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MONOLITHIC ZIRCONIUM DIOXIDE AS A FULL CONTOUR RESTORATIVE MATERIAL

With Special Emphasis on the Optical and Mechanical Properties

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بسم الله الرحمن الرحيم

"In the name of God, the Most Gracious, the Most Merciful"

To my beloved family and mentors,
for their endless support.

ABSTRACT

Taiseer Sulaiman

Monolithic zirconium dioxide as a full contour restorative material: With special emphasis on the optical and mechanical properties

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Full contour monolithic zirconia restorations have shown an increased popularity in the dental field over the recent years, owing to its mechanical and acceptable optical properties. However, many features of the restoration are yet to be researched and supported by clinical studies to confirm its place among the other indirect restorative materials

This series of *in vitro* studies aimed at evaluating and comparing the optical and mechanical properties, light cure irradiance, and cement polymerization of multiple monolithic zirconia material at variable thicknesses, environments, treatments, and stabilization.

Five different monolithic zirconia materials, four of which were partially stabilized and one fully stabilized were investigated. The optical properties in terms of surface gloss, translucency parameter, and contrast ratio were determined via a reflection spectrophotometer at variable thicknesses, coloring, sintering method, and after immersion in an acidic environment. Light cure irradiance and radiant exposure were quantified through the specimens at variable thicknesses and the degree of conversion of two dual-cure cements was determined via Fourier Transform Infrared spectroscopy. Bi-axial flexural strength was evaluated to compare between the partially and fully stabilized zirconia prepared using different coloring and sintering methods. Surface characterization was performed using a scanning electron microscope and a spinning disk confocal microscope.

The surface gloss and translucency of the zirconia investigated were brand and thickness dependent with the translucency values decreasing as the thickness increased. Staining decreased the translucency of the zirconia and enhanced surface gloss as well as the flexural strength of the fully stabilized zirconia but had no effect on partially stabilized zirconia. Immersion in a corrosive acid increased surface gloss and decreased the translucency of some zirconia brands. Zirconia thickness was inversely related to the amount of light irradiance, radiant exposure, and degree of monomer conversion. Type of sintering furnace had no effect on the optical and mechanical properties of zirconia.

Monolithic zirconia maybe classified as a semi-translucent material that is well influenced by the thickness, limiting its use in the esthetic zones. Conventional acid-base reaction, autopolymerizing and dual-cure cements are recommended for its cementation. Its desirable mechanical properties give it a high potential as a restoration for posterior teeth. However, close monitoring with controlled clinical studies must be determined before any definite clinical recommendations can be drawn.

Keywords: Monolithic zirconia, Dental ceramics, Dual-cure cements, Mechanical properties, Optical properties, Erosive gastric acid, Light-cure irradiance, Radiant exposure.

TIIVISTELMÄ

Monoliittinen zirkonium dioksidi anatomiseen muotoon tehtyjen restauraatioiden materiaalina: kokeellisia tutkimuksia materiaalin optisista ja mekaanisista ominaisuuksista.

Turun yliopisto, Lääketieteellinen tiedekunta, Hammaslääketieteen laitos, Hammasprotetiikan oppiaine, Kansallinen suun terveystieteiden tohtoriohjelma- FINDOS Turku

Zirkonian suosio on kasvanut viime vuosina lopulliseen muotoonsa valmistetuissa hammasproteettisissa rakenteissa materiaalin optisten ja mekaanisten ominaisuuksien parannuttua. Zirkoniarakenteet vaativat kuitenkin lisää materiaalitutkimuksia sekä kliinisistä kokemuksista saatavaa näyttöä ennen kuin materiaali vahvistaa paikkansa muiden epäsuorissa restauraatioissa käytettyjen materiaalien joukossa.

Näiden tutkimusten tavoitteena on ollut verrata erilaisten monoliittisten zirkonia materiaalien optisia ja mekaanisia ominaisuuksia ja valokovetuksen toimivuutta sekä selvittää materiaalin paksuuden, pintakäsittelyn ja stabilointiasteen vaikutusta niihin.

