 N the PEKK/LC groups showed the least damaged crowns among the other YZ/LC and Metal/LC groups. On the other hand, YZ/LC had most of its samples severely damaged and 6 out of 10 crowns showed fracture that was through the zirconia and the composite veneer. This substructure fracture was only seen in the zirconia group under 522 N and was not recorded in any other group in all loads used. On the other hand, PEKK crowns were the only substructure material to show damage in the occlusal surface under the indenter after damaging the composite veneer while still having the whole crown intact as one structure.

The large mismatch in elastic modulus between the substructure and the veneering material leads to higher tensile stresses on the substructure that eventually could lead to crown failure (Rekow et al., 2007). Hence it is a likely explanation that the PEKK with a modulus of elasticity of 5.1 GPa outperformed the zirconia and metal-based crowns in this evaluation because of the difference in elastic modulus between the zirconia (210 GPa) and metal (218 GPa) (Tiossi et al., 2013) with the light cured composite veneer (4.5 GPa).

This is also confirmed in a finding from a previous study where the Finite Element Analysis (FEA) showed a higher stress generated on the zirconia substructure when veneered with light cured composite (4.5 GPa) in comparison to porcelain (66.5 GPa) veneered zirconia crowns (Alsadon, 2012).

In other similar studies performed on bilayered zirconia crowns veneered with porcelain, the majority of crown failures were observed as veneer chipping (Coelho et al., 2009a, Rosentritt et al., 2009b, Belli et al., 2013). This is in accordance with the YZ/LC group tested under 2.5 Kg load where all the fractures were within the veneer. The difference between fractures with this group and other studies of bilayered zirconia porcelain crowns is the visible debonding of the composite veneer against the cohesive fracture of the porcelain veneer in those studies. It was shown in previous studies that the best method for bonding indirect composite veneer to zirconia substructure was to use primers containing hydrophobic phosphate monomer (MDP) (Kobayashi et al., 2009, Fushiki et al., 2015). A possible explanation of the zirconia composite delamination is that the bond was affected by the test environment under temperature controlled circulated water, even when using MDP contained primer. This was also concluded in a study by Komine et al. (2013) who tested the effect of thermocycling on zirconia composite veneered discs. This clearly gives the porcelain more advantage when it comes to bonding to zirconia in comparison to the indirect light cured composite. On the other hand, the porcelain showed a high percentage failure rate and is considered one of the main weak points in porcelain veneered zirconia crowns as mentioned before in the literature (Sailer et al., 2006, Manicone et al., 2007, Denry and Kelly, 2008, Hammond, 2009, Koutayas et al., 2009, Sailer et al., 2015). This was not the case when having metal substructure veneered with porcelain as they showed higher survival

rates than the zirconia based ones (Silva et al., 2010, Hosseini et al., 2012, Larsson et al., 2015).

The PEKK/LC groups showed the best results in this evaluation against the zirconia and metal based crowns. The PEKK and the light cured composite showed a very good bond unlike the other groups where the fracture code in both PEKK groups (5 and 7.5 Kg) were recoded as minor fractures code 1 and code 2. A study by Fuhrmann et al. (2014) tested the bonding of different polyaryletherketones based dental polymers to resin under different conditioning methods and different thermocycling times have revealed that PEKK showed the most durable bonding among other groups for all thermocycling times and with every conditioning method. Also when taking a closer look at the fractured samples, the code 1 PEKK/LC crowns show that the composite veneer went through different fractures layers before reaching and exposing the PEKK layer were the internal fractures from the indent can be seen on the PEKK surface. On the contrary, the zirconia and metal groups showed a fracture through the entire thickness of composite layer before causing veneer delamination.

8.7. Conclusions:

In the limitation of this work, the following conclusions could be drawn from the work done in this chapter:

- PEKK composite veneered molar crowns showed the highest fatigue limit pattern and value against other zirconia and metal composite molar crowns.
- For the Fatigue Life, PEKK composite veneered molar crowns showed comparable results under its fatigue limit load and superior results under 522 N against zirconia and metal composite veneered molar crowns.
- No significant difference could be found in the facture mode under different loads (PEKK/LC the highest at 682 N) between groups in the fatigue life evaluation.
- PEKK composite veneered molar crowns showed significantly minor fractures in comparison to zirconia and metal composite veneered groups under the same load fatigue life evaluation at 522 N.

Chapter 9

General Discussion

From the outcomes of this research, it can be clearly seen that PEKK has considerable potential as a substructure material for crowns and it could replace other well known materials such as alloys and zirconia. The findings could be of interest to the end users, patients, dental technicians and dentists who wishes to have a better understanding of such novel material against well-known substructure materials in the field.

To recapitulate, the following aspects were of interest to this research:

- Material handling and manufacturing process in the dental laboratory.
- Influence of the material on the aesthetics of the end product.
- The structural integrity of a restoration when processed and bonded to different materials as the final product.
- The durability of the restoration in comparison with other known restorations.

1) Material handling and manufacturing process in the dental laboratory:

The material was available in the form of polymer ingots for hot pressing using DEKEMA furnaces and later Cendres+Métaux pressing furnaces that have cooling features. Nevertheless, such furnaces are not always available in dental laboratories, where ceramic pressing furnaces are the most commonly used pressing devices. The cost of purchasing new equipment and providing any training required for new processing techniques may therefore limit the capacity of dental laboratories and clinics to try out new materials available in the market.

To address this issue, an attempt was made to optimise a protocol for pressing PEKK in a common ceramic pressing furnace and a pressing protocol was achieved.

The material is also available as disc blanks for CAD/CAM production, samples of which were made available for the current study after the pressing protocol was studied. These were used to conduct mechanical tests using the configured pressing protocol with the ceramic pressing furnace to see whether the pressing protocol had affected the properties of the material. No significant difference was found between the pressed and milled samples after testing the biaxial flexural strength and hardness. Furthermore, optical evaluation of both the pressed and milled PEKK samples showed no significant difference in any CIE L*a*b colour values.

Furthermore, after going through all the crowns manufacturing for this study, it could be concluded that the manufacturing process of PEKK involved fewer steps and less time to fabricate the full contoured composite veneered crowns in comparison to the manufacturing process of other zirconia and metal based crowns. Table 34 outlines different processing routes and materials involved and approx. time required for crowns manufacturing.

Table 34: Different processing routes of different substructure materials used in this study (highlighted in blue) and other possible routes (highlighted in green) with the approx. time required for crowns manufacturing

Substructure	Metal		Zirconia	PEKK	
Steps	CAD Laser Sinter Condition	CAD (30 min) Mill (wax) (30 min) Invest (90 min) Lost wax/cast (90 min) Divest (30 min) Condition (30 min)	CAD (30 min) Mill (60 min) Finish (15 min) Sinter (360 min) Condition (15 min)	CAD (30 min) Mill (30 min) Condition (30 min)	CAD (30 min) Mill (wax) (30 min) Invest (90 min) Lost wax/press (90 min) Divest (15 min) Condition (30 min)
Veneer	Composite	Composite (30 min)	Composite (30 min)	Composite (30 min)	Composite (30 min)
Total time	--	**5½ hours**	**8½ hours**	**2 hours**	**5¼ hours**

2) Influence of the material on the aesthetics of the end product:

A major factor in the evaluation of any dental prosthesis is its appearance and how well it blends into the oral cavity. The underlying substructure plays an important role in the final appearance of any prosthesis when covered with a veneering material such as feldspathic porcelain or composite. One question that has not been addressed with PEKK based restorations is how well they perform in aesthetics evaluations compared to other well known bilayered restoration materials such as zirconia and metal.

Based on this research, bonding different substructure materials to the same light cured composite did not show any significant difference in the colour

values. However, PEKK showed very little in the way of translucency, being closer to metal than zirconia, when tested against a white background. This point should be taken into account when considering PEKK/composite restorations for single anterior maxillary teeth in particular where no masking of underlying tooth or substructure is needed and a natural shade/translucency as adjacent teeth is required.

3) The structural integrity of a restoration when processed and bonded to different materials as the final product:

Structural integrity evaluation, as opposed to standard mechanical testing, takes into consideration the complex shape of the crown and how differently the materials will perform when bonded in different layers. One of the testing methods involves subjecting a crown (fully contoured as fabricated for patients) to occlusal forces through an antagonist indenter (ball shaped, rod or tooth shaped) until fracture and the data is captured by measuring the load at fracture in Newtons. This testing method was used not intending to replicate the forces inside the mouth, but instead to evaluate the complex design and shape of the crown.

Light cured composite crowns of different substructure materials: PEKK, zirconia and metal, were evaluated and each group was divided into two sub groups based on the central fossa and buccal cusp occlusal force positions.

The PEKK groups both showed comparable results to the metal groups and significantly better results than both zirconia groups. This finding could be

compared with results of different studies on zirconia and metal based crowns veneered with both composite and porcelain.

Assessing these results by comparing them with the known mechanical properties of the materials, where in purely mechanical tests such as biaxial flexural strength zirconia shows higher values than PEKK, highlights the value of conducting structural integrity tests of the manufactured, shaped and bonded restoration.

After mechanical testing of materials, structural integrity testing of restorations, a further consideration is longevity.

4) The durability of the restoration in comparison with other known restorations:

The ideal solution for this this is to gain data through in-vivo clinical studies. The difficulties in gaining data through such studies are:

- Time required: Case needs to be followed and reviewed for 5 years.
- Numbers of cases.
- Cost.
- Patient participation.
- Clinicians wanting to use a known reliable solution.
- Ethical considerations of providing a material, which may be compromised in comparison to the gold standard solution.

In order to provide further data and to inform the knowledge base for any novel material, attempts are made to replicate the mouth motion in-vitro by

fabricating mouth motion simulators or chewing machines. Ageing, and the build up of stresses from chewing forces are both important factors in determining how long a restoration will last inside the mouth. Ageing is affected by the moistness, acidity and temperature of the environment and can weaken the performance of material and cause failure. In this study, a custom-made fatigue chewing machine was used to determine two parameters: fatigue limit and fatigue life. The machine allows a reproducible load to be applied for a know number of cycles in a temperature controlled aqueous environment. The stresses caused by dynamic cyclic loading caused the restorations to weaken and eventually fail and not necessarily in accordance with their mechanical properties as reported from mechanical tests performed on the individual substructure material or the structural integrity tests.

The fatigue limit of the PEKK group was higher than for both the zirconia and metal groups. The majority of fractures occurred within the composite veneer as cohesive fractures, which was to be expected, as this is usually the case in bilayered dental restorations.

In terms of fatigue life, all the chosen loads in both sub-groups were considered in the higher range of any possible chewing loads in the molar area. The PEKK group showed the highest fatigue life when comparing all groups under the same load. This is considered advantageous as it clearly shows that the PEKK based crown system as a whole, in particular the bond between veneer and substructure, performs together as one structure and is

suitable for the kind of environment and loads to be expected inside the mouth.

Also worth noting is the significant difference that emerged in the fatigue life experiment in the mode of fracture of PEKK crowns, with only a minor dent occurring in the composite veneer. Hence, it offers a more serviceable crown inside the mouth in terms of eliminating the need to replace the whole crown. After all, changing the failed crown means further tooth preparation that can eventually cause the remaining tooth structure to break or even being extracted (Sharif et al., 2010).

When fabricating bilayered dental restorations, many factors play important roles in determining the success and longevity of the restoration. These may relate to the fabrication process, including the tooth preparation and substructure design, thickness of the veneer, cementing regime and surface finish (Aboushelib et al., 2008). Similarly, big mismatch in properties of the substructure and veneering could cause veneer delamination e.g. difference in the coefficient of thermal expansion CTE between substructure and ceramic veneer (Aboushelib et al., 2006, Saito et al., 2010, De Jager et al., 2005).

The findings in this research support the studies previously mentioned in that the performance of symmetrical samples in laboratory tests does not necessarily correspond with that of the material inside the oral cavity after being processed and shaped as a restoration (Jones et al., 1985, Kelly, 1995, Padipatvuthikul and Mair, 2008, Heintze, 2007, Bayne, 2007, Bayne, 2012). This

conclusion is supported with few examples from this study. According to Ferracane (2013), compressive strength and flexural strength are important properties in evaluating different materials, and when taking PEKK and zirconia as examples, the latter obviously outperforms PEKK with compressive strength (>2000 MPa) and flexural strength (>900 MPa) against PEKK's flexural strength (200 MPa) and compressive strength (>200 MPa). This was not the case when testing crowns made with substructures of these materials with PEKK significantly outperforming zirconia in the structural integrity and fatigue longevity tests. Furthermore, metal and PEKK crowns showed the latter outperforming metal based crowns in the fatigue testing.

For this study, the PEKK's 'crown system' involving different bonded layers of veneer, substructure, cement and the underlying abutment was clearly seen to have performed better as a whole structure in:

- Time required to fabricate the crown and ease of handling.
- Resisting occlusal and fatigue fracture and veneer delamination.

In addition to these positive findings, the appearance is not different than other zirconia and metal substructures when veneered with the same light cured composite.

Few explanations could be thought the causes of the PEKK based samples being a reliable crown system under different testing conditions in this study in comparison to the other zirconia and metal based samples:

1) Fracture toughness:

The fracture toughness plays an important in the success of a restoration subjected to high stress and this could explain the PEKK samples outperforming the zirconia ones. Such property could be considered a vital indicator of a restoration's ability to be intact and resist fracture inside the mouth, especially when assuming restorations could hold some imperfections (Ferracane, 2013). No figures of PEKK's fracture toughness could be found in the literature however, PEKK have been reported to show higher mechanical properties than PEEK, including fracture toughness (Mazur et al., 2014, Wang et al., 1993, Damestani et al., 2016). PEEK's fracture toughness could range, depending on the processing, from 2-8 $MPa.m^{1/2}$ (Kurtz, 2012).

2) Elastic modulus:

PEKK is less dense and more elastic resembling dentine more than other restorative materials such as metal and ceramics. Having a low elastic modulus permits PEKK a greater resilience and when combined with a veneer, cement and abutment of a close elasticity resulting in a uniform structure allowing stress to evenly distribute through different layers. This was not the case with the zirconia and metal based groups where the elasticity mismatch is great and hence zones of concentrated stresses could generate leading to crown's failure. The crown failure in the zirconia group in this study can be related to previous reports attributing it possibly to concentration of tensile stresses in the zirconia substructure from

compressive stresses generated within the veneer caused by the mismatch in the elastic modulus between the substructure and veneer hence could explain the cohesive fracture of the veneer and substructure (Guazzato et al., 2004, Rekow et al., 2007, Dundar et al., 2007, Aboushelib et al., 2008, Silva et al., 2010, Millen et al., 2012, Alsadon, 2012).

3) Bonding to substructure:

In this study, bonding between PEKK and the composite veneer and resin cement was achieved using a multifunctional methacrylate (MMA) based primers following the manufacturer's recommendation.

Fuhrmann et al. (2014) found that the best bond between resin cement and PEKK was achieved with MMA based primer, which agrees with results from other studies on the highest bond between composite and PEEK substructures when using MMA based primers (Stawarczyk et al., 2013b, Stawarczyk et al., 2015, Stawarczyk et al., 2014a, Keul et al., 2014, Rosentritt et al., 2015). The previous studies report bonding values in the same range as found with resin bonding to different substructures such as metal and zirconia (Sabatini et al., 2013, Taufall et al., 2016).

For the veneer bonding, Pekkton® ivory manufacturer's manual provides strength values for bonding between PEKK and composite veneer, with MMA based primer recording high values with different composite veneering materials, whilst the bonding value of VITA VM LC composite using visio.link primer (same as in this study) was the lowest amongst other composite materials using the same primer. Such information encourages evaluation of

bonding of other composite veneers to PEKK to assess their performance when shaped into crowns, rather than solely relying on results based on tests done on standard geometric samples.

Now after showing that using PEKK as a substructure material has demonstrated good results in the structural integrity and durability, a further investigation is how will such crowns fit inside the mouth. This could include evaluating the marginal and internal fit of PEKK crowns under different designs, thicknesses and fabrication methods i.e. hot pressed and milled, and after different conditions such as aging, thermocycling and cyclic loading. In relation to that, promising findings were found in two recently emerged studies by Bae et al. (2016) and Park et al. (2016) where they compared the marginal and internal fit of CAD/CAM milled PEKK crowns using two and three dimensional analysis methods. They have concluded that PEKK crowns showed better marginal and internal fit than the zirconia counterpart and PEKK crowns fitting were within clinically acceptable levels.

In this study, one type of light cured composite was used for all groups to eliminate any other variables other than the substructure materials. As the PEKK group in this research showed promising results, it is worth noting that the fracture toughness of the used composite veneer is around 0.97 MPa.$m^{1/2}$ (Nguyen et al., 2012), which is much lower than all the substructure materials used in this study and also lower than other composites available in the market. This finding agrees with studies mentioned before in the literature that mechanical properties such as fracture toughness do not correlate to composites' fatigue resistance and hence should not be used to speculate

their fatigue behaviour once in function inside the mouth (Belli et al., 2014, Lohbauer et al., 2003).

With the advances in composite resins, composites with higher fracture toughness should be evaluated when veneered on to PEKK substructures. The evaluation should take into consideration aging and cyclic fatigue as their negative effects on resin composites have been demonstrated, with indirect composites showing better results than their direct counterparts (Drummond et al., 2009, Hahnel et al., 2010). Furthermore, the degree of infiltration of resin fillers in the resin matrix plays an important role in determining the level of fatigue resistance of the restoration (Curtis et al., 2009). The size and volume of the filler also have an important effect on the mechanical properties of the composite but do so to an extent by reducing its plasticity and hence its inability to resist fractures with less plastic deformation (Thomaidis et al., 2013).

Other important evaluations could focus on, and are not limited to, the wear behaviour of the composite veneer as it is considered an important feature for both the restoration and the opposing natural teeth (Mehta et al., 2012). Such wear behaviour is affected by the mastication forces inside the mouth, the occlusal scheme, acidity, diet, parafunctional habits, antagonist material and with time it could cause restoration failure and in some cases wear to the opposing natural teeth (Elmaria et al., 2006). Using different veneering composites (e.g. flowable and condensable) with different properties and using different fabrication methods (e.g. conventional hand layered,

CAD/CAM milled and remanufactured veneers) for veneering PEKK substructures could be considered for future evaluations.

Chapter 10

General Conclusions

With the limitation of this research, the following general conclusions could be drawn:

1. It was possible to hot press Pekkton® ivory using a standard ceramic pressing furnace without any significant differences in on the produced samples in L*a*b* colour values, biaxial flexural strength and hardness values in comparison to samples produced via CAD/CAM milling.
2. Having PEKK as a substructure material did not cause any significant difference in in the L*a*b* and very low acceptable ΔE colour difference when veneered with the same composite veneer, against zirconia and metal substructures. However, zirconia substructure gave a little more translucency with composite veneer and even more with porcelain veneer in comparison with composite veneered PEKK and metal laminates.
3. The fracture resistance of PEKK composite veneered crowns showed significantly higher strength than zirconia based crowns, and comparable results to metal-based crowns with no significant difference.
4. The fatigue limit of PEKK composite veneered crowns was the highest pattern and value against other zirconia and metal composite molar crowns.
5. The fatigue Life of PEKK composite veneered crowns showed comparable results under its fatigue limit load and superior results under 522 N against zirconia and metal composite veneered molar crowns in their survival rate.

6. The fracture mode of PEKK composite veneered crowns in the fatigue life experiment was significantly different than the other zirconia and metal group and hence could be considered as more serviceable crowns.
7. The fabrication process of PEKK crowns via CAD/CAM milling involved fewer steps and was the easiest and fastest among the other zirconia and metal crowns fabricated for this study.

Chapter 11

Future work

Several ideas for future work related to this research can be summarised below:

- Evaluate the fracture toughness of PEKK and other substructure materials to see if any correlation to the outcomes of this study could be established.
- Investigate minimal crown preparation and compare with different preparations or restorations materials.
- Analyse the stress on the restoration using different substructure and veneering materials and/or different restoration designs and thickness using Finite Element Analysis (FEA) method.
- Repeat the mechanical testing done in this research with the variable being the composite veneer on the PEKK substructure. Different indirect composite veneers with different properties, e.g. filler and matrix could be closely evaluated.
- Bonding trials between different composite veneers and PEKK substructure and compare to other restorative systems e.g. zirconia/porcelain and PFM crowns.
- Bonding trials between PEKK substructures and resin cements.
- Evaluate fracture toughness of PEKK and other substructure materials e.g. PEEK, zirconia and metal under different conditions e.g. aging and cyclic loading.
- Solubility test PEKK under different liquids evaluating both its resistance to staining and acids.
- Cost effectiveness in comparison with other available restorative systems.

- A randomised controlled clinical trial (gold standard) following on from an initial pilot study.

Chapter 12

References

Abernethy, R. B. 2008. *The new Weibull handbook : reliability & statistical analysis for predicting life, safety, risk, support costs, failures, and forecasting warranty claims, substantiation and accelerated testing, using Weibull, Log normal, Crow-AMSAA, Probit, and Kaplan-Meier models,* North Palm Beach, Fla., R.B. Abernethy.

Aboushelib, M. N., De Jager, N., Kleverlaan, C. J. & Feilzer, A. J. 2007. Effect of loading method on the fracture mechanics of two layered all-ceramic restorative systems. *Dental Materials,* 23**,** 952-9.

Aboushelib, M. N. & Elsafi, M. H. 2016. Survival of resin infiltrated ceramics under influence of fatigue. *Dental Materials,* 32**,** 529-34.

Aboushelib, M. N., Feilzer, A. J., De Jager, N. & Kleverlaan, C. J. 2008. Prestresses in bilayered all-ceramic restorations. *Journal of Biomedical Materials Research. Part B, Applied Biomaterials,* 87**,** 139-45.

Aboushelib, M. N., Kleverlaan, C. J. & Feilzer, A. J. 2006. Microtensile bond strength of different components of core veneered all-ceramic restorations. Part II: Zirconia veneering ceramics. *Dental Materials,* 22**,** 857-63.

Al Wazzan, K. A. 2004. The visible portion of anterior teeth at rest. *The Journal of Contemporary Dental Practice,* 5**,** 53-62.

Al-Hazaimeh, N. & Gutteridge, D. L. 2001. An in vitro study into the effect of the ferrule preparation on the fracture resistance of crowned teeth incorporating prefabricated post and composite core restorations. *International Endodontic Journal,* 34**,** 40-6.

Al-Makramani, B. M., Razak, A. A. & Abu-Hassan, M. I. 2009. Comparison of the load at fracture of Turkom-Cera to Procera AllCeram and In-Ceram all-ceramic restorations. *Journal of Prosthodontics,* 18**,** 484-8.

Al-Wahadni, A. & Gutteridge, D. L. 2002. An in vitro investigation into the effects of retained coronal dentine on the strength of a tooth restored with a cemented post and partial core restoration. *International Endodontic Journal,* 35**,** 913-8.

Alghazali, N., Burnside, G., Moallem, M., Smith, P., Preston, A. & Jarad, F. D. 2012. Assessment of perceptibility and acceptability of color difference of denture teeth. *Journal of Dentistry,* 40 Suppl 1**,** e10-7.

Alsadon, O. 2012. *Investigating and Optimising Composite Veneered Zirconia Laminates.* MPhil Thesis, The University of Sheffield.

Alsadon, O., Patrick, D., Johnson, A., Pollington, S. & Wood, D. 2017. Fracture resistance of zirconia-composite veneered crowns in comparison with zirconia-porcelain crowns. *Dental Materials Journal*.

Alvim, H. H., Alecio, A. C., Vasconcellos, W. A., Furlan, M., De Oliveira, J. E. & Saad, J. R. 2007. Analysis of camphorquinone in composite resins as a function of shade. *Dental Materials,* 23**,** 1245-9.

Andersson, M. & Oden, A. 1993. A new all-ceramic crown. A dense-sintered, high-purity alumina coping with porcelain. *Acta Odontologica Scandinavica,* 51**,** 59-64.

Andreiotelli, M., Wenz, H. J. & Kohal, R. J. 2009. Are ceramic implants a viable alternative to titanium implants? A systematic literature review. *Clinical Oral Implants Research,* 20 Suppl 4**,** 32-47.

Anusavice, K. J. 2012. Standardizing failure, success, and survival decisions in clinical studies of ceramic and metal-ceramic fixed dental prostheses. *Dental Materials,* 28**,** 102-11.

Anusavice, K. J. & Phillips, R. W. 2003. *Phillips' science of dental materials,* St. Louis, Mo., Saunders.

Ardu, S., Gutemberg, D., Krejci, I., Feilzer, A. J., Di Bella, E. & Dietschi, D. 2011. Influence of water sorption on resin composite color and color variation amongst various composite brands with identical shade code: an in vitro evaluation. *Journal of Dentistry,* 39 Suppl 1**,** e37-44.

Att, W., Kurun, S., Gerds, T. & Strub, J. R. 2006. Fracture resistance of single-tooth implant-supported all-ceramic restorations: an in vitro study. *The Journal of Prosthetic Dentistry,* 95**,** 111-6.

Attia, A., Lehmann, F. & Kern, M. 2011. Influence of surface conditioning and cleaning methods on resin bonding to zirconia ceramic. *Dental Materials,* 27**,** 207-13.

Attwood, T. E., Dawson, P. C., Freeman, J. L., Hoy, L. R. J., Rose, J. B. & Staniland, P. A. 1981. Synthesis and Properties of Polyaryletherketones. *Polymer,* 22**,** 1096-1103.

Azzopardi, N., Moharamzadeh, K., Wood, D. J., Martin, N. & Van Noort, R. 2009. Effect of resin matrix composition on the translucency of experimental dental composite resins. *Dental Materials,* 25**,** 1564-8.

Bae, J.-M., Kim, K.-N., Hattori, M., Hasegawa, K., Yoshinari, M., Kawada, E. & Oda, Y. 2004. Fatigue strengths of particulate filler composites reinforced with fibers. *Dental Materials Journal,* 23**,** 166-74.

Bae, S. Y., Park, J. Y., Jeong, I. D., Kim, H. Y., Kim, J. H. & Kim, W. C. 2016. Three-dimensional analysis of marginal and internal fit of copings fabricated with polyetherketoneketone (PEKK) and zirconia. *Journal of Prosthodontic Research*.

Bagis, B. & Turgut, S. 2013. Optical properties of current ceramics systems for laminate veneers. *Journal of Dentistry,* 41**,** e24-e30.

Bagley, D. & Bell, M. 2002. Method for producing sealing and anti-extrusion components for use in downhole tools and components produced thereby. Google Patents.

Bakaeen, L. G., Winkler, S. & Neff, P. A. 2001. The effect of implant diameter, restoration design, and occlusal table variations on screw loosening of posterior single-tooth implant restorations. *The Journal of Oral Implantology,* 27**,** 63-72.

Bakke, M., Michler, L., Han, K. & Moller, E. 1989. Clinical significance of isometric bite force versus electrical activity in temporal and masseter muscles. *Scandinavian Journal of Dental Research,* 97**,** 539-51.

Baldassarri, M., Zhang, Y., Thompson, V., Rekow, E. D. & Stappert, C. F. J. 2011. Reliability and failure modes of implant-supported zirconium-oxide fixed dental prostheses related to veneering techniques. *Journal of Dentistry,* 39**,** 489-498.

Baldissara, P., Llukacej, A., Ciocca, L., Valandro, F. L. & Scotti, R. 2010. Translucency of zirconia copings made with different CAD/CAM systems. *The Journal of Prosthetic Dentistry,* 104**,** 6-12.

Baran, G., Boberick, K. & Mccool, J. 2001. Fatigue of restorative materials. *Critical Reviews in Oral Biology and Medicine,* 12**,** 350-60.

Barcellos, R. R., Correia, D. P. D., Farina, A. P., Mesquita, M. F., Ferraz, C. C. R. & Cecchin, D. 2013. Fracture resistance of endodontically treated teeth restored with intra-radicular post: the effects of post system and dentine thickness. *Journal of Biomechanics,* 46**,** 2572-7.

Barizon, K. T. L., Bergeron, C., Vargas, M. A., Qian, F., Cobb, D. S., Gratton, D. G. & Geraldeli, S. 2013. Ceramic Materials for Porcelain Veneers. Part I: Correlation between Translucency Parameters and Contrast Ratio. *Journal of Prosthetic Dentistry,* 110**,** 397-401.

Barzilay, I., Myers, M. L., Cooper, L. B. & Graser, G. N. 1988. Mechanical and Chemical Retention of Laboratory Cured Composite to Metal-Surfaces. *Journal of Prosthetic Dentistry,* 59**,** 131-137.

Bates, J. F., Stafford, G. D. & Harrison, A. 1976. Masticatory function - a review of the literature. III. Masticatory performance and efficiency. *Journal of Oral Rehabilitation,* 3**,** 57-67.

Bates, M. N. 2006. Mercury amalgam dental fillings: an epidemiologic assessment. *International Journal of Hygiene and Environmental Health,* 209**,** 309-16.

Bayne, S. C. 2007. Dental restorations for oral rehabilitation - testing of laboratory properties versus clinical performance for clinical decision making. *Journal of Oral Rehabilitation,* 34**,** 921-32.

Bayne, S. C. 2012. Correlation of clinical performance with 'in vitro tests' of restorative dental materials that use polymer-based matrices. *Dental materials,* 28**,** 52-71.

Bechir, E. S., Bechir, A., Gioga, C., Manu, R., Burcea, A. & Dascalu, I. T. 2016. The Advantages of BioHPP Polymer as Superstructure Material in Oral Implantology. *Materialele Plastice,* 53**,** 394-398.

Beham, G. 1991. IPS-Empress: a new ceramic technology. *ZWR,* 100**,** 404-8.

Belli, R., Frankenberger, R., Appelt, A., Schmitt, J., Baratieri, L. N., Greil, P. & Lohbauer, U. 2013. Thermal-induced residual stresses affect the lifetime of zirconia-veneer crowns. *Dental Materials,* 29**,** 181-90.

Belli, R., Petschelt, A. & Lohbauer, U. 2014. Are linear elastic material properties relevant predictors of the cyclic fatigue resistance of dental resin composites? *Dental Materials,* 30**,** 381-91.

Bello, A. & Jarvis, R. H. 1997. A review of esthetic alternatives for the restoration of anterior teeth. *The Journal of Prosthetic Dentistry,* 78**,** 437-40.

Bernardini, F., Tuniz, C., Coppa, A., Mancini, L., Dreossi, D., Eichert, D., Turco, G., Biasotto, M., Terrasi, F., De Cesare, N., Hua, Q. & Levchenko, V. 2012. Beeswax as dental filling on a neolithic human tooth. *PloS one,* 7**,** e44904.

Beuer, F., Aggstaller, H., Edelhoff, D. & Gernet, W. 2008. Effect of preparation design on the fracture resistance of zirconia crown copings. *Dental Materials Journal,* 27**,** 362-7.

Bindl, A. & Mormann, W. H. 2004. Survival rate of mono-ceramic and ceramic-core CAD/CAM-generated anterior crowns over 2-5 years. *European Journal of Oral Sciences,* 112**,** 197-204.

Blair, F. M., Wassell, R. W. & Steele, J. G. 2002. Crowns and other extra-coronal restorations: preparations for full veneer crowns. *British Dental Journal,* 192**,** 561-4, 567-71.

Blatz, M. B., Sadan, A. & Kern, M. 2003. Resin-ceramic bonding: a review of the literature. *The Journal of Prosthetic Dentistry,* 89**,** 268-74.

Boff, L. L., Oderich, E., Cardoso, A. C. & Magne, P. 2014. Fatigue resistance and failure mode of adhesively restored custom metal-composite resin premolar implant abutments. *The International Journal of Oral & Maxillofacial Implants,* 29**,** 364-73.

Bonfante, E. A. & Coelho, P. G. 2016. A Critical Perspective on Mechanical Testing of Implants and Prostheses. *Advances in Dental Research,* 28**,** 18-27.

Bonfante, E. A., Coelho, P. G., Guess, P. C., Thompson, V. P. & Silva, N. R. F. A. 2010. Fatigue and damage accumulation of veneer porcelain pressed on Y-TZP. *Journal of Dentistry,* 38**,** 318-24.

Bonner, W. H. 1962. Aromatic polyketones and preparation. USA Patents.

Bowen, R. L. 1962. *Dental filling material comprising vinyl-silane treated fused silica and a binder consisting of the reaction product of bisphenol and glycidyl methacrylate*. USA patent application 3 066 112.

Bremner, M. 1959. False teeth for the millions. *The story of dentistry Brooklyn: Dental Items of Interest*.

Brosh, T., Porat, N., Vardimon, A. D. & Pilo, R. 2011. Appropriateness of viscoelastic soft materials as in vitro simulators of the periodontal ligament. *Journal of Oral Rehabilitation,* 38**,** 929-39.

Buchalla, W., Attin, T., Hilgers, R. D. & Hellwig, E. 2002. The effect of water storage and light exposure on the color and translucency of a hybrid and a microfilled composite. *Journal of Prosthetic Dentistry,* 87**,** 264-270.

Buonocore, M. G. 1955. A simple method of increasing the adhesion of acrylic filling materials to enamel surfaces. *J Dent Res,* 34**,** 849-53.

Burke, F. J. 1999. Maximising the fracture resistance of dentine-bonded all-ceramic crowns. *Journal of Dentistry,* 27**,** 169-73.

Burke, F. J. 2007. Four year performance of dentine-bonded all-ceramic crowns. *British Dental Journal,* 202**,** 269-73.

Burke, F. J. & Watts, D. C. 1994. Fracture resistance of teeth restored with dentin-bonded crowns. *Quintessence international (Berlin, Germany : 1985),* 25**,** 335-40.

Butz, F., Heydecke, G., Okutan, M. & Strub, J. R. 2005. Survival rate, fracture strength and failure mode of ceramic implant abutments after chewing simulation. *Journal of Oral Rehabilitation,* 32**,** 838-843.

Calamia, J. R. & Simonsen, R. J. 1984. Effect of Coupling Agents on Bond Strength of Etched Porcelain. *Journal of Dental Research,* 63**,** 179-179.

Casson, A. M., Glyn Jones, J. C., Youngson, C. C. & Wood, D. J. 2001. The effect of luting media on the fracture resistance of a flame sprayed all-ceramic crown. *Journal of Dentistry,* 29**,** 539-44.

Celik, E. U., Aladag, A., Turkun, L. S. & Yilmaz, G. 2011. Color changes of dental resin composites before and after polymerization and storage in water. *Journal of Esthetic and Restorative Dentistry,* 23**,** 179-88.

Cellik, G., Uludag, B., Usumez, A., Sahin, V., Ozturk, O. & Goktug, G. 2008. The effect of repeated firings on the color of an all-ceramic system with two different veneering porcelain shades. *Journal of Prosthetic Dentistry,* 99**,** 203-208.

Chevalier, J. 2006. What future for zirconia as a biomaterial? *Biomaterials,* 27**,** 535-43.

Choi, M. S., Lee, Y. K., Lim, B. S., Rhee, S. H. & Yang, H. C. 2005. Changes in surface characteristics of dental resin composites after polishing. *Journal of Materials Science-Materials in Medicine,* 16**,** 347-53.

Coelho, P. G., Bonfante, E. A., Silva, N. R., Rekow, E. D. & Thompson, V. P. 2009a. Laboratory simulation of Y-TZP all-ceramic crown clinical failures. *Journal of Dental Research,* 88**,** 382-6.

Coelho, P. G., Silva, N. R., Bonfante, E. A., Guess, P. C., Rekow, E. D. & Thompson, V. P. 2009b. Fatigue testing of two porcelain-zirconia all-ceramic crown systems. *Dental Materials,* 25**,** 1122-7.

Conrad, H. J., Seong, W. J. & Pesun, G. J. 2007. Current ceramic materials and systems with clinical recommendations: A systematic review. *Journal of Prosthetic Dentistry,* 98**,** 389-404.

Conserva, E., Menini, M., Tealdo, T., Bevilacqua, M., Ravera, G., Pera, F. & Pera, P. 2009. The use of a masticatory robot to analyze the shock absorption capacity of different restorative materials for prosthetic implants: a preliminary report. *The International Journal of Prosthodontics,* 22**,** 53-5.