Tutkimukseen valittiin neljä osittain stabiloitua ja yksi kokonaan stabiloitu zirkonia materiaali. Optiset ominaisuudet arvioitiin materiaalin pinnan kiillon, läpikuultavuuden ja kontrastisuhteen perusteella. Analyysit tehtiin heijastus spektrofotometrilla ottaen huomioon tutkittavan materiaalin paksuus, värjäys, sintrausmenetelmä sekä happoaltistuksen vaikutus. Kahden zirkoniarakenteiden kiinnittämiseen käytettävän kaksoiskovetteisen kiinnityssementtien toimivuus testattiin eripaksuisilla testikappaleilla määrittämällä kovetusvalon irradianssi ja säteilyn läpäisevyys sekä sementin kovettumisaste. Mittaukset suoritettiin FTIR spektroskopiaa käyttämällä. Biaksiaalista taivutusluujuusmittausta käytettiin selvittämään värjäyksen ja erilaisten sintrausmenetelmien vaikutus osittain tai kokonaan stabiloitujen zirkonia materiaalien mekaanisiin ominaisuuksiin. Materiaalien pintarakenteet arvioitiin pyyhkäisyelektroni ja konfokaali mikroskopiaa käyttämällä.

Tutkittavien materiaalien pintakiilto ja läpikuultavuus riippuivat materiaalityypistä ja paksuudesta, joka oli kääntäen verrannollinen läpikuultavuuteen. Materiaalin värjäys vähensi zirkonian läpikuultavuutta, mutta paransi kokonaan stabiloidun zirkonian pintakiiltoa ja mekaanista lujuutta. Vastaavaa vaikutusta ei todettu osittain stabiloidulla zirkonialla. Altistaminen syövyttävälle hapolle lisäsi joidenkin tutkittavien materiaalien pinnan kiiltoa, mutta vähensi niiden läpikuultavuutta. Zirkoniamateriaalin paksuus oli kääntäisesti verrannollinen valon irradianssiin, säteilyn läpäisevyyteen ja sementin kovettumisasteeseen. Sintrausmenetelmällä ei todettu olevan vaikutusta materiaalien optisiin tai mekaanisiin ominaisuuksiin.

Monoliittiset zirkoniamateriaalit voidaan luokitella osittain läpikuultaviksi materiaaleiksi, mikä rajoittaa niiden käyttöä esteettisesti vaativilla alueilla. Perinteisiä ja kaksoiskovetteisia sementtejä voidaan suositella zirkoniarakenteiden kiinnittämiseen. Hyvien mekaanisten ominaisuuksiensa ansiosta lopulliseen anatomiseen muotoon tehtyjä zirkonia rakenteita voidaan käyttää takahammasalueiden restauroinneissa. Kontrolloituja kliinisiä tutkimuksia kuitenkin tarvitaan ennen kuin lopullisia johtopäätöksiä zirkonian käyttäytymisestä voidaan esittää.

Avainsanat: Monoliittinen zirkonia, Hammaskeraami, Kaksoiskovetteinen sementti, Mekaaninen ominaisuus, Optinen ominaisuus, Vatsahappo, Valokovetus, Irradianssi, Sätelyn läpäisevyys.

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LIST OF ABBREVIATIONS

°C	Degree Celsius
ANOVA	Analysis of variance
CAD/CAM	Computer aided design/computer-assisted manufacturing
CR	Contrast ratio
DC	Degree of conversion
EDX	Energy dispersive x-ray spectroscopy
FSZ	Fully stabilized zirconia
FTIR	Fourier transform infrared spectroscopy
GERD	Gastroesophageal reflux disease
HCl	Hydrochloric acid
hrs	Hours
LTD	Low temperature degradation
mins	Minutes
MPa	Mega Pascal
n	Number of specimens
PSZ	Partially stabilized zirconia
SD	Standard deviation
secs	Seconds
SEM	Scanning electron microscope
TIE	Total irradiant energy
TP	Translucency parameter
XRD	X-ray diffraction
Y-TZP	Yttria-stabilized tetragonal zirconia polycrystals

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following original articles, which are referred to in the text by the Roman numerals I–IV.