Cook, S. D. & Rust-Dawicki, A. M. 1995. Preliminary evaluation of titanium-coated PEEK dental implants. *Journal of Oral Implantology,* 21**,** 176-81.

Coornaert, J., Adriaens, P. & De Boever, J. 1984. Long-term clinical study of porcelain-fused-to-gold restorations. *Journal of Prosthetic Dentistry,* 51**,** 338-42.

Copponnex, T. 2011. New material approaches in dental technology. *meditec.*

Copponnex, T. & Decarmine, A. 2009. Reevaluating thermoplastics. How good is PEEK, really, for aesthetic and long-term structural applications. *European Medical Device Technology.*

Coray, R., Zeltner, M. & Ozcan, M. 2016. Fracture strength of implant abutments after fatigue testing: A systematic review and a meta-analysis. *Journal of the Mechanical Behavior of Biomedical Materials,* 62**,** 333-46.

Corvelli, A., Biermann, P. & Roberts, J. 1997. Design, analysis, and fabrication of a composite segmental bone replacement implant. *Journal of Advanced Materials,* 28**,** 2-8.

Costa-Palau, S., Torrents-Nicolas, J., Brufau-De Barbera, M. & Cabratosa-Termes, J. 2014. Use of Polyetheretherketone in the Fabrication of a Maxillary Obturator Prosthesis: A Clinical Report. *Journal of Prosthetic Dentistry,* 112**,** 680-682.

Craig, R. G. & Powers, J. M. 2002. *Restorative dental materials,* St. Louis, Mo. ; London, Mosby.

Culp, L. 1999. Empress 2. First year clinical results. *J Dent Technol,* 16**,** 12-5.

Curtis, A. R., Palin, W. M., Fleming, G. J., Shortall, A. C. & Marquis, P. M. 2009. The mechanical properties of nanofilled resin-based composites: the impact of dry and wet cyclic pre-loading on bi-axial flexure strength. *Dental Materials,* 25**,** 188-97.

Da Col Dos Santos Pinto, G., Dias, K. C., Cruvinel, D. R., Da Fonseca Roberti Garcia, L. & Consani, S. 2013. Influence of finishing/polishing on color stability and surface roughness of composites submitted to accelerated artificial aginga. *Indian Journal of Dental Research,* 24.

Damestani, Y., Galan-Hoffman, D. E., Ortiz, D., Cabrales, P. & Aguilar, G. 2016. Inflammatory response to implantation of transparent nanocrystalline yttria-stabilized zirconia using a dorsal window chamber model. *Nanomedicine,* 12**,** 1757-1763.

De Jager, N., Pallav, P. & Feilzer, A. J. 2005. The influence of design parameters on the FEA-determined stress distribution in CAD-CAM produced all-ceramic dental crowns. *Dental Materials,* 21**,** 242-251.

Deligeorgi, V., Mjor, I. A. & Wilson, N. H. 2001. An overview of reasons for the placement and replacement of restorations. *Primary Dental Care,* 8**,** 5-11.

Della Bona, A. & Kelly, J. R. 2008. The clinical success of all-ceramic restorations. *Journal of the American Dental Association,* 139 Suppl**,** 8S-13S.

Della Bona, A., Pecho, O. E. & Alessandretti, R. 2015. Zirconia as a Dental Biomaterial. *Materials,* 8**,** 4978-4991.

Delong, R. & Douglas, W. H. 1983. Development of an Artificial Oral Environment for the Testing of Dental Restoratives - Bi-Axial Force and Movement Control. *Journal of Dental Research,* 62**,** 32-36.

Delong, R. & Douglas, W. H. 1991. An artificial oral environment for testing dental materials. *IEEE Transactions on Biomedical Engineering,* 38**,** 339-45.

Denry, I. & Kelly, J. R. 2008. State of the art of zirconia for dental applications. *Dental Materials,* 24**,** 299-307.

Denry, I. L. 1996. Recent advances in ceramics for dentistry. *Critical Reviews in Oral Biology and Medicine,* 7**,** 134-43.

Derand, T., Molin, M. & Kvam, K. 2005. Bond strength of composite luting cement to zirconia ceramic surfaces. *Dental Materials,* 21**,** 1158-62.

Diamantopoulou, S., Papazoglou, E., Margaritis, V., Lynch, C. D. & Kakaboura, A. 2013. Change of optical properties of contemporary resin composites after one week and one month water ageing. *Journal of Dentistry,* 41**,** e62-e69.

Diaz-Arnold, A. M., Schneider, R. L. & Aquilino, S. A. 1989. Bond strengths of intraoral porcelain repair materials. *Journal of Prosthetic Dentistry,* 61**,** 305-9.

Dieter, G. E. 1961. *Mechanical metallurgy,* New York ; London, McGraw-Hill Book Co.

Dittmer, M. P., Kohorst, P., Borchers, L. & Stiesch, M. 2010. Influence of the supporting structure on stress distribution in all-ceramic FPDs. *The International Journal of Prosthodontics,* 23**,** 63-8.

Dong, J. K., Luthy, H., Wohlwend, A. & Scharer, P. 1992. Heat-pressed ceramics: technology and strength. *International Journal of Prosthodontics,* 5**,** 9-16.

Donovan, T. E. 2009. Porcelain-fused-to-metal (PFM) alternatives. *Journal of Esthetic and Restorative Dentistry,* 21**,** 4-6.

Douglas, R. D., Steinhauer, T. J. & Wee, A. G. 2007. Intraoral determination of the tolerance of dentists for perceptibility and acceptability of shade mismatch. *The Journal of Prosthetic Dentistry,* 97**,** 200-8.

Drummond, J. L., Lin, L., Al-Turki, L. A. & Hurley, R. K. 2009. Fatigue behaviour of dental composite materials. *Journal of Dentistry,* 37**,** 321-30.

Dundar, M., Ozcan, M., Gokce, B., Comlekoglu, E., Leite, F. & Valandro, L. F. 2007. Comparison of two bond strength testing methodologies for bilayered all-ceramics. *Dental Materials,* 23**,** 630-6.

Dunne, S. M., Gainsford, I. D. & Wilson, N. H. 1997. Current materials and techniques for direct restorations in posterior teeth. Part 1: Silver amalgam. *International Dental Journal,* 47**,** 123-36.

Duret, F. & Preston, J. D. 1991. CAD/CAM imaging in dentistry. *Current Opinion in Dentistry,* 1**,** 150-4.

Eid, D. E.-S. 1971. A new material for partial dentures. An unbreakable thermoplastic resin paraformaldehyde and its Co-polymers. *Egyptian Dental Journal,* 17**,** 1-22.

Elmaria, A., Goldstein, G., Vijayaraghavan, T., Legeros, R. Z. & Hittelman, E. L. 2006. An evaluation of wear when enamel is opposed by various ceramic materials and gold. *The Journal of Prosthetic Dentistry,* 96**,** 345-53.

Evans, D. B. 1996. A castable glass-ceramic pontic for the partial veneer fixed partial denture. *The International Journal of Prosthodontics,* 9**,** 248-53.

Ferracane, J. L. 1995. Current trends in dental composites. *Critical Reviews in Oral Biology and Medicine,* 6**,** 302-18.

Ferracane, J. L. 2011. Resin composite--state of the art. *Dental Materials,* 27**,** 29-38.

Ferracane, J. L. 2013. Resin-based composite performance: Are there some things we can't predict? *Dental Materials,* 29**,** 51-58.

Ferrario, V. F., Sforza, C., Serrao, G., Dellavia, C. & Tartaglia, G. M. 2004. Single tooth bite forces in healthy young adults. *Journal of Oral Rehabilitation,* 31**,** 18-22.

Fradeani, M., Aquilano, A. & Corrado, M. 2002. Clinical experience with In-Ceram Spinell crowns: 5-year follow-up. *International Journal of Periodontics & Restorative Dentistry,* 22**,** 525-33.

Fradeani, M. & Redemagni, M. 2002. An 11-year clinical evaluation of leucite-reinforced glass-ceramic crowns: a retrospective study. *Quintessence international (Berlin, Germany : 1985),* 33**,** 503-10.

Freese, A. S. 1959. Porcelain fused to iridio-platinum crowns. *The Journal of Prosthetic Dentistry,* 9**,** 847-850.

Fuhrmann, G., Steiner, M., Freitag-Wolf, S. & Kern, M. 2014. Resin bonding to three types of polyaryletherketones (PAEKs)-durability and influence of surface conditioning. *Dental Materials,* 30**,** 357-63.

Fusayama, T., Hirano, T. & Kono, A. 1971. Discoloration test of acrylic resin fillings by an organic dye. *The Journal of Prosthetic Dentistry,* 25**,** 532-9.

Fushiki, R., Komine, F., Honda, J., Kamio, S., Blatz, M. B. & Matsumura, H. 2015. Long-term Bond Strength between Layering Indirect Composite Material and Zirconia Coated with Silicabased Ceramics. *The Journal of Adhesive Dentistry,* 17**,** 273-81.

Gardner, K. H., Hisao, B. S. & Faron, K. L. 1994. Polymorphism in Poly(Aryl Ether Ketone)S. *Polymer,* 35**,** 2290-2295.

Garoushi, S., Lassila, L. V., Tezvergil, A. & Vallittu, P. K. 2007. Static and fatigue compression test for particulate filler composite resin with fiber-reinforced composite substructure. *Dental Materials,* 23**,** 17-23.

Geller, W. & Kwiatkowski, S. J. 1987. The Willi's glas crown: a new solution in the dark and shadowed zones of esthetic porcelain restorations. *Quintessence Dental Technology,* 11**,** 233-42.

Ghevalier, J., Drouin, J. M. & Cales, B. 1997. Low temperature ageing behavior of zirconia hip joint heads. *Bioceramics, Vol 10***,** 135-138.

Glenn, J. 1982. Composition and properties of unfilled and composite resin restorative materials. *Biocompatibility of Dental Materials,* 3**,** 98-130.

Goldstein, G. R. 1985. Light-activated composite resin as an adjunct to the fabrication of fixed partial denture prosthesis. *The Journal of Prosthetic Dentistry,* 53**,** 161-3.

Gordon, M., Laufer, B. Z. & Metzger, Z. 1985. Composite-veneered amalgam restorations. *The Journal of Prosthetic Dentistry,* 54**,** 759-62.

Gorgas, F. 1891. Vulcano-plastic work. *Harris' principles and practice of dentistry. 12th ed. Philadelphia: Blakiston P, Son and Co*.

Gouveia, T. H., Público, J. C., Ambrosano, G., Paulillo, L. A., Aguiar, F. H. & Lima, D. A. 2016. Evaluation of physical properties of a nanocomposite after aging, bleaching and staining. *Journal of Applied Biomaterials & Functional Materials,* 14.

Green, S. & Schlegel, J. A polyaryletherketone biomaterial for use in medical implant applications. Conference Proceedings, Polymers for the Medical Industry, 14th-15th May, 2001.

Grieznis, L., Apse, P. & Soboleva, U. 2006. The effect of 2 different diameter cast posts on tooth root fracture resistance in vitro. *Stomatologija,* 8**,** 30-2.

Guazzato, M., Proos, K., Quach, L. & Swain, M. V. 2004. Strength, reliability and mode of fracture of bilayered porcelain/zirconia (Y-TZP) dental ceramics. *Biomaterials,* 25**,** 5045-52.

Guazzato, M., Quach, L., Albakry, M. & Swain, M. V. 2005. Influence of surface and heat treatments on the flexural strength of Y-TZP dental ceramic. *Journal of Dentistry,* 33**,** 9-18.

Guess, P. C., Zavanelli, R. A., Silva, N. R. F. A., Bonfante, E. A., Coelho, P. G. & Thompson, V. P. 2010. Monolithic CAD/CAM lithium disilicate versus veneered Y-TZP crowns: comparison of failure modes and reliability after fatigue. *The International Journal of Prosthodontics,* 23**,** 434-42.

Gueth, J.-F., Zuch, T., Zwinge, S., Engels, J., Stimmelmayr, M. & Edelhoff, D. 2013. Optical properties of manually and CAD/CAM-fabricated polymers. *Dental Materials Journal,* 32**,** 865-871.

Guo, J., Tian, B., Wei, R., Wang, W., Zhang, H., Wu, X., He, L. & Zhang, S. 2014. Investigation of the time-dependent wear behavior of veneering ceramic in porcelain fused to metal crowns during chewing simulations. *Journal of the Mechanical Behavior of Biomedical Materials,* 40**,** 23-32.

Hahnel, S., Henrich, A., Burgers, R., Handel, G. & Rosentritt, M. 2010. Investigation of mechanical properties of modern dental composites after artificial aging for one year. *Operative Dentistry,* 35**,** 412-9.

Hammond, B. D. 2009. Critical appraisal. Intraoral repair of fractured ceramic restorations. *J Esthet Restor Dent,* 21**,** 275-84.

Han, K.-H., Lee, J.-Y., Shin, S. W., Han, K.-H., Lee, J.-Y. & Shin, S. W. 2016. Implant-and Tooth-Supported Fixed Prostheses Using a High-Performance Polymer (Pekkton) Framework. *International Journal of Prosthodontics,* 29.

Harada, R., Takemoto, S., Hattori, M., Yoshinari, M., Oda, Y. & Kawada, E. 2015. The influence of colored zirconia on the optical properties of all-ceramic restorations. *Dental Materials Journal,* 34**,** 918-924.

Hayashi, M., Takahashi, Y., Imazato, S. & Ebisu, S. 2006. Fracture resistance of pulpless teeth restored with post-cores and crowns. *Dental Materials,* 22**,** 477-85.

Heffernan, M. J., Aquilino, S. A., Diaz-Arnold, A. M., Haselton, D. R., Stanford, C. M. & Vargas, M. A. 2002. Relative translucency of six all-ceramic systems. Part I: core materials. *The Journal of Prosthetic Dentistry,* 88**,** 4-9.

Heimer, S., Schmidlin, P. R. & Stawarczyk, B. 2016. Discoloration of PMMA, composite, and PEEK. *Clinical Oral Investigations***,** 1-10.

Heintze, S., Eser, A., Monreal, D. & Rousson, V. 2017. Using a chewing simulator for fatigue testing of metal ceramic crowns. *Journal of the Mechanical Behavior of Biomedical Materials,* 65**,** 770-780.

Heintze, S. D. 2007. Systematic reviews: I. The correlation between laboratory tests on marginal quality and bond strength. II. The correlation between marginal quality and clinical outcome. *The Journal of Adhesive Dentistry,* 9 Suppl 1**,** 77-106.

Heintze, S. D. & Rousson, V. 2010. Survival of zirconia-and metal-supported fixed dental prostheses: a systematic review. *International Journal of Prosthodontics,* 23.

Heintze, S. D., Zellweger, G. & Zappini, G. 2007. The relationship between physical parameters and wear of dental composites. *Wear,* 263**,** 1138-1146.

Helmer, J. D. & Driskell, T. D. 1969. Research on bioceramics. *Symposium on Use of Ceramics as Surgical Implants.* South Carolina, USA: Clemson University.

Hengchang, X., Vingerling, P. A., Wenyi, L., Gang, Z. & Tong, W. 1990. Wear of composite resin in vitro: a testing machine with rubber plate. Preliminary results. *Journal of Oral Rehabilitation,* 17**,** 107-15.

Heuer, A., Lange, F., Swain, M. & Evans, A. 1986. Transformation toughening: an overview. *Journal of the American Ceramic Society,* 69**,** i-iv.

Holand, W., Schweiger, M., Frank, M. & Rheinberger, V. 2000. A comparison of the microstructure and properties of the IPS Empress (R) 2 and the IFS Empress (R) glass-ceramics. *Journal of Biomedical Materials Research,* 53**,** 297-303.

Honda, J., Komine, F., Kamio, S., Taguchi, K., Blatz, M. B. & Matsumura, H. 2016. Fracture resistance of implant–supported screw–retained zirconia–based molar restorations. *Clinical Oral Implants Research*.

Hooshmand, T., Van Noort, R. & Keshvad, A. 2002. Bond durability of the resin-bonded and silane treated ceramic surface. *Dental Materials,* 18**,** 179-88.

Horn, H. R. 1983. Porcelain Laminate Veneers Bonded to Etched Enamel. *Dental Clinics of North America,* 27**,** 671-684.

Hosoya, Y., Shiraishi, T., Odatsu, T., Ogata, T., Miyazaki, M. & Powers, J. M. 2010. Effects of specular component and polishing on color of resin composites. *Journal of Oral Science,* 52**,** 599-607.

Hosoya, Y., Shiraishi, T., Oshiro, M., Ando, S., Miyazaki, M. & Powers, J. M. 2009. Effects of specular component on color differences of different filler type resin composites after aging. *Journal of Dentistry,* 37**,** 585-90.

Hosseini, M., Kleven, E. & Gotfredsen, K. 2012. Fracture mode during cyclic loading of implant-supported single-tooth restorations. *Journal of Prosthetic Dentistry,* 108**,** 74-83.

Isgro, G., Addison, O. & Fleming, G. J. 2011. Transient and residual stresses induced during the sintering of two dentin ceramics. *Dental Materials,* 27**,** 379-85.

Jalalian, E., Atashkar, B. & Rostami, R. 2011. The effect of preparation design on the fracture resistance of zirconia crown copings (computer associated design/computer associated machine, CAD/CAM system). *Journal of Dentistry,* 8**,** 123-9.

Janda, R., Roulet, J.-F., Kaminsky, M., Steffin, G. & Latta, M. 2004. Color stability of resin matrix restorative materials as a function of the method of light activation. *European Journal of Oral Sciences,* 112**,** 280-5.

Johnston, W. M. & Kao, E. C. 1989. Assessment of appearance match by visual observation and clinical colorimetry. *Journal of Dental Research,* 68**,** 819-22.

Johnston, W. M., Ma, T. & Kienle, B. H. 1995. Translucency parameter of colorants for maxillofacial prostheses. *The International Journal of Prosthodontics,* 8**,** 79-86.
Joiner, A. 2004. Tooth colour: a review of the literature. *Journal of Dentistry,* 32 Suppl 1**,** 3-12.
Jones, D. P., Leach, D. C. & Moore, D. R. 1985. Mechanical-Properties of Poly(Ether-Ether-Ketone) for Engineering Applications. *Polymer,* 26**,** 1385-1393.
Jordan, R. E. 1993. *Esthetic composite bonding : techniques and materials,* St Louis ; London, Mosby.
Kamio, S., Komine, F., Taguchi, K., Iwasaki, T., Blatz, M. B. & Matsumura, H. 2015. Effects of framework design and layering material on fracture strength of implant-supported zirconia-based molar crowns. *Clinical Oral Implants Research,* 26**,** 1407-13.
Kassem, A. S., Atta, O. & El-Mowafy, O. 2012. Fatigue resistance and microleakage of CAD/CAM ceramic and composite molar crowns. *Journal of Prosthodontics,* 21**,** 28-32.
Keilig, L., Katzenbach, A., Weber, A., Stark, H. and Bourauel, C., 2014. Fatigue testing of crowns made from a high performance polymer. *Clinical Oral Implants Research*, *25*, p.322.
Kelly, J. R. 1995. Perspectives on strength. *Dental Materials,* 11**,** 103-10.
Kelly, J. R. 1999. Clinically relevant approach to failure testing of all-ceramic restorations. *Journal of Prosthetic Dentistry,* 81**,** 652-61.
Kelly, J. R. 2004. Dental ceramics: current thinking and trends. *Dental Clinics of North America,* 48**,** viii.
Kelly, J. R. & Benetti, P. 2011. Ceramic materials in dentistry: historical evolution and current practice. *Australian Dental Journal,* 56 Suppl 1**,** 84-96.
Kelly, J. R., Benetti, P., Rungruanganunt, P. & Bona, A. D. 2012. The slippery slope: critical perspectives on in vitro research methodologies. *Dental Materials,* 28**,** 41-51.
Kelly, J. R. & Denry, I. 2008. Stabilized zirconia as a structural ceramic: An overview. *Dental Materials,* 24**,** 289-298.
Kelly, J. R., Nishimura, I. & Campbell, S. D. 1996. Ceramics in dentistry: Historical roots and current perspectives. *Journal of Prosthetic Dentistry,* 75**,** 18-32.
Kemmish, D. 2010. *Update on the technology and applications of polyaryletherketones,* Shrewsbury, iSmithers.
Kern, M., Barloi, A. & Yang, B. 2009. Surface conditioning influences zirconia ceramic bonding. *Journal of Dental Research,* 88**,** 817-22.
Kern, M., Douglas, W. H., Fechtig, T., Strub, J. R. & Delong, R. 1993. Fracture strength of all-porcelain, resin-bonded bridges after testing in an artificial oral environment. *Journal of Dentistry,* 21**,** 117-21.
Kern, M. & Lehmann, F. 2012. Influence of surface conditioning on bonding to polyetheretherketon (PEEK). *Dental Materials,* 28**,** 1280-3.
Keul, C., Liebermann, A., Schmidlin, P. R., Roos, M., Sener, B. & Stawarczyk, B. 2014. Influence of PEEK surface modification on surface properties and

bond strength to veneering resin composites. *The Journal of Adhesive Dentistry,* 16**,** 383-92.
Khashayar, G., Dozic, A., Kleverlaan, C. J., Feilzer, A. J. & Roeters, J. 2014. The influence of varying layer thicknesses on the color predictability of two different composite layering concepts. *Dental Materials,* 30**,** 493-8.
Kheradmandan, S., Koutayas, S. O., Bernhard, M. & Strub, J. R. 2001. Fracture strength of four different types of anterior 3-unit bridges after thermo-mechanical fatigue in the dual-axis chewing simulator. *Journal of Oral Rehabilitation,* 28**,** 361-369.
Kilicarslan, M. A., Kedici, P. S., Kucukesmen, H. C. & Uludag, B. C. 2004. In vitro fracture resistance of posterior metal-ceramic and all-ceramic inlay-retained resin-bonded fixed partial dentures. *The Journal of Prosthetic Dentistry,* 92**,** 365-70.
Kim, B.-J. & Lee, Y.-K. 2009. Influence of the shade designation on the color difference between the same shade-designated resin composites by the brand. *Dental Materials,* 25**,** 1148-54.
Kim, H. K. & Kim, S. H. 2014. Effect of the number of coloring liquid applications on the optical properties of monolithic zirconia. *Dental Materials,* 30**,** e229-37.
Kim, I.-J. & Lee, Y.-K. 2007. Changes in color and color parameters of dental resin composites after polymerization. *Journal of Biomedical Materials Research Part B, Applied Biomaterials,* 80**,** 541-6.
Kim, J. H., Kim, J. W., Myoung, S. W., Pines, M. & Zhang, Y. 2008. Damage maps for layered ceramics under simulated mastication. *Journal of Dental Research,* 87**,** 671-5.
Knosp, H., Holliday, R. J. & Corti, C. W. 2003. Gold in dentistry: Alloys, uses and performance. *Gold Bulletin,* 36**,** 93-101.
Kobayashi, K., Komine, F., Blatz, M. B., Saito, A., Koizumi, H. & Matsumura, H. 2009. Influence of priming agents on the short-term bond strength of an indirect composite veneering material to zirconium dioxide ceramic. *Quintessence international,* 40**,** 545-51.
Kohal, R. J., Klaus, G. & Strub, J. R. 2006. Zirconia-implant-supported all-ceramic crowns withstand long-term load: a pilot investigation. *Clinical Oral Implants Research,* 17**,** 565-71.
Kohorst, P., Herzog, T. J., Borchers, L. & Stiesch-Scholz, M. 2007. Load-bearing capacity of all-ceramic posterior four-unit fixed partial dentures with different zirconia frameworks. *European Journal of Oral Sciences,* 115**,** 161-6.
Koishi, Y., Tanoue, N., Matsumura, H. & Atsuta, M. 2001. Colour reproducibility of a photo-activated prosthetic composite with different thickness. *Journal of Oral Rehabilitation,* 28**,** 799-804.
Kokubo, Y., Tsumita, M., Sakurai, S., Suzuki, Y., Tokiniwa, Y. & Fukushima, S. 2011. Five-year clinical evaluation of In-Ceram crowns fabricated using GN-I (CAD/CAM) system. *Journal of Oral Rehabilitation,* 38**,** 601-7.
Komine, F., Koizuka, M., Fushiki, R., Taguchi, K., Kamio, S. & Matsumura, H. 2013. Post-thermocycling shear bond strength of a gingiva-colored

indirect composite layering material to three implant framework materials. *Acta Odontologica Scandinavica,* 71**,** 1092-100.
Komine, F., Taguchi, K., Fushiki, R., Kamio, S., Iwasaki, T. & Matsumura, H. 2014. In vitro comparison of fracture load of implant-supported, zirconia-based, porcelain- and composite-layered restorations after artificial aging. *Dental Materials Journal,* 33**,** 607-613.
Körber, K. & Ludwig, K. 1983. The maximum bite force as a critical factor for fixed partial dentures. *Dental-Labor* 31**,** 60.
Kosmac, T., Oblak, C., Jevnikar, P., Funduk, N. & Marion, L. 2000. Strength and reliability of surface treated Y-TZP dental ceramics. *Journal of Biomedical Materials Research,* 53**,** 304-13.
Koutayas, S. O., Vagkopoulou, T., Pelekanos, S., Koidis, P. & Strub, J. R. 2009. Zirconia in dentistry: part 2. Evidence-based clinical breakthrough. *European Journal of Esthetic Dentistry,* 4**,** 348-80.
Koyama, T., Sato, T. & Yoshinari, M. 2012. Cyclic fatigue resistance of yttria-stabilized tetragonal zirconia polycrystals with hot isostatic press processing. *Dental Materials Journal,* 31**,** 1103-10.
Kursoglu, P., Karagoz Motro, P. F. & Kazazoglu, E. 2015. Translucency of ceramic material in different core-veneer combinations. *Journal of Prosthetic Dentistry,* 113**,** 48-53.
Kurtz, S. M. 2012. *PEEK biomaterials handbook,* Oxford UK ; Waltham, MA, William Andrew.
Kurtz, S. M. & Devine, J. N. 2007. PEEK biomaterials in trauma, orthopedic, and spinal implants. *Biomaterials,* 28**,** 4845-69.
Land, C. 1903. Porcelain dental arts. *Dental Cosmos,* 45**,** 615-620.
Larsson, C., Drazic, M., Nilsson, E. & Vult Von Steyern, P. 2015. Fracture of porcelain-veneered gold-alloy and zirconia molar crowns using a modified test set-up. *Acta Biomaterialia Odontologica Scandinavica,* 1**,** 35-42.
Larsson, C., El Madhoun, S., Wennerberg, A. & Vult Von Steyern, P. 2012. Fracture strength of yttria-stabilized tetragonal zirconia polycrystals crowns with different design: an in vitro study. *Clinical Oral Implants Research,* 23**,** 820-6.
Lee, M. H., Min, B. K., Son, J. S. & Kwon, T. Y. 2016. Influence of Different Post-Plasma Treatment Storage Conditions on the Shear Bond Strength of Veneering Porcelain to Zirconia. *Materials,* 9.
Lee, W. E. & Rainforth, W. M. 1994. *Ceramic microstructures : property control by processing,* London, Chapman & Hall.
Lee, Y.-K., Cha, H.-S. & Ahn, J.-S. 2007. Layered color of all-ceramic core and veneer ceramics. *The Journal of prosthetic dentistry,* 97**,** 279-86.
Lee, Y.-K., Lim, B.-S., Rhee, S.-H., Yang, H.-C. & Powers, J. M. 2004. Changes of optical properties of dental nano-filled resin composites after curing and thermocycling. *Journal of Biomedical Materials Research Part B, Applied Biomaterials,* 71**,** 16-21.
Lee, Y. K., Lim, B. S. & Kim, C. W. 2002. Effect of surface conditions on the color of dental resin composites. *Journal of Biomedical Materials Research,* 63**,** 657-63.

Lee, Y. K., Lim, B. S. & Kim, C. W. 2005. Difference in the colour and colour change of dental resin composites by the background. *Journal of Oral Rehabilitation,* 32**,** 227-33.

Lee, Y. K., Lim, B. S., Kim, C. W. & Powers, J. M. 2001. Comparison of color of resin composites of white and translucent shades with two shade guides. *Journal of Esthetic and Restorative Dentistry,* 13**,** 179-86.

Liebermann, A., Keul, C., Bahr, N., Edelhoff, D., Eichberger, M., Roos, M. & Stawarczyk, B. 2013. Impact of plasma treatment of PMMA-based CAD/CAM blanks on surface properties as well as on adhesion to self-adhesive resin composite cements. *Dental Materials,* 29**,** 935-44.

Lin, S. K., Lee, Y. L. & Lu, M. W. 2001. Evaluation of the staircase and the accelerated test methods for fatigue limit distributions. *International Journal of Fatigue,* 23**,** 75-83.

Lindauer, S. J. & Shoff, R. C. 1998. Comparison of Essix and Hawley retainers. *Journal of Clinical Orthodontics,* 32**,** 95.

Little, D. A. 1982. The relevance of prosthodontics and the science of dental materials to the practice of dentistry. *Journal of Dentistry,* 10**,** 300-10.

Lohbauer, U., Von Der Horst, T., Frankenberger, R., Kramer, N. & Petschelt, A. 2003. Flexural fatigue behavior of resin composite dental restoratives. *Dental Materials,* 19**,** 435-40.

Lorenzoni, F. C., Martins, L. M., Silva, N. R. F. A., Coelho, P. G., Guess, P. C., Bonfante, E. A., Thompson, V. P. & Bonfante, G. 2010. Fatigue life and failure modes of crowns systems with a modified framework design. *Journal of Dentistry,* 38**,** 626-634.

Ma, R. & Tang, T. 2014. Current strategies to improve the bioactivity of PEEK. *International Journal of Molecular Sciences,* 15**,** 5426-5445.

Macculloch, W. T. 1968. Advances in dental ceramics. *Br Dent J,* 124**,** 361-5.

Maekawa, M., Kanno, Z., Wada, T., Hongo, T., Doi, H., Hanawa, T., Ono, T. & Uo, M. 2015. Mechanical properties of orthodontic wires made of super engineering plastic. *Dental Materials Journal,* 34**,** 114-119.

Magne, P., Schlichting, L. H., Maia, H. P. & Baratieri, L. N. 2010. In vitro fatigue resistance of CAD/CAM composite resin and ceramic posterior occlusal veneers. *Journal of Prosthetic Dentistry,* 104**,** 149-57.

Mahmood, D. J. H., Linderoth, E. H. & Vult Von Steyern, P. 2011. The influence of support properties and complexity on fracture strength and fracture mode of all-ceramic fixed dental prostheses. *Acta Odontologica Scandinavica,* 69**,** 229-37.

Mair, L., Langfield, A., Walton, R. & Mansour, Y. 2011. Correlation of shear strength, fatigue limit and fatigue life of six high impact denture resins. *Dental Materials,* 27**,** e64-e65.

Malament, K. A. & Grossman, D. G. 1987. The cast glass-ceramic restoration. *Journal of Prosthetic Dentistry,* 57**,** 674-83.

Manicone, P. F., Rossi Iommetti, P. & Raffaelli, L. 2007. An overview of zirconia ceramics: basic properties and clinical applications. *Journal of Dentistry,* 35**,** 819-26.

Marchack, B. W., Sato, S., Marchack, C. B. & White, S. N. 2011. Complete and partial contour zirconia designs for crowns and fixed dental

prostheses: a clinical report. *The Journal of Prosthetic Dentistry,* 106**,** 145-52.
Margolis, J. M. 1985. *Engineering thermoplastics: properties and applications*, CRC Press.
Matinlinna, J. P., Heikkinen, T., Ozcan, M., Lassila, L. V. & Vallittu, P. K. 2006. Evaluation of resin adhesion to zirconia ceramic using some organosilanes. *Dental Materials,* 22**,** 824-31.
Matsumura, H., Kawahara, M., Tanaka, T. & Atsuta, M. 1991. Surface Preparations for Metal Frameworks of Composite Resin Veneered Prostheses Made with an Adhesive Opaque Resin. *Journal of Prosthetic Dentistry,* 66**,** 10-15.
Mazur, R. L., Oliveira, P. C., Rezende, M. C. & Botelho, E. C. 2014. Environmental effects on viscoelastic behavior of carbon fiber/PEKK thermoplastic composites. *Journal of Reinforced Plastics and Composites,* 33**,** 749-757.
Mccabe, J. F. & Walls, A. 2008. *Applied dental materials,* Oxford, Blackwell.
Mclaren, E. A. 1998. All-ceramic alternatives to conventional metal-ceramic restorations. *Compendium,* 19**,** 307-25.
Mclean, J. & Hughes, T. 1965. The reinforcement of dental porcelain with ceramic oxides. *British Dental Journal,* 119**,** 251.
Mehl, C., Ludwig, K., Steiner, M. & Kern, M. 2010. Fracture strength of prefabricated all-ceramic posterior inlay-retained fixed dental prostheses. *Dental Materials,* 26**,** 67-75.
Mehta, S. B., Banerji, S., Millar, B. J. & Suarez-Feito, J. M. 2012. Current concepts on the management of tooth wear: part 1. Assessment, treatment planning and strategies for the prevention and the passive management of tooth wear. *British Dental Journal,* 212**,** 17-27.
Michalakis, K. X., Stratos, A., Hirayama, H., Kang, K., Touloumi, F. & Oishi, Y. 2009. Fracture resistance of metal ceramic restorations with two different margin designs after exposure to masticatory simulation. *The Journal of Prosthetic Dentistry,* 102**,** 172-8.
Millen, C. S., Reuben, R. L. & Ibbetson, R. J. 2012. The effect of coping/veneer thickness on the fracture toughness and residual stress of implant supported, cement retained zirconia and metal-ceramic crowns. *Dental Materials,* 28**,** e250-8.
Miyazaki, T., Hotta, Y., Kunii, J., Kuriyama, S. & Tamaki, Y. 2009. A review of dental CAD/CAM: current status and future perspectives from 20 years of experience. *Dental Materials Journal,* 28**,** 44-56.
Moritz, T., Eiselt, W. & Moritz, K. 2006. Electrophoretic deposition applied to ceramic dental crowns and bridges. *Journal of Materials Science,* 41**,** 8123-8129.
Mormann, W. H., Brandestini, M., Lutz, F. & Barbakow, F. 1989. Chairside computer-aided direct ceramic inlays. *Quintessence Int,* 20**,** 329-39.
Mount, G. J. & Hume, W. R. 1998. *Preservation and restoration of tooth structure,* London, Mosby.

Najeeb, S., Zafar, M. S., Khurshid, Z. & Siddiqui, F. 2016. Applications of polyetheretherketone (PEEK) in oral implantology and prosthodontics. *Journal of Prosthodontic Research,* 60**,** 12-19.

Naumann, M., Preuss, A. & Rosentritt, M. 2006. Effect of incomplete crown ferrules on load capacity of endodontically treated maxillary incisors restored with fiber posts, composite build-ups, and all-ceramic crowns: an in vitro evaluation after chewing simulation. *Acta Odontologica Scandinavica,* 64**,** 31-6.

Naumann, M., Sterzenbach, G. & Proschel, P. 2005. Evaluation of load testing of postendodontic restorations in vitro: linear compressive loading, gradual cycling loading and chewing simulation. *Journal of Biomedical Materials Research Part B Applied Biomaterials,* 74**,** 829-34.

Nawafleh, N., Hatamleh, M. M., Öchsner, A. & Mack, F. 2016. The Impact of Core/Veneer Thickness Ratio and Cyclic Loading on Fracture Resistance of Lithium Disilicate Crown. *Journal of Prosthodontics*.

Negrutiu, M., Sinescu, C., Romanu, M., Pop, D. & Lakatos, S. 2005. Thermoplastic resins for flexible framework removable partial dentures. *Timisoara Medical Journal* 55**,** 295-299.

Neiva, G., Yaman, P., Dennison, J. B., Razzoog, M. E. & Lang, B. R. 1998. Resistance to fracture of three all-ceramic systems. *Journal of Esthetic and Restorative Dentistry,* 10**,** 60-6.

Nelson, S. J., Ash, M. M., Ash, M. M. D. a. P. & Occlusion 2010. *Wheeler's dental anatomy, physiology, and occlusion,* Philadelphia, Pa. ; London, Saunders.

Nelson, W. B. 2009. *Accelerated testing: statistical models, test plans, and data analysis*, John Wiley & Sons.