I.   **Sulaiman TA**, Abdulmajeed AA, Donovan TE, Ritter AV, Vallittu PK, Närhi TO, Lassila LV. Optical properties and light irradiance of monolithic zirconia at variable thicknesses. Dental Materials, 2015.

II.   **Sulaiman TA**, Abdulmajeed AA, Donovan TE, Ritter AV, Vallittu PK, Lassila LV, Närhi TO. The degree of conversion of dual-polymerizing cements light-polymerized through monolithic zirconia of different thicknesses and types. Journal of Prosthetic Dentistry, 2015.

III.   **Sulaiman TA**, Abdulmajeed AA, Donovan TE, Vallittu PK, Närhi TO, Lassila LV. The effect of staining and vacuum sintering on optical and mechanical properties of a partially and fully stabilized monolithic zirconia. In press, Dental Materials Journal, 2015.

IV.   **Sulaiman TA**, Abdulmajeed AA, Donovan TE, Shahramian K, Leena Hupa, Lippo V. Lassila, Vallittu PK, Närhi TO. Impact of simulated gastric acid on surface topography and optical properties of monolithic zirconia. In press, Dental Materials, 2015.

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1. INTRODUCTION

Over the past decade there has been an increasing demand for metal-free restorations (e.g. ceramics and resin composites) to replace full cast gold or metal-based restorations mainly due to cost, esthetics, and biosafety. Most of the all-ceramic crowns are now fabricated using computer aided design/computer-assisted manufacturing (CAD/CAM) enabling to some extent control of time and cost. Despite this new era of all ceramic restorations, these restorations must be on a par with porcelain fused to metal restorations, the gold standard of fixed prosthodontics, and that these ceramic systems should prove success in independent clinical trials of 95% over a 3-5 year period (Schärer, 1997).

All-ceramic material belong to one of the following classes (Kelly & Benetti, 2011): (1) predominantly glassy materials, mainly known as aluminosilicate glasses such as feldspathic porcelains; (2) particle filled glasses, where fillers (e.g. leucite) are added and uniformly distributed by 'dispersion strengthening' such as IPS Empress Esthetic (Ivoclar Vivadent AG; Schaan, Liechtenstein); (3) polycrystalline ceramics, where there is no glassy components; the atoms are densely packed into regular arrays, rendering them tougher and stronger than glassy ceramics, such as Lava (3M-ESPE, St. Paul, MN).

Zirconia ceramics have been used in fixed dental prosthesis over the past 20 years, first introduced as a substructure. This polycrystalline ceramic demonstrates superior mechanical properties, biocompatibility, and ease of fabrication via CAD/CAM technology. However, an early issue emerged as a chipping of the veneering porcelain, which was reported in many studies (Larsson *et al.,* 2006; Raigrodski *et al.,* 2006; Sailer *et al.,* 2006, 2007). It was evident in the literature that the zirconia substructure rarely suffered from any fracture, due to its high strength owing to the 'transformation toughening' phenomenon as well as its relatively high fracture toughness and flexural strength, rendering zirconia the strongest amongst all dental ceramics available today.