Nguyen, J.-F., Migonney, V., Ruse, N. D. & Sadoun, M. 2012. Resin composite blocks via high-pressure high-temperature polymerization. *Dental Materials,* 28**,** 529-34.

Nickerson, D. 1976. History of the Munsell Color System, Company, and Foundation. Ill*. *Color Research & Application,* 1**,** 121-130.

Nie, E. M., Chen, X. Y., Zhang, C. Y., Qi, L. L. & Huang, Y. H. 2012. Influence of masticatory fatigue on the fracture resistance of the pulpless teeth restored with quartz-fiber post-core and crown. *International Journal of Oral Science,* 4**,** 218-20.

Oderich, E., Boff, L. L., Cardoso, A. C. & Magne, P. 2012. Fatigue resistance and failure mode of adhesively restored custom implant zirconia abutments. *Clinical Oral Implants Research,* 23**,** 1360-1368.

Oh, W.-S. & Anusavice, K. J. 2002. Effect of connector design on the fracture resistance of all-ceramic fixed partial dentures. *The Journal of Prosthetic Dentistry,* 87**,** 536-42.

Orr, J. F. & Mitchell, C. A. 1996. The evaluation of post-retained crowns using a custom-designed fatigue machine. *Journal of Oral Rehabilitation,* 23**,** 179-185.

Ozcan, M., Cura, C. & Valandro, L. F. 2011. Early bond strength of two resin cements to Y-TZP ceramic using MPS or MPS/4-META silanes. *Odontology/The Society of the Nippon Dental University,* 99**,** 62-7.

Ozcan, M., Nijhuis, H. & Valandro, L. F. 2008. Effect of various surface conditioning methods on the adhesion of dual-cure resin cement with MDP functional monomer to zirconia after thermal aging. *Dental Materials Journal,* 27**,** 99-104.

Ozcellik, T. B., Yillmaz, B., Ozcan, I. & Kircelli, C. 2008. Colorimetric analysis of opaque porcelain fired to different base metal alloys used in metal ceramic restorations. *Journal of Prosthetic Dentistry,* 99**,** 193-202.

Padipatvuthikul, P. & Mair, L. 2009. Fatigue fracture in resin-bonded ceramic disks. *Dental Materials,* 25**,** e31.

Padipatvuthikul, P. & Mair, L. H. 2008. Comparison of Shear Bond Strength, Fatigue Limit and Fatigue Life in resin-bonded metal to enamel bonds. *Dental Materials,* 24**,** 674-80.

Paravina, R. D., Ontiveros, J. C. & Powers, J. M. 2002. Curing-dependent changes in color and translucency parameter of composite bleach shades. *Journal of Esthetic and Restorative Dentistry,* 14**,** 158-66.

Park, J.-Y., Lee, J.-J., Bae, S.-Y., Kim, J.-H. & Kim, W.-C. 2016. In vitro assessment of the marginal and internal fits of interim implant restorations fabricated with different methods. *The Journal of Prosthetic Dentistry,* 116**,** 536-542.

Passia, N., Ghazal, M. & Kern, M. 2016. Long-term retention behaviour of resin matrix attachment systems for overdentures. *Journal of the Mechanical Behavior of Biomedical Materials,* 57**,** 88-94.

Pecho, O. E., Ghinea, R., Ionescu, A. M., Cardona Jde, L., Paravina, R. D. & Perez Mdel, M. 2012. Color and translucency of zirconia ceramics, human dentine and bovine dentine. *Journal of Dentistry,* 40 Suppl 2**,** e34-40.

Petridis, H., Garefis, P., Hirayama, H., Kafantaris, N. M. & Koidis, P. T. 2004. Bonding indirect resin composites to metal: Part 2. Effect of alloy surface treatment on elemental composition of alloy and bond strength. *International Journal of Prosthodontics,* 17**,** 77-82.

Peutzfeldt, A. 1997. Resin composites in dentistry: the monomer systems. *European Journal of Oral Sciences,* 105**,** 97-116.

Peyton, F. A. 1975. History of resins in dentistry. *Dent Clin North Am,* 19**,** 211-22.

Peyton, F. A. & Craig, R. G. 1963. Current Evaluation of Plastics in Crown and Bridge Prosthesis. *Journal of Prosthetic Dentistry,* 13**,** 743-&.

Phoenix, R. D., Mansueto, M. A., Ackerman, N. A. & Jones, R. E. 2004. Evaluation of mechanical and thermal properties of commonly used denture base resins. *Journal of Prosthodontics,* 13**,** 17-27.

Piconi, C., Burger, W., Richter, H. G., Cittadini, A., Maccauro, G., Covacci, V., Bruzzese, N., Ricci, G. A. & Marmo, E. 1998. Y-TZP ceramics for artificial joint replacements. *Biomaterials,* 19**,** 1489-94.

Piconi, C. & Maccauro, G. 1999. Zirconia as a ceramic biomaterial. *Biomaterials,* 20**,** 1-25.

Piddock, V., Marquis, P. M. & Wilson, H. J. 1986. Comparison of the Strengths of Aluminous Porcelain Fired on to Platinum and Palladium Foils. *Journal of Oral Rehabilitation,* 13**,** 31-37.

Pincus, C. R. 1938. Building mouth personality *Journal of South California Dental Association* 14**,** 125-9.

Ponitz, R. J. 1971. Invisible retainers. *American Journal of Orthodontics,* 59**,** 266-272.
Powers, J. M., Sakaguchi, R. L. & Craig, R. G. R. D. M. 2006. *Craig's Restorative Dental Materials,* St. Louis, Mo. ; [London], Mosby Elsevier.
Preis, V., Behr, M., Hahnel, S., Handel, G. & Rosentritt, M. 2012. In vitro failure and fracture resistance of veneered and full-contour zirconia restorations. *Journal of Dentistry,* 40**,** 921-8.
Probster, L. & Diehl, J. 1992. Slip-casting alumina ceramics for crown and bridge restorations. *Quintessence International,* 23**,** 25-31.
Raigrodski, A. J. 2004. Contemporary materials and technologies for all-ceramic fixed partial dentures: a review of the literature. *Journal of Prosthetic Dentistry,* 92**,** 557-62.
Rathke, A., Tymina, Y. & Haller, B. 2009. Effect of different surface treatments on the composite-composite repair bond strength. *Clinical Oral Investigations,* 13**,** 317-23.
Rattacaso, R. M., Da Fonseca Roberti Garcia, L., Aguilar, F. G., Consani, S. & De Carvalho Panzeri Pires-De-Souza, F. 2011. Bleaching agent action on color stability, surface roughness and microhardness of composites submitted to accelerated artificial aging. *European Journal of Dentistry,* 5**,** 143-9.
Reich, S., Wichmann, M., Nkenke, E. & Proeschel, P. 2005. Clinical fit of all-ceramic three-unit fixed partial dentures, generated with three different CAD/CAM systems. *European Journal of Oral Sciences,* 113**,** 174-9.
Rekow, D. & Thompson, V. P. 2007. Engineering long term clinical success of advanced ceramic prostheses. *Journal of Materials Science-Materials in Medicine,* 18**,** 47-56.
Rekow, D., Zhang, Y. & Thompson, V. 2007. Can material properties predict survival of all-ceramic posterior crowns? *Compendium of continuing education in dentistry (Jamesburg, N J : 1995),* 28**,** 362-8; quiz 369, 386.
Rekow, E. D. 2006. Dental CAD/CAM systems: a 20-year success story. *Journal of the American Dental Association,* 137 Suppl**,** 5S-6S.
Rekow, E. D., Silva, N. R., Coelho, P. G., Zhang, Y., Guess, P. & Thompson, V. P. 2011. Performance of dental ceramics: challenges for improvements. *Journal of Dental Research,* 90**,** 937-52.
Rimmer, S. 2006. Modern dental ceramics: an overview. *International Dentistry SA,* 8**,** 32-40.
Rinne, H. 2009. *The Weibull distribution : a handbook,* Boca Raton, Fla. ; London, CRC.
Rochette, A. L. 1975. Ceramic Restoration Bonded by Etched Enamel and Resin for Fractured Incisors. *Journal of Prosthetic Dentistry,* 33**,** 287-293.
Rosentritt, M., Behr, M., Gebhard, R. & Handel, G. 2006. Influence of stress simulation parameters on the fracture strength of all-ceramic fixed-partial dentures. *Dental Materials,* 22**,** 176-82.

Rosentritt, M., Behr, M. & Preis, V. 2016. A Critical Evaluation of Fatigue Studies for Restorative Materials in Dentistry. *Current Oral Health Reports,* 3**,** 221-228.

Rosentritt, M., Naumann, M., Hahnel, S., Handel, G. & Reill, M. 2009a. Evaluation of tooth analogs and type of restoration on the fracture resistance of post and core restored incisors. *Journal of Biomedical Materials Research. Part B, Applied Biomaterials,* 91**,** 272-6.

Rosentritt, M., Plein, T., Kolbeck, C., Behr, M. & Handel, G. 2000. In vitro fracture force and marginal adaptation of ceramic crowns fixed on natural and artificial teeth. *The International Journal of Prosthodontics,* 13**,** 387-91.

Rosentritt, M., Preis, V., Behr, M., Sereno, N. & Kolbeck, C. 2015. Shear bond strength between veneering composite and PEEK after different surface modifications. *Clinical Oral Investigations,* 19**,** 739-44.

Rosentritt, M., Steiger, D., Behr, M., Handel, G. & Kolbeck, C. 2009b. Influence of substructure design and spacer settings on the in vitro performance of molar zirconia crowns. *Journal of Dentistry,* 37**,** 978-83.

Rueggeberg, F. A. 2002. From vulcanite to vinyl, a history of resins in restorative dentistry. *Journal of Prosthetic Dentistry,* 87**,** 364-379.

Ruiz, L. & Readey, M. J. 1996. Effect of heat-treatment on grain size, phase assemblage, and mechanical properties of 3 mol% Y-TZP. *Journal of the American Ceramic Society,* 79**,** 2331-2340.

Ruyter, I. E., Nilner, K. & Moller, B. 1987. Color stability of dental composite resin materials for crown and bridge veneers. *Dental Materials,* 3**,** 246-51.

Sabatini, C., Patel, M. & D'silva, E. 2013. In vitro shear bond strength of three self-adhesive resin cements and a resin-modified glass ionomer cement to various prosthodontic substrates. *Operative Dentistry,* 38**,** 186-96.

Sadowsky, S. J. 2006. An overview of treatment considerations for esthetic restorations: A review of the literature. *Journal of Prosthetic Dentistry,* 96**,** 433-442.

Sahin, V., Uludag, B., Usumez, A. & Ozkir, S. E. 2010. The Effect of Repeated Firings on the Color of an Alumina Ceramic System with Two Different Veneering Porcelain Shades. *Journal of Prosthetic Dentistry,* 104**,** 372-378.

Sailer, I., Feher, A., Filser, F., Luthy, H., Gauckler, L. J., Scharer, P. & Franz Hammerle, C. H. 2006. Prospective clinical study of zirconia posterior fixed partial dentures: 3-year follow-up. *Quintessence International,* 37**,** 685-93.

Sailer, I., Makarov, N. A., Thoma, D. S., Zwahlen, M. & Pjetursson, B. E. 2015. All-ceramic or metal-ceramic tooth-supported fixed dental prostheses (FDPs)? A systematic review of the survival and complication rates. Part I: Single crowns (SCs). *Dental Materials,* 31**,** 603-623.

Sailer, I., Pjetursson, B. E., Zwahlen, M. & Hammerle, C. H. F. 2007. A systematic review of the survival and complication rates of all-ceramic

and metal-ceramic reconstructions after an observation period of at least 3 years. Part II: Fixed dental prostheses. *Clinical oral implants research,* 18 Suppl 3**,** 86-96.

Saito, A., Komine, F., Blatz, M. B. & Matsumura, H. 2010. A Comparison of Bond Strength of Layered Veneering Porcelains to Zirconia and Metal. *Journal of Prosthetic Dentistry,* 104**,** 247-257.

Sakaguchi, R. L., Douglas, W. H., Delong, R. & Pintado, M. R. 1986. The wear of a posterior composite in an artificial mouth: a clinical correlation. *Dental Materials,* 2**,** 235-40.

Sakaguchi, R. L. & Powers, J. M. 2012. *Craig's Restorative Dental Materials*, Elsevier Limited.

Sarafianou, A., Seimenis, I. & Papadopoulos, T. 2008. Effectiveness of different adhesive primers on the bond strength between an indirect composite resin and a base metal alloy. *Journal of Prosthetic Dentistry,* 99**,** 377-387.

Sarrett, D. C. 2005. Clinical challenges and the relevance of materials testing for posterior composite restorations. *Dental Materials,* 21**,** 9-20.

Schaerer, P., Sato, T. & Wohlwend, A. 1988. A comparison of the marginal fit of three cast ceramic crown systems. *Journal of Prosthetic Dentistry,* 59**,** 534-42.

Scherrer, S. S. & De Rijk, W. G. 1992. The effect of crown length on the fracture resistance of posterior porcelain and glass-ceramic crowns. *International Journal of Prosthodontics,* 5**,** 550-7.

Schindler, H. J., Stengel, E. & Spiess, W. E. 1998. Feedback control during mastication of solid food textures--a clinical-experimental study. *The Journal of Prosthetic Dentistry,* 80**,** 330-6.

Schmalz, G. & Garhammer, P. 2002. Biological interactions of dental cast alloys with oral tissues. *Dental Materials,* 18**,** 396-406.

Schmidlin, P. R., Stawarczyk, B., Wieland, M., Attin, T., Hammerle, C. H. & Fischer, J. 2010. Effect of different surface pre-treatments and luting materials on shear bond strength to PEEK. *Dental Materials,* 26**,** 553-9.

Schwitalla, A. & Muller, W. D. 2013. PEEK Dental Implants: A Review of the Literature. *Journal of Oral Implantology,* 39**,** 743-749.

Schwitalla, A. D., Spintig, T., Kallage, I. & Müller, W.-D. 2016. Pressure behavior of different PEEK materials for dental implants. *Journal of the Mechanical Behavior of Biomedical Materials,* 54**,** 295-304.

Schwitalla, A. D., Spintig, T., Kallage, I. & Muller, W. D. 2015. Flexural behavior of PEEK materials for dental application. *Dental Materials,* 31**,** 1377-84.

Scotti, R., Catapano, S. & D'elia, A. 1995. A clinical evaluation of In-Ceram crowns. *International Journal of Prosthodontics,* 8**,** 320-3.

Scurria, M. S., Bader, J. D. & Shugars, D. A. 1998. Meta-analysis of fixed partial denture survival: prostheses and abutments. *The Journal of Prosthetic Dentistry,* 79**,** 459-64.

Segal, B. S. 2001. Retrospective assessment of 546 all-ceramic anterior and posterior crowns in a general practice. *Journal of Prosthetic Dentistry,* 85**,** 544-50.

Seghi, R. R. & Sorensen, J. A. 1995. Relative flexural strength of six new ceramic materials. *International Journal of Prosthodontics,* 8**,** 239-46.
Shah, K., Holloway, J. A. & Denry, I. L. 2008. Effect of coloring with various metal oxides on the microstructure, color, and flexural strength of 3Y-TZP. *Journal of Biomedical Materials Research Part B, Applied Biomaterials,* 87**,** 329-37.
Shahdad, S. A. & Kennedy, J. G. 1998. Bond strength of repaired anterior composite resins: an in vitro study. *Journal of Dentistry,* 26**,** 685-94.
Sharif, M. O., Fedorowicz, Z., Tickle, M. & Brunton, P. A. 2010. Repair or replacement of restorations: do we accept built in obsolescence or do we improve the evidence? *British Dental Journal,* 209**,** 171-4.
Shembish, F. A., Tong, H., Kaizer, M., Janal, M. N., Thompson, V. P., Opdam, N. J. & Zhang, Y. 2016. Fatigue resistance of CAD/CAM resin composite molar crowns. *Dental Materials,* 32**,** 499-509.
Shibata, M., Yosomiya, R., Wang, J., Zheng, Y., Zhang, W. & Wu, Z. 1997. Relationship between molecular structure and thermal properties of poly (aryl ether ketone) s. *Macromolecular Rapid Communications,* 18**,** 99-105.
Shillingburg, H. T. 1997. *Fundamentals of fixed prosthodontics,* Chicago, Quintessence Pub. Co.
Shiraishi, T., Wood, D. J., Shinozaki, N. & Van Noort, R. 2011. Optical properties of base dentin ceramics for all-ceramic restorations. *Dental Materials,* 27**,** 165-72.
Shokry, T. E., Shen, C., Elhosary, M. M. & Elkhodary, A. M. 2006. Effect of core and veneer thicknesses on the color parameters of two all-ceramic systems. *The Journal of Prosthetic Dentistry,* 95**,** 124-9.
Silva, N. R., Bonfante, E. A., Zavanelli, R. A., Thompson, V. P., Ferencz, J. L. & Coelho, P. G. 2010. Reliability of metalloceramic and zirconia-based ceramic crowns. *Journal of Dental Research,* 89**,** 1051-6.
Skinner, H. B. 1988. Composite technology for total hip arthroplasty. *Clinical Orthopaedics and Related Research***,** 224-36.
Smith, B. G. N. & Howe, L. C. 2007. *Planning and making crowns and bridges,* Abingdon, Informa Healthcare.
Soares, C. J., Pizi, E. C., Fonseca, R. B. & Martins, L. R. 2005. Influence of root embedment material and periodontal ligament simulation on fracture resistance tests. *Brazilian Oral Research,* 19**,** 11-6.
Solow, R. A. 1999. Composite veneered acrylic resin provisional restorations for complete veneer crowns. *The Journal of Prosthetic Dentistry,* 82**,** 515-7.
Sorrentino, R., Triulzio, C., Tricarico, M. G., Bonadeo, G., Gherlone, E. F. & Ferrari, M. 2016. In vitro analysis of the fracture resistance of CAD-CAM monolithic zirconia molar crowns with different occlusal thickness. *Journal of the Mechanical Behavior of Biomedical Materials,* 61**,** 328-333.
Southan, D. E. 1970. The development and characteristics of dental porcelain. *Australian Dental Journal,* 15**,** 103-7.