To avoid the issue of porcelain veneer chipping and taking advantage of zirconia's strength, the idea of fabricating a crown made of full zirconia material was conceived, eliminating the veneering porcelain and relying on stains and glazes to help achieve zirconia's esthetic appearance. Ever since, the applications of full contour zirconia in the dental field have been immense, including single and multiple unit restorations, abutments, full arch implant supported prosthesis, and orthodontic brackets (Anusavice, 2013). With these high premature recommendations for its use, mainly driven by the manufacturers, it is of crucial importance to fully investigate monolithic zirconia material in terms of blank fabrication, pre-sintered stage machining, methods of sintering, surface treatments, and most importantly thermal degradation, as it still threatens the potential longevity and success of zirconia material. With well-engineered *in vitro* studies that will

lay the foundation to orchestrate proper randomized clinical trials; and only then, it will be possible to offer clinical guidance and recommendations for zirconia restorations.

Further exploring the optical, chemical, and mechanical behavior of monolithic zirconia material and whether these are influenced by different manufacturing vendors, thicknesses, staining and how it will interact with an acidic environment were the main emphases of the present research project.

2. REVIEW OF LITERATURE

2.1. History of zirconia

Zirconia, formally known as zirconium dioxide (ZrO_2), is a white crystalline oxide of zirconium. Zirconium, a metal, comes from the Persian word *Zargon* that means golden in color (Piconi and Maccauro, 1999). Martin Heinrich Klaproth, a German chemist, isolated the oxide of zirconium from zircon (which is zirconium silicate, ZrSiO4) in 1789. Natural zirconium contains also radioactive isotopes. Most commonly used compound in stabilization of phase structures of zirconia is yttrium oxide, metal element which was first time found by Finnish chemist Johan Gadolin at the University of Turun Akatemia in 1794. Metallic zirconium was first prepared in 1824 by Jons J. Berzelius, a Swedish chemist (Heiserman, 1992). The discovery of zirconia's potentials (i.e. unique chemical, mechanical, and electrical properties) led to its use in many applications as heat insulators, knife blades, oxygen sensors, and fuel cells (Anusavice, 2013).

The use of zirconia was not explored for medical use until 1969, when Helmer and Driskell wrote the first paper on the use of zirconia as a biomedical application (Helmer & Driskell, 1969). Alumina then, was used in many implant restorations, but suffered from low fracture toughness which lead to its replacement with zirconia especially after the revolutionary discovery of the transformation toughening of zirconia in the mid-1970's (Garvie *et al.*, 1975) and eventually, zirconia was first introduced as a femoral head for hip replacement in orthopedics by Christel *et al.* in the late 1980's (Christel *et al.,* 1988). Hundreds of thousands of zirconia femoral heads have been placed ever since, till the early 2000's where many of these femoral heads began to fail owing it to the element of thermal degradation (aging) of zirconia. Manufactures claimed it was limited, till 400 femoral heads failed in one year, leading to a state of confusion and panic among the orthopedic surgeons and patients (Chevalier, 2006). This lead to a catastrophic impact for the use of zirconia whereby the market sales dropped 90% between 2000 and 2001. Surprisingly, the dental community saw the potentials of zirconia, and started their research and development to build on its mechanical and esthetic properties to make it more accessible for dental applications. Zirconia restorations were first introduced in prosthetic dentistry as a core material and then layered by feldspathic porcelain. It had many desirable esthetic properties and strength which enabled it to be used either as single or multiple unit bridges. Chipping of the layering porcelain, was the main issue that faced layered zirconia restorations, and fracture of the core was never reported (Kelly & Benetti, 2011). From that scenario the concept of a full contour monolithic zirconia restoration was emerged. However, there is still a great need for extensive research to be able to conclude clinical recommendations. Clarke best underlined this turmoil of events*;* the absence of

rigorous scientific clarifications on thermal degradation has led to a series of misleading interpretations and confusion to the history of zirconia (Clarke *et al.,* 2003).

2.2.   Zirconia processing

2.2.1. Blank fabrication

Blank fabrication is the first and very crucial step in the fabrication process of zirconia. The following factors may portray in the final zirconia property:

- *Powder chemical purity:* it has been documented that the more impurities incorporated in the zirconia powder will lead to a greater grain size and favors more yttria transport, depleting the tetragonal grains rendering more cubic phase formation, which in turn results in a less stable and a more transformation susceptible zirconia (Stoto *et al.,* 1991 and Chevalier *et al.,* 2004).