Spear, F. & Holloway, J. 2008. Which all-ceramic system is optimal for anterior esthetics? *Journal of the American Dental Association,* 139**,** 19S-24S.

Sproesser, O., Schmidlin, P. R., Uhrenbacher, J., Eichberger, M., Roos, M. & Stawarczyk, B. 2014. Work of adhesion between resin composite cements and PEEK as a function of etching duration with sulfuric acid and its correlation with bond strength values. *International Journal of Adhesion and Adhesives,* 54**,** 184-190.

Spyropoulou, P.-E., Giroux, E. C., Razzoog, M. E. & Duff, R. E. 2011. Translucency of shaded zirconia core material. *The Journal of Prosthetic Dentistry,* 105**,** 304-7.

Stavridakis, M. M., Papazoglou, E., Seghi, R. R., Johnston, W. M. & Brantley, W. A. 2000. Effect of different high-palladium metal-ceramic alloys on the color of opaque porcelain. *Journal of Prosthodontics,* 9**,** 71-6.

Stawarczyk, B., Bahr, N., Beuer, F., Wimmer, T., Eichberger, M., Gernet, W., Jahn, D. & Schmidlin, P. R. 2014a. Influence of plasma pretreatment on shear bond strength of self-adhesive resin cements to polyetheretherketone. *Clinical Oral Investigations,* 18**,** 163-70.

Stawarczyk, B., Beuer, F., Wimmer, T., Jahn, D., Sener, B., Roos, M. & Schmidlin, P. R. 2013a. Polyetheretherketone-a suitable material for fixed dental prostheses? *Journal of Biomedical Materials Research Part B, Applied Biomaterials,* 101**,** 1209-16.

Stawarczyk, B., Egli, R., Roos, M., Ozcan, M. & Hammerle, C. H. 2011. The impact of in vitro aging on the mechanical and optical properties of indirect veneering composite resins. *Journal of Prosthetic Dentistry,* 106**,** 386-98.

Stawarczyk, B., Jordan, P., Schmidlin, P. R., Roos, M., Eichberger, M., Gernet, W. & Keul, C. 2014b. PEEK surface treatment effects on tensile bond strength to veneering resins. *The Journal of Prosthetic Dentistry,* 112**,** 1278-88.

Stawarczyk, B., Keul, C., Beuer, F., Roos, M. & Schmidlin, P. R. 2013b. Tensile bond strength of veneering resins to PEEK: impact of different adhesives. *Dental Materials Journal,* 32**,** 441-8.

Stawarczyk, B., Özcan, M., Hallmann, L., Roos, M., Trottmann, A. & Hämmerle, C. H. 2012. Impact of air–abrasion on fracture load and failure type of veneered anterior Y–TZP crowns before and after chewing simulation. *Journal of Biomedical Materials Research Part B: Applied Biomaterials,* 100**,** 1683-1690.

Stawarczyk, B., Schmid, P., Roos, M., Eichberger, M. & Schmidlin, P. R. 2016. Spectrophotometric Evaluation of Polyetheretherketone (PEEK) as a Core Material and a Comparison with Gold Standard Core Materials. *Materials,* 9**,** 491.

Stawarczyk, B., Thrun, H., Eichberger, M., Roos, M., Edelhoff, D., Schweiger, J. & Schmidlin, P. R. 2015. Effect of different surface pretreatments and adhesives on the load-bearing capacity of veneered 3-unit PEEK FDPs. *The Journal of Prosthetic Dentistry,* 114**,** 666-73.

Steele, J. & O'sullivan, I. 2011. Executive summary: adult dental health survey 2009. *Leeds: NHS Information Centre for Health and Social Care*.

Steiner, M., Mitsias, M. E., Ludwig, K. & Kern, M. 2009. In vitro evaluation of a mechanical testing chewing simulator. *Dental Materials,* 25**,** 494-9.

Stevenson, B. & Ibbetson, R. 2010. The effect of the substructure on the colour of samples/restorations veneered with ceramic: a literature review. *Journal of Dentistry,* 38**,** 361-8.

Suarez, M. J., Lozano, J. F., Paz Salido, M. & Martinez, F. 2004. Three-year clinical evaluation of In-Ceram Zirconia posterior FPDs. *Int J Prosthodont,* 17**,** 35-8.

Sulaiman, T. A., Abdulmajeed, A. A., Donovan, T. E., Ritter, A. V., Vallittu, P. K., Narhi, T. O. & Lassila, L. V. 2015. Optical properties and light irradiance of monolithic zirconia at variable thicknesses. *Dental Materials,* 31**,** 1180-7.

Sundh, A. & Sjogren, G. 2004. A comparison of fracture strength of yttrium-oxide- partially-stabilized zirconia ceramic crowns with varying core thickness, shapes and veneer ceramics. *J Oral Rehabil,* 31**,** 682-8.

Suttor, D., Hauptmann, H., Schnagl, R. & Frank, S. 2004. Coloring ceramics by way of ionic or complex-containing solutions. Google Patents.

Swab, J. J. 1991. Low-Temperature Degradation of Y-Tzp Materials. *Journal of Materials Science,* 26**,** 6706-6714.

Taggart, W. H. 1911. METHOD FOR MAKING DENTAL INLAY-EILLINGS AND THE LIKE. Google Patents.

Taguchi, K., Komine, F., Fushiki, R., Blatz, M. B., Kamio, S. & Matsumura, H. 2014. Fracture resistance of single-tooth implant-supported zirconia-based indirect composite-layered molar restorations. *Clinical Oral Implants Research,* 25**,** 983-91.

Tannous, F., Steiner, M., Shahin, R. & Kern, M. 2012. Retentive forces and fatigue resistance of thermoplastic resin clasps. *Dental Materials,* 28**,** 273-8.

Tarozzo, L. S. A., De Mattos, M. D., Ribeiro, R. F. & Semprini, M. 2003. Comparison of retentive systems for composites used as alternatives to porcelain in fixed partial dentures. *Journal of Prosthetic Dentistry,* 89**,** 572-578.

Taufall, S., Eichberger, M., Schmidlin, P. R. & Stawarczyk, B. 2016. Fracture load and failure types of different veneered polyetheretherketone fixed dental prostheses. *Clinical Oral Investigations*.

Tetelman, E. D. & Babbush, C. A. 2008. A new transitional abutment for immediate aesthetics and function. *Implant Dentistry,* 17**,** 51-8.

Thomaidis, S., Kakaboura, A., Mueller, W. D. & Zinelis, S. 2013. Mechanical properties of contemporary composite resins and their interrelations. *Dental Materials,* 29**,** e132-41.

Tinschert, J., Natt, G., Mautsch, W., Augthun, M. & Spiekermann, H. 2001. Fracture resistance of lithium disilicate-, alumina-, and zirconia-based three-unit fixed partial dentures: a laboratory study. *International Journal of Prosthodontics,* 14**,** 231-8.

Tiossi, R., Vasco, M. a. A., Lin, L., Conrad, H. J., Bezzon, O. L., Ribeiro, R. F. & Fok, A. S. L. 2013. Validation of finite element models for strain analysis of implant-supported prostheses using digital image correlation. *Dental Materials,* 29**,** 788-96.

Toksavul, S. & Toman, M. 2007. A short-term clinical evaluation of IPS Empress 2 crowns. *International Journal of Prosthodontics,* 20**,** 168-72.

Tortopidis, D., Lyons, M. F., Baxendale, R. H. & Gilmour, W. H. 1998. The variability of bite force measurement between sessions, in different positions within the dental arch. *Journal of Oral Rehabilitation,* 25**,** 681-6.

Truninger, T. C., Stawarczyk, B., Leutert, C. R., Sailer, T. R., Hämmerle, C. H. & Sailer, I. 2012. Bending moments of zirconia and titanium abutments with internal and external implant–abutment connections after aging and chewing simulation. *Clinical Oral Implants Research,* 23**,** 12-18.

Tsitrou, E. A., Helvatjoglu-Antoniades, M. & Van Noort, R. 2010. A preliminary evaluation of the structural integrity and fracture mode of minimally prepared resin bonded CAD/CAM crowns. *Journal of Dentistry,* 38**,** 16-22.

Uhrenbacher, J., Schmidlin, P. R., Keul, C., Eichberger, M., Roos, M., Gernet, W. & Stawarczyk, B. 2014. The effect of surface modification on the retention strength of polyetheretherketone crowns adhesively bonded to dentin abutments. *The Journal of prosthetic dentistry,* 112**,** 1489-97.

Um, C. M. & Ruyter, I. E. 1991. Staining of resin-based veneering materials with coffee and tea. *Quintessence International,* 22**,** 377-86.

Ural, C., Kulunk, T., Kulunk, S., Kurt, M. & Baba, S. 2010. Determination of resin bond strength to zirconia ceramic surface using different primers. *Acta Odontologica Scandinavica,* 69**,** 48-53.

Vagkopoulou, T., Koutayas, S. O., Koidis, P. & Strub, J. R. 2009. Zirconia in dentistry: Part 1. Discovering the nature of an upcoming bioceramic. *European Journal of Esthetic Dentistry,* 4**,** 130-51.

Vallittu, P. K. 1998. The effect of glass fiber reinforcement on the fracture resistance of a provisional fixed partial denture. *The Journal of Prosthetic Dentistry,* 79**,** 125-30.

Van Noort, R. 2007. *Introduction to dental materials,* Edinburgh ; New York, Mosby.

Van Noort, R. 2012. The future of dental devices is digital. *Dent Mater,* 28**,** 3-12.

Venclikova, Z., Benada, O., Bartova, J., Joska, L. & Mrklas, L. 2007. Metallic pigmentation of human teeth and gingiva: morphological and immunological aspects. *Dental Materials Journal,* 26**,** 96-104.

Vichi, A., Ferrari, M. & Davidson, C. L. 2004. Color and opacity variations in three different resin-based composite products after water aging. *Dental Materials,* 20**,** 530-4.

Vichi, A., Louca, C., Corciolani, G. & Ferrari, M. 2011. Color related to ceramic and zirconia restorations: A review. *Dental Materials,* 27**,** 97-108.

Wagner, W. C. & Chu, T. M. 1996. Biaxial flexural strength and indentation fracture toughness of three new dental core ceramics. *Journal of Prosthetic Dentistry,* 76**,** 140-144.

Walmsley, A. D. 2007. *Restorative dentistry,* Edinburgh, Churchill Livingstone.
Walter, M. H., Wolf, B. H., Wolf, A. E. & Boening, K. W. 2006. Six-year clinical performance of all-ceramic crowns with alumina cores. *International Journal of Prosthodontics,* 19**,** 162-3.
Waltimo, A. & Kononen, M. 1993. A novel bite force recorder and maximal isometric bite force values for healthy young adults. *Scandinavian Journal of Dental Research,* 101**,** 171-5.
Wang, T. J., Xie, Y. M. & Sherwood, P. M. A. 1993. X-Ray Photoelectron Spectroscopic Studies of Poly(Ether Ketone Ketone) - Core-Level and Valence-Band Studies and Valence-Band Interpretation by X-Alpha Calculations. *Chemistry of Materials,* 5**,** 1007-1011.
Wataha, J. C. 2000. Biocompatibility of dental casting alloys: a review. *The Journal of Prosthetic Dentistry,* 83**,** 223-34.
Williams, D., Mcnamara, A. & Turner, R. 1987. Potential of polyetheretherketone (PEEK) and carbon-fibre-reinforced PEEK in medical applications. *Journal of Materials Science Letters,* 6**,** 188-190.
Wimmer, T., Erdelt, K.-J., Eichberger, M., Roos, M., Edelhoff, D. & Stawarczyk, B. 2014. Influence of abutment model materials on the fracture loads of three-unit fixed dental prostheses. *Dental Materials Journal,* 33**,** 717-24.
Wiskott, H. W., Nicholls, J. I. & Belser, U. C. 1995. Stress fatigue: basic principles and prosthodontic implications. *The International Journal of Prosthodontics,* 8**,** 105-16.
Wiskott, H. W. A., Meyer, M., Perriard, J. & Scherrer, S. S. 2007. Rotational fatigue-resistance of seven post types anchored on natural teeth. *Dental Materials,* 23**,** 1412-9.
Yildirim, M., Fischer, H., Marx, R. & Edelhoff, D. 2003. In vivo fracture resistance of implant-supported all-ceramic restorations. *The Journal of Prosthetic Dentistry,* 90**,** 325-31.
Yilmaz, B., Ozcelik, T. B. & Wee, A. G. 2009. Effect of Repeated Firings on the Color of Opaque Porcelain Applied on Different Dental Alloys. *Journal of Prosthetic Dentistry,* 101**,** 395-404.
Yoshida, K., Taira, Y., Matsumura, H. & Atsuta, M. 1993. Effect of Adhesive Metal Primers on Bonding a Prosthetic Composite Resin to Metals. *Journal of Prosthetic Dentistry,* 69**,** 357-362.
Yu, B., Ahn, J.-S. & Lee, Y.-K. 2009a. Measurement of translucency of tooth enamel and dentin. *Acta Odontologica Scandinavica,* 67**,** 57-64.
Yu, B., Ahn, J. S., Lim, J. I. & Lee, Y. K. 2009b. Influence of TiO2 nanoparticles on the optical properties of resin composites. *Dental Materials,* 25**,** 1142-7.
Yucel, M. T., Yondem, I., Aykent, F. & Eraslan, O. 2012. Influence of the supporting die structures on the fracture strength of all-ceramic materials. *Clinical Oral Investigations,* 16**,** 1105-10.
Yun, J. Y., Ha, S. R., Lee, J. B. & Kim, S. H. 2010. Effect of sandblasting and various metal primers on the shear bond strength of resin cement to Y-TZP ceramic. *Dental Materials,* 26**,** 650-8.

Zahran, M., El-Mowafy, O., Tam, L., Watson, P. A. & Finer, Y. 2008. Fracture strength and fatigue resistance of all-ceramic molar crowns manufactured with CAD/CAM technology. *Journal of Prosthodontics,* 17**,** 370-7.

Zankuli, M. A., Silikas, N. & Devlin, H. 2015. The Effect of Cyclic Loading on the Compressive Strength of Core Build–Up Materials. *Journal of Prosthodontics,* 24**,** 549-552.

Zhang, Y. 2014. Making yttria-stabilized tetragonal zirconia translucent. *Dental Materials,* 30**,** 1195-203.

Zhi-Yue, L. & Yu-Xing, Z. 2003. Effects of post-core design and ferrule on fracture resistance of endodontically treated maxillary central incisors. *The Journal of Prosthetic Dentistry,* 89**,** 368-73.

Chapter 13

Appendices

13.1.1. Fracture resistance detailed results

Table 35: Fracture resistance N of all groups when load applied on the central fossa. *These samples withstood the maximum limit of the universal tester of 2100 N without detecting any signs of fracture.

Load on central fossa			
Sample no.	Group 1: PEKK/LC	Group 2: Metal/LC*	Group 3: YZ/LC
1	1511	>2100	2045
2	1943	>2100	1524
3	2100	>2100	1754
4	2100	>2100	1453
5	2109	>2100	1913
6	1672	>2100	1611
7	1689	>2100	1593
8	2100	>2100	1657
9	2100	>2100	1890
10	2061	>2100	1870
Average	**1938.5**	0	**1731**
SD	227.2	0	193.2

Table 36: Fracture resistance N of all groups when load applied on buccal cusp.

Load on buccal cusp			
Sample no.	Group 4: PEKK/LC	Group 5: Metal/LC	Group 6: YZ/LC
1	1667.9	1052.9	594
2	1613	2086	645.4
3	1285	1151.7	686
4	1557	1423	791
5	1258	1782	380
6	1268	1136	491
7	1413	1394	526
8	1320	1327	673.4
9	1591	859	675
10	1189	1630	548
Average	**1416.19**	**1384.16**	**600.98**
SD	175.6	367.8	118.1

13.1.2. Fatigue machine's load calibration

Table 37: Detailed load calibration figures for the fatigue machine.

Weight Kg	Load N
0 (lever's weight)	178
0.5	214
1	250
1.5	284
2	319
2.5	353
3	388
3.5	422
4	457
4.5	489
5	522
5.5	554
6	586
6.5	619
7	652
7.5	682
8	715
8.5	754
9	792
9.5	812
10	845
10.5	881
11	917
11.5	956
12	986
12.5	1021

13	1058

13.1.3. IADR poster, March 2015, Boston, USA

The University Of Sheffield.

Evaluation of the Optical Properties of PEKK Based Restorations

Poster#3667

Omar Alsadon[1,2], Duncan Wood[1], David Patrick[1], Thierry Copponnex[3] and Sarah Pollington[1]

[1]School of Clinical Dentistry, Sheffield University, United Kingdom. [2]College of Applied Medical Sciences, King Saud University, Saudi Arabia*. [3]Cendres+Métaux SA, Switzerland.

o.alsadon@sheffield.ac.uk

School of Clinical Dentistry, University of Sheffield, United Kingdom

Introduction

Poly-aryl-ether-ketone (PAEK) thermoplastic biomaterial polymers have been successfully applied in different medical applications and from them comes a poly-ether-ketone-ketone (PEKK) based polymer which have been recently introduced to dentistry as a restorative material for fixed prostheses as both monolithic and bi-layered structures, the latter veneered with composite resin. To date there is little published data about the aesthetics of such bi-layered structures.

Objectives

To evaluate the spectral reflectance and color of PEKK based thermoplastic polymer (Pekkton®§) as a material used for fabricating indirect restorations when veneered with light cured composite in comparison with equivalent zirconia-composite and metal-composite bilayers to assess the effect of different substructure materials on the same veneering material and similar bi-layer structures i.e. zirconia-porcelain.

Materials and Methods

Groups: 1) PEKK and Composite (PEKK-LC) | 2) Metal and Composite (Metal-LC) | 3) Zirconia and Composite (YZ-LC) | 4) Zirconia and Porcelain (YZ-VM9)

Substructures

PEKK: Disc shaped samples were produced of wax and processed into PEKK polymer, using the lost wax technique. PEKK discs were divested before being finished and polished using diamond bur and carbide abrasive paper P400 under water.

Brand: **Pekkton® ivory, Cendres+Métaux SA, CH** Lot No. 175701

Figure 1

Metal: Disc shaped wax samples were invested and casted with a ceramic alloy. After divesting and sprue cutting, the metal discs were finished and polished using carbide bur and carbide abrasive paper P400 under water.

Brand: **Talladium Tilite V, Talladium, Inc, USA** Lot No. 042011

Figure 2

Zirconia: A CAD/CAM block was sectioned using a diamond blade in a precision diamond saw and was submerged in light YZ coloring liquid for 2 minutes before sintering to achieve the best shade matching the composite veneer.

Brand: **In-Ceram YZ®, VITA Zahnfabrik GmbH, DE** Lot No. 10921

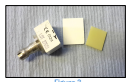


Figure 3

Veneers

Composite: Light cured composite resin (UDMA, TEGMA, Silica, primary particle (40- 50nm)) of A2 shade was used in this research.
The bonding surface was shot-blasted with 50μ Alumina particles and cleaned before applying primer to enhance bonding between substructure and veneer. Different primers were used according to the substructure materials recommendation as follows:
1) PEKK: visio.link®, Bredent GmbH & Co. KG, Germany.
2) Zirconia: Monobond® Plus, Ivoclar Vivadent AG, Liechtenstein.
3) Metal (Kuraray Alloy primer® , KURARAY CO., LTD, Japan).
The composite was built starting with the opaque layer masking the substructure followed with dentine paste and light cured using Coltolux75®, Coltène Whaledent, CH unit. All samples were polished using waterproof carbide abrasive paper P400 and P600 respectively to a thickness of 1.3mm (minimal manufacturer clinical recommendation 0.8mm for substructure and 0.5mm for the veneer).

Brand: **Vita VM LC®, VITA Zahnfabrik GmbH, DE** Lot No. 33211

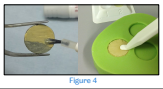


Figure 4

Porcelain: High-fusing, fine structure feldspathic ceramic (2M2 shade) for veneering zirconia substructure was fired using using a porcelain furnace (VITA VACUMAT 40T, VITA Zahnfabrik H. Rauter GmbH & Co.KG, Germany). Samples were polished using waterproof carbide abrasive paper P400 and P600 respectively.

Brand: **Vita VM9®, VITA Zahnfabrik GmbH, DE** Lot No. 32380

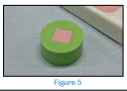


Figure 5

A spectrophotometer (CM-2600d Konica Minolta Sensing, Inc., Japan) was used to determine the spectral reflectance of each material over white and black backgrounds using a D65 illuminant. CIE L*a*b* color coordinates and color difference (ΔE) were determined from the reflectance data. Each group consisted of three samples (n=3) wide enough to cover the spectrophotometer's target mask opening of 3mm (Figure 6). Each sample was measured three times in different positions (9 readings per group). Results were compared with one-way ANOVA and paired t-test using statistical data analyzing software Minitab 15 for Widows XP (Minitab Ltd., UK).

Figure 6

Results

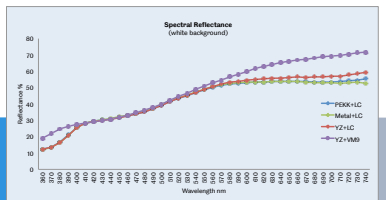


Figure 7: Spectral Reflectance data curve of the laminate samples (1.3mm) under white background.

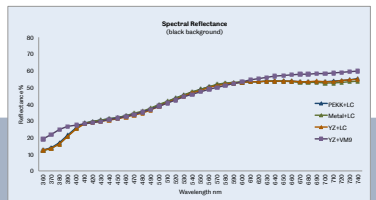


Figure 8: Spectral Reflectance data curve of the laminate samples (1.3mm) under black background.

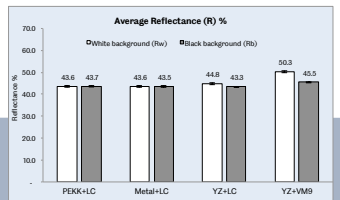


Figure 9: Average Reflectance (%) of the laminates under white (Rw) and black background (Rb).

Table 1: CIE L*a*b* values of the laminate samples of 1.3mm thickness under black and white background.
Groups with different superscript letters indicate significant differences (P<0.05) and groups with same superscript letters indicate no significant difference (P>0.05).

Group	L*		a*		b*	
	white	black	white	black	white	black
PEKK-LC	74.51^{a} ± 0.11	74.26^{a} ± 0.15	2.31^{a} ± 0.3	2.29^{a} ± 0.26	17.81^{a} ± 0.72	17.83^{a} ± 0.56
Metal-LC	74.5^{a} ± 0.22	74.49^{a} ± 0.27	1.93^{a} ± 0.18	1.9^{a} ± 0.22	18.2^{a} ± 0.45	18.2^{a} ± 0.46
YZ-LC	74.67^{a} ± 0.35	74.1^{a} ± 0.21	3.17^{a} ± 0.72	2.4^{a} ± 0.14	19.21^{a} ± 0.69	18.65^{a} ± 0.65
YZ-VM9	76.4^{b} ± 0.51	73.99^{a} ± 0.14	6.15^{b} ± 0.23	3.85^{b} ± 0.27	21.64^{b} ± 0.77	18.12^{a} ± 0.4

Table 2: Color difference (ΔE) between different groups determined using white and black backgrounds CIE L*a*b values.
*LC and VM9 groups (veneers) were tested solely as single layers.

Groups	ΔE	
	White	Black
PEKK-LC & Metal-LC	0.40	0.28
PEKK-LC & YZ-LC	1.30	0.60
Metal-LC & YZ-LC	1.61	0.78
YZ-LC & YZ-VM9	4.22	1.55
PEKK-LC & YZ-VM9	5.51	1.75
*LC & VM9	4.13	4.70

Conclusions

- Having different substructure material did not cause any significant difference in optical properties between all composite veneered groups.
- Different results were found between light cured composite resin and porcelain of the same shade when evaluated both solely and bonded to underlying substructure.

* This research is part of a sponsored PhD course for the presenter by King Saud University, Saudi Arabia.

§ The researchers would like to thank Cendres+Métaux for their support and for providing Pekkton® ivory.

13.1.4. BSODR poster September 2015, Cardiff, Wales.

The University Of Sheffield.

Structural Integrity of Poly-Ether-Ketone-Ketone (PEKK) Based Bi-layered Molar Crowns

BSODR Annual General Meeting 14th-16th September 2015 Cardiff City Hall

School of Clinical Dentistry, University of Sheffield, United Kingdom

Omar Alsadon[1,2], Duncan Wood[1], David Patrick[1], Thierry Copponnex[3] and Sarah Pollington[1]

[1]School of Clinical Dentistry, Sheffield University, United Kingdom. [2]College of Applied Medical Sciences, King Saud University, Saudi Arabia*. [3]Cendres+Métaux SA, Switzerland.

o.alsadon@sheffield.ac.uk

Introduction

Poly-aryl-ether-ketone (PAEK) thermoplastic biomaterial polymers have been successfully applied in different medical applications and from them comes a poly-ether-ketone-ketone (PEKK) based polymer which have been recently introduced to dentistry as a restorative material for fixed prostheses as both monolithic and bi-layered structures, the latter veneered with composite resin. To date there is little published data about the structural integrity of such bi-layered crowns.

Objectives

To evaluate the occlusal fracture resistance of mandibular molar crowns made from a Poly-Ether-Ketone-Ketone (PEKK) based polymer (Pekkton®ivory) when veneered with light-cured composite. The crowns will be tested and compared with equivalent zirconia-composite and metal-composite bi-layered crowns to assess the effect of different substructure materials on the structural integrity of these bi-layered crowns when veneered with the same material.

Materials and Methods

A mandibular first molar was prepared (1.5mm reduction) and duplicated using silicon to produce abutments from polyurethane (AlphaDie MF, Schutz Dental Group, Germany). It was then mounted in a base of the same material with the use of a light bodied impression material (President, Coltene/Whaledent, Switzerland) to simulate the periodontal ligament. The prepared tooth was scanned and a software was used to design the coping (exocad GmbH, Germany). All copings were CAD/CAM milled (wax copings to be casted for Metal-LC group) using (Roland DWX50, Roland DGA Corp. USA). Three groups of crowns (n=20) were fabricated with different substructure materials as follows:

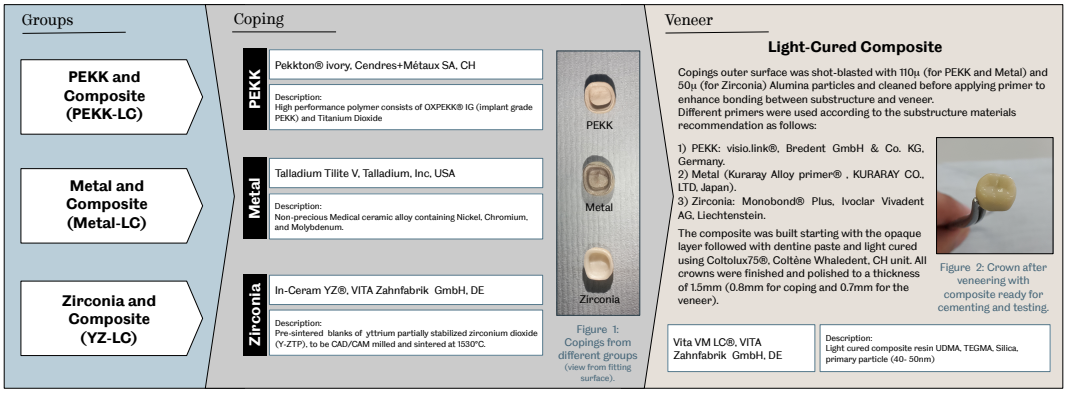


Figure 1: Copings from different groups (view from fitting surface).

Figure 2: Crown after veneering with composite ready for cementing and testing.

All crowns were cemented using resin cement (Multilink Automix, Ivoclar Vivadent AG, Liechtenstein) under 40N pressure for 3 minutes[1]. Each sample set was divided into two groups (central fossa or buccal cusp n=10) to allow the effect of different occlusal loading to be compared. A Lloyd LRX universal testing machine was used to apply a static load through a 4mm diameter ball steel indenter at a crosshead speed of 1mm/min with a latex sheet between crown and indenter. The force was measured in Newtons (N) and mode of fracture was also recorded and categorised according to Burke's classification[2].

Results

The fracture strength results of all groups are shown in Figure 3 and IBM SPSS Statistics 22 software was used to compare them using one-way ANOVA and Games-Howell tests to determine any significant difference between groups. The recorded mode of fracture for all groups can be seen in Table 1 and significance difference between groups were determined using Kruskul-Wallis and Mann-Whitney tests. Figure 4 shows some examples of crowns after the test.

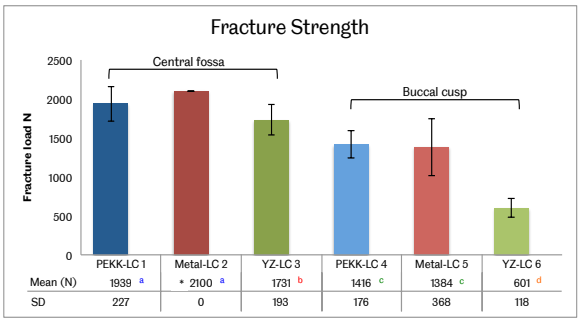


Figure 3: Fracture strength results in Newtons for all groups. *These samples withstood the maximum limit of the universal tester of 2100N without detecting any signs of fracture. Different superscript letters indicate significant differences (P<0.05) and groups with same superscript letters indicate no significant difference (P>0.05).

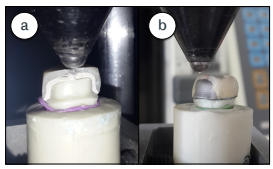


Figure 4: a) PEKK-LC crown with severe fracture. b) Metal-LC crown with code 2 veneer fracture.

Table 1: Mode of fracture for all tested crowns following Burke's classification (1 minimal fracture and 5 severe fracture). The letter "v" indicate fracture within the veneer only e.g.. Figure 4b. *These samples showed no signs of fracture. Different superscript letters indicate significant differences (P<0.05) and groups with same superscript letters indicate no significant difference (P>0.05).

Groups		Fracture Code				
		1	2	3	4	5
Central fossa	PEKK-LC 1[a]	4	0	1	1	4
	Metal-LC 2*	0	0	0	0	0
	YZ-LC 3[a]	0	0	1	3	6
Buccal cusp	PEKK-LC 4[a]	0	1	3	2	4
	Metal-LC 5[b]	0	8v	1v	1v	0
	YZ-LC 6[b]	0	10v	0	0	0

Conclusion

The occlusal fracture resistance of PEKK based crowns showed significantly higher strength than zirconia based crowns, and comparable results to metal-based crowns with no significant difference.

References

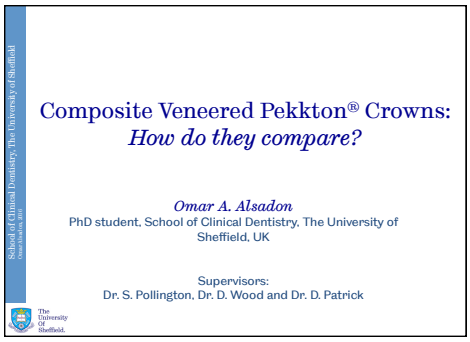
1- Tsitrou, E A., Northeast, S E and van Noort. R. "Evaluation of the marginal fit of three margin designs of resin composite crowns using CAD/CAM." Journal of Dentistry 35.1 (2007): 68-73.
2- Burke, F. J. T. "Maximising the fracture resistance of dentine-bonded all-ceramic crowns." Journal of Dentistry 27.3 (1999): 169-173.

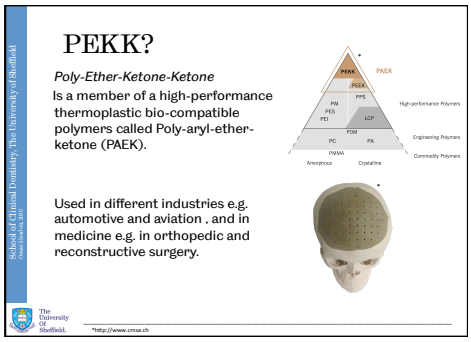
* This research is part of a sponsored PhD course for the presenter by King Saud University, Saudi Arabia.

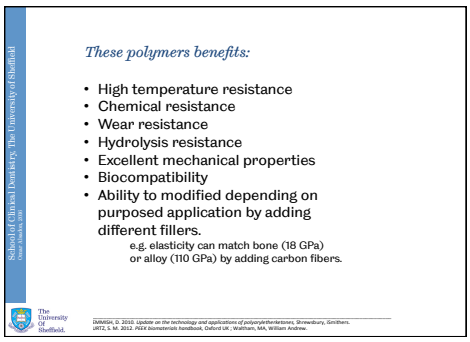
§ The researchers would like to thank Cendres+Métaux for their support and for providing Pekkton® ivory.

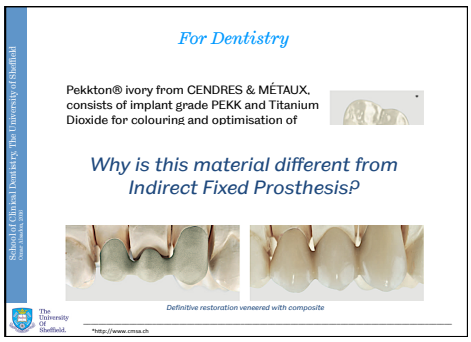
13.1.5. Pekkton Circle presentation, September 2016, Biel-Bienne, Switzerland.

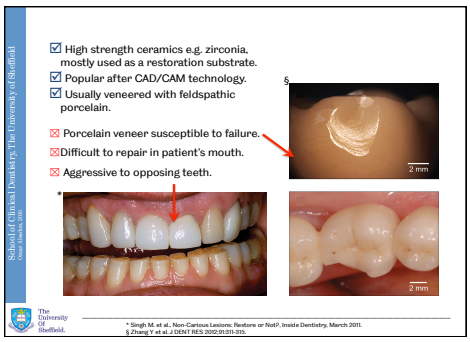
04/10/2016

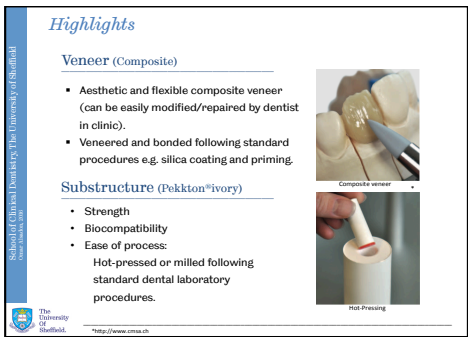












04/10/2016

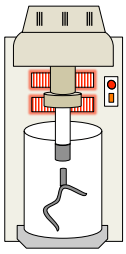
Aim

Assess PEKK based bi-layered crowns veneered with composite against other crowns in the aspects of:

- Aesthetics
- Structural integrity
- Durability

Objectives

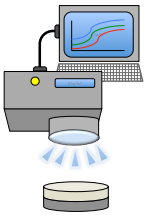
Pressing methodology
To optimise the pressing parameters of PEKK using a standard ceramic pressing furnace



Objectives

Pressing methodology
To press PEKK using standard ceramic pressing furnace

Aesthetics
Optical properties and translucency of PEKK/composite bi-layered samples against other zirconia and metal based bi-layered groups.

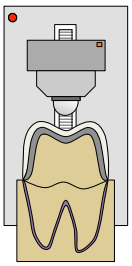


Objectives

Pressing methodology
To press PEKK using standard ceramic pressing furnace

Aesthetics
Optical properties and translucency of PEKK/composite bi-layered samples against other zirconia based bi-layered groups.

Structural integrity
Fracture resistance of the PEKK/composite crowns will be tested with other zirconia based bi-layered crowns.



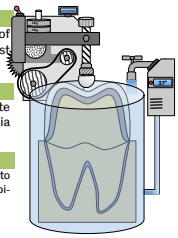
Objectives

Pressing methodology
To press PEKK using standard ceramic pressing furnace

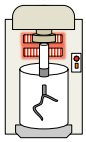
Aesthetics
Optical properties and translucency of PEKK/composite bi-layered samples against other zirconia based bi-layered groups.

Structural integrity
Fracture resistance of the PEKK/composite crowns will be tested with other zirconia based bi-layered crowns.

Durability
Evaluated by subjecting bi-layered crowns to fatigue testing with other zirconia based bi-layered crowns.



I: Pressing methodology: Optimising pressing parameters



04/10/2016

I: Pressing methodology

Initial pressing trials using standard ceramic pressing furnace
(IVOCLAR EP3000 pressing furnace)

Pilot pressing

Symbol	Parameter	Value range
B	Standby temperature	100-700 °C
t	Temperature increase rate	10-140 °C/min
T	Holding temperature	100-1200 °C
H	Holding time (min : sec)	00:00-60:00
E	Abort speed	0-100000 µm/min

Pressing parameters for IVOCLAR EP3000.

Electrical thermometer measuring ring's temperature after wax burn-out

*http://www.cmsa.ch

I: Pressing methodology

Initial pressing trials using standard ceramic pressing furnace
(IVOCLAR EP3000 pressing furnace)

✖ Mould too hot

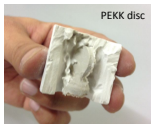
✖ No press

✖ Investment ring crack

✖ Incomplete press

I: Pressing methodology

Ring size & plunger	Wax burn-out preheating furnace	Ivoclar EP3000	
		Cooling	Pressing
100g & disposable plunger	850°C 45min	365°C (standby & holding temp.) → 25min → end program	362°C (standby & holding temp.) → 7min → press (abort speed 100)



PEKK disc

Crown coping

II: Aesthetics
Optical Properties

II: Aesthetics
Methods

PEKK

Pekkton® Ivory, Cendres+Metaux SA, CH

Metal

Talladium Title V, Talladium, Inc, USA

Zirconia

In-Ceram YZB, VITA Zahnfabrik GmbH, DE

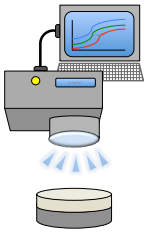
+ Composite

Spectrophotometer

Sample groups fabricated following manufacturer guidelines for each material and finished with P400-P800 abrasive paper.

* Following manufacture thickness recommendation for crowns.

II: Aesthetics
Methods



Bi-layers groups

- PEKK + Composite
- Zirconia + Composite
- Metal + Composite

RESULTS

- CIE L*a*b*
- Colour difference (ΔE)
- Spectral Reflectance and average reflectance

04/10/2016

II: Aesthetics

Results

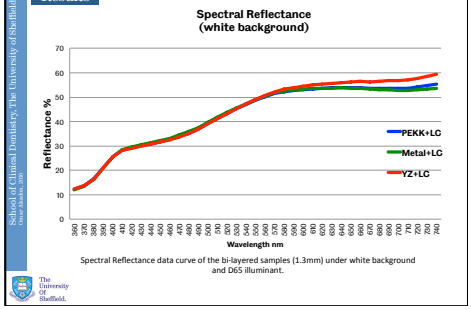
CIE L*a*b* values of the bi-layered samples of 1.3mm thickness under black and white background

Groups with different superscript letters indicate significant differences (P<0.05).

Material	L* Lightness		a* Red-green		b* Blue-yellow	
	Black	White	Black	White	Black	White
PEKK/Composite	74.26[a]	74.51[a]	2.29[a]	2.31[a]	17.83[a]	17.81[a]
Zirconia/Composite	74.1[a]	74.67[a]	2.4[a]	3.17[a]	18.65[a]	19.21[a]
Metal/Composite	74.5[a]	74.5[a]	1.9[a]	1.93[a]	18.2[a]	18.2[a]

II: Aesthetics

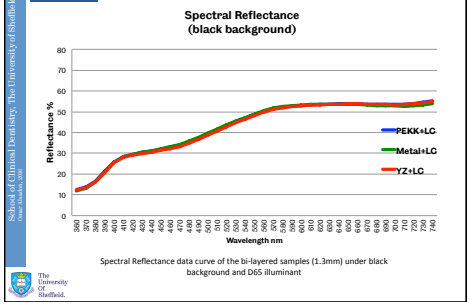
Results



Spectral Reflectance data curve of the bi-layered samples (1.3mm) under white background and D65 illuminant.

II: Aesthetics

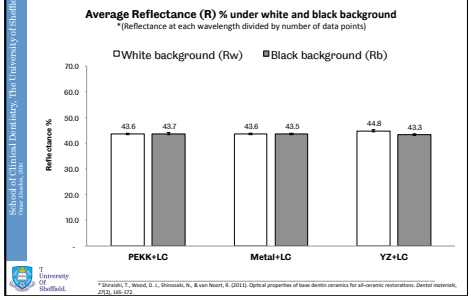
Results



Spectral Reflectance data curve of the bi-layered samples (1.3mm) under black background and D65 illuminant

II: Aesthetics

Results



* Shirakiri, T., Wood, D. J., Shinozaki, N., & van Noort, R. (2011). Optical properties of base dentin ceramics for all-ceramic restorations. *Dental materials*, *27*(2), 165-172.

II: Aesthetics

Results

Colour difference ΔE between composite veneered groups

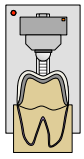
$[\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}]^*$

Groups	ΔE	
	White	Black
PEKK-LC & Metal-LC	0.40	0.28
PEKK-LC & YZ-LC	1.30	0.60

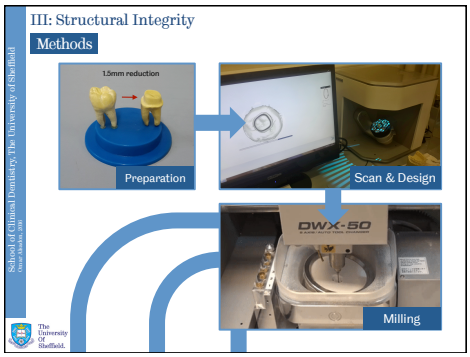
ΔE= **1.0** could be noticeable
ΔE= up to **3.3** is Acceptable

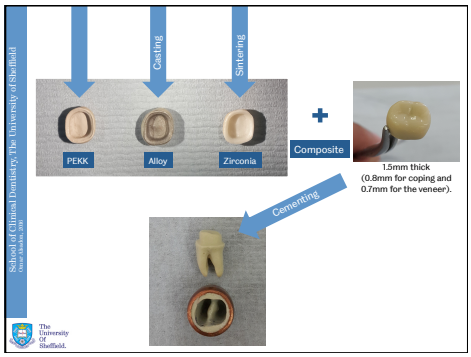
- Commission Internationale de l'Eclairage. (2004). *Colorimetry: Technical Report*. Central Bureau of the CIE.
- UM, C. M. & RUYTER, I. E. 1991. Staining of resin-based veneering materials with coffee and tea. *Quintessence international (Berlin, Germany : 1985)*, 22, 377-86.

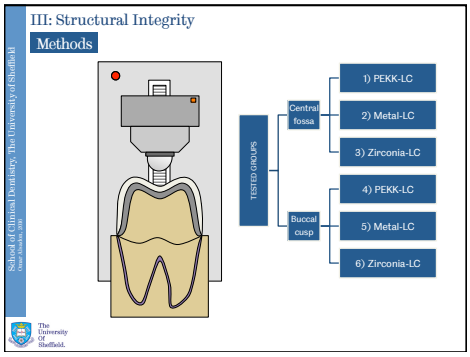
III: Structural Integrity
Occlusal Fracture Resistance

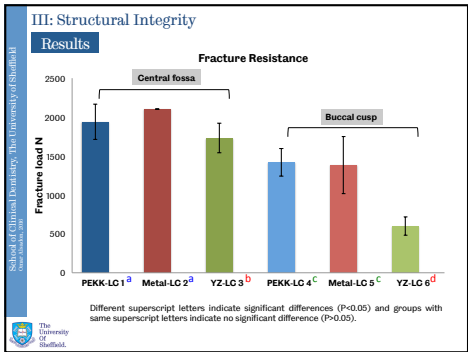


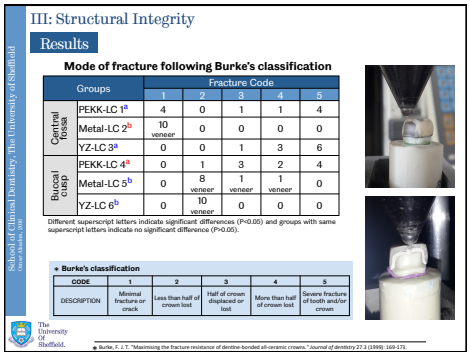
04/10/2016

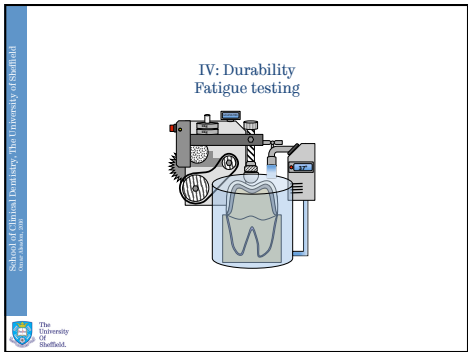

III: Structural Integrity
Methods
1.5mm reduction
Preparation
Scan & Design
DWX-50
Milling


Casting
Sintering
PEKK
Alloy
Zirconia
Composite
1.5mm thick
(0.8mm for coping and
0.7mm for the veneer).
Cementing

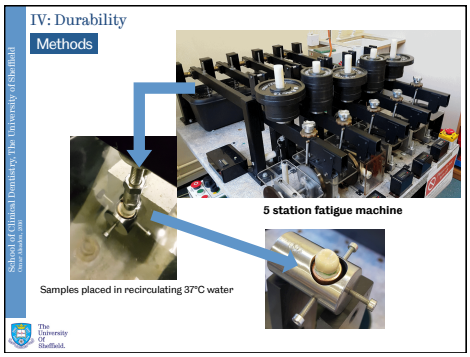

III: Structural Integrity
Methods
TESTED GROUPS
Central fossa
Buccal cusp
1) PEKK-LC
2) Metal-LC
3) Zirconia-LC
4) PEKK-LC
5) Metal-LC
6) Zirconia-LC

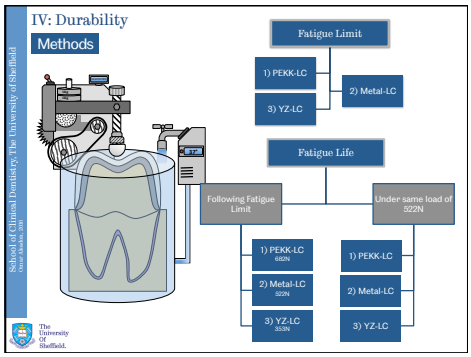

III: Structural Integrity
Results
Fracture Resistance
Central fossa
Buccal cusp
Fracture load N
2500
2000
1500
1000
500
0
PEKK-LC 1 a
Metal-LC 2 a
YZ-LC 3 b
PEKK-LC 4 c
Metal-LC 5 c
YZ-LC 6 d
Different superscript letters indicate significant differences (P<0.05) and groups with same superscript letters indicate no significant difference (P>0.05).

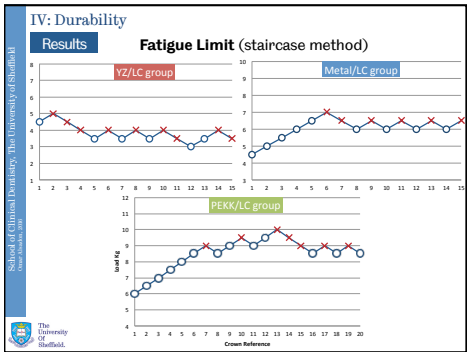

III: Structural Integrity
Results
Mode of fracture following Burke's classification
Groups
Fracture Code
1 2 3 4 5
Central fossa
PEKK-LC 1 a 4 0 1 1 4
Metal-LC 2 b 10 veneer 0 0 0 0
YZ-LC 3 a 0 0 1 3 6
Buccal cusp
PEKK-LC 4 a 0 1 3 2 4
Metal-LC 5 b 0 8 veneer 1 veneer 1 veneer 0
YZ-LC 6 b 0 10 veneer 0 0 0
Different superscript letters indicate significant differences (P<0.05) and groups with same superscript letters indicate no significant difference (P>0.05).
Burke's classification
CODE 1 2 3 4 5
DESCRIPTION Minimal fracture or crack Less than half of crown lost Half of crown displaced or lost More than half of crown lost Severe fracture of tooth and/or crown

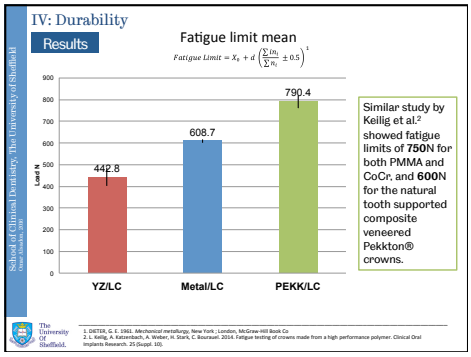

IV: Durability
Fatigue testing

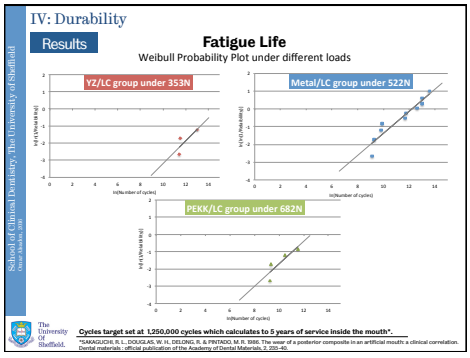
04/10/2016

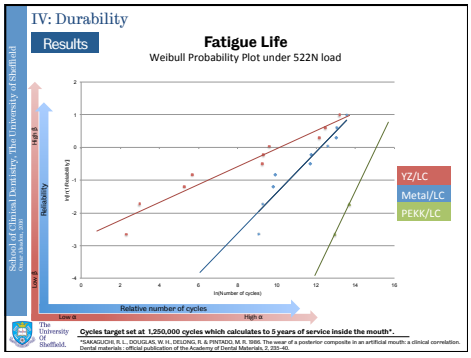

IV: Durability
Methods
5 station fatigue machine
Samples placed in recirculating 37°C water
School of Clinical Dentistry, The University of Sheffield


IV: Durability
Methods
Fatigue Limit
1) PEKK-LC
2) Metal-LC
3) YZ-LC
Fatigue Life
Following Fatigue Limit
Under same load of 522N
1) PEKK-LC 682N
2) Metal-LC 322N
3) YZ-LC 353N
1) PEKK-LC
2) Metal-LC
3) YZ-LC
School of Clinical Dentistry, The University of Sheffield


IV: Durability
Results
Fatigue Limit (staircase method)
YZ/LC group
Metal/LC group
PEKK/LC group
Load N
Crown Reference
School of Clinical Dentistry, The University of Sheffield


IV: Durability
Results
Fatigue limit mean
790.4
608.7
442.8
YZ/LC
Metal/LC
PEKK/LC
Load N
Similar study by Kellig et al.[2] showed fatigue limits of 750N for both PMMA and CoCr, and 600N for the natural tooth supported composite veneered Pekkton® crowns.
School of Clinical Dentistry, The University of Sheffield


IV: Durability
Results
Fatigue Life
Weibull Probability Plot under different loads
YZ/LC group under 353N
Metal/LC group under 522N
PEKK/LC group under 682N
Cycles target set at 1,250,000 cycles which calculates to 5 years of service inside the mouth*.
School of Clinical Dentistry, The University of Sheffield

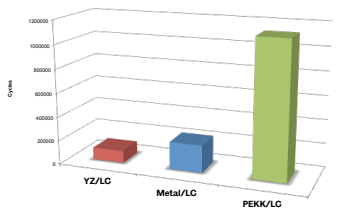

IV: Durability
Results
Fatigue Life
Weibull Probability Plot under 522N load
Reliability
Relative number of cycles
YZ/LC
Metal/LC
PEKK/LC
Cycles target set at 1,250,000 cycles which calculates to 5 years of service inside the mouth*.
School of Clinical Dentistry, The University of Sheffield

IV: Durability

Results

Fatigue Life

Average survived cycles under 522N load



Cycles target set at 1,250,000 cycles which calculates to 5 years of service inside the mouth*.

*SAKAGUCHI, R. L., DOUGLAS, W. H., DELONG, R., & PINTADO, M. R. 1986. The wear of a posterior composite in an artificial mouth: a clinical correlation. Dental materials : official publication of the Academy of Dental Materials, 2, 235–40.

IV: Durability

Results

Fatigue Life

Mode of fracture following Burke's classification

	Groups		Fracture Code 1	2	3	4	5
Different loads	353N	YZ-LC[a]	7 veneer	0	1 veneer	0	2 veneer
	522N	Metal-LC[b]	2 veneer	2 veneer	4 veneer	2 veneer	0
	682N	PEKK-LC[a]	5 veneer	4 veneer	0	0	1 veneer

	Groups		Fracture Code 1	2	3	4	5
Same load 522N		YZ-LC[b]	0	0	3 veneer	1	6
		Metal-LC[b]	2 veneer	2 veneer	4 veneer	2 veneer	0
		PEKK-LC[a]	8 veneer	2 veneer	0	0	0

Burke's classification

CODE	1	2	3	4	5
DESCRIPTION	Minimal fracture or crack	Less than half of crown lost	Half of crown displaced or lost	More than half of crown lost	Severe fracture of tooth and/or crown

Burke, F. J. T. "Maximising the fracture resistance of dentine-bonded all-ceramic crowns." *Journal of dentistry* 27.3 (1999): 169-173.

Conclusions

Pilot study

PEKK successfully pressed using a standard dental lab ceramic pressing furnace.

Aesthetics

Having different substructure material did not cause any significant difference in optical properties between PEKK, zirconia and metal composite veneered groups

Structural integrity

The fracture resistance of PEKK based crowns showed significantly higher strength than zirconia based crowns, and comparable results to metal-based crowns with no significant difference.

Durability

PEKK crowns showed the highest fatigue limit. For the Fatigue Life, PEKK crowns showed comparable results under it's fatigue limit load and superior results under 522N against zirconia and metal based crowns.

Thank You

Future work

- Investigate minimal preparation possibility.
- Finite Element Analysis.
- Bonding trials between veneer and coping.
- Bonding trials between PEKK and resin cement.
- Cost effectiveness.
- Clinical trials.