- *Granule characteristics and type of pressing:* typical crystallite size in the zirconia powders is around 30-40 nm, from which agglomerates of 20-80 μm are then produced. When the processing is uniaxially pressed and due to the lack of intense compaction compared to the isostatic pressing, these coarse agglomerates leave micropores at the grain boundaries, which can render the zirconia more susceptible to low temperature degradation (LTD) by water diffusion (Swain, 2014). The pre-sintered zirconia blanks at this stage can influence the machinability of the zirconia, the form that chippings can take, and the final sharpness of zirconia (Filser *et al.,* 2003).

2.2.2. Sintering process

The sintering times and temperatures have a direct impact on zirconia's grain size, amount of cubic phase and yttrium distribution that in turn has an effect on zirconia's mechanical and optical properties (Denry & Kelly, 2014). It has been well-documented that as the sintering temperatures increase so does the grain size. Larger grains have less boundaries that can enhance the translucency of the zirconia but render them more susceptible to transformation, thus it may benefit the optical properties but affect its stability (Denry & Kelly, 2014).

Sintering consists of at least two heat-activated processes, densification and grain growth. The most common method for sintering zirconia would be the use of conventional furnaces at temperatures between 1350-1600°C and holding times ranging from 2-4 hrs. Multiple alternative methods for sintering zirconia have been introduced such as microwave sintering, spark plasma sintering, and use of vacuum furnaces, all aiming to improve the mechanical and esthetic properties of the zirconia, and to some extent save on sintering time and energy. In a vacuum furnace, the absence of air or other gases

prevents heat transfer with the product through convection and removes a source of contamination. Yet, some manufacturers claim that use of vacuum furnaces can enhance mechanical properties and increase the translucency of the zirconia. As many features of zirconia are yet to be clinically proven, information regarding the effects of LTD on the clinical performance of dental zirconia has never been reported in the clinical trials. There rather seems to be many factors that can trigger LTD as low-grade powders, high sintering temperatures, and aqueous environments (Keuper *et al.,* 2013).

2.2.3. Zirconia coloring (staining)

Zirconia, and its inherent opacity, and whether it will ever mimic the color and translucency of the natural dentition, is arguably one of the biggest challenges facing the clinical acceptance of monolithic zirconia. From a ceramic-engineering point of view, it would be best to add the coloring oxides to the powders before it is pressed. Color-doping of the powder is another possibility. The large number of shades required makes these techniques rather challenging and costly. Infiltration of metal salts at low concentration has been used to color zirconia (Suttor *et al.,* 2004). Non-uniform colors and limited diffusion depth have been reported as some setbacks to this technique (Oh *et al.,* 2012).

In a study determining the effect of staining zirconia framework in its pre-sintered stage with different colors on its mechanical properties and surface microhardness the authors concluded that there was a minor reduction in the strength and microhardness of zirconia after staining, and the staining of zirconia led to some dimensional changes which can affect the fitting accuracy of the final restoration (Hjerppe *et al.,* 2008).

The mentioned coloring methods can have an effect through crystallographic and microstructural changes that can in turn affect the mechanical properties of zirconia. Minimum data in the literature is available on the effect of zirconia coloring via metal-salts on its esthetic and mechanical properties.

2.3.   Material properties

2.3.1. Transformation toughening phenomenon

Zirconia, a polymorph, exists at room temperature in its monoclinic (*m*) form (pure zirconia). As temperature rises to 1170°C it transforms into its tetragonal (*t*) form and then to its cubic (*c*) form at temperatures reaching approximately 2370°C, with melting point at temperatures more than 2716°C (Subbarao, 1981). As foreseen by Garvie *et al.*, pure zirconia undergoes phase transformation upon cooling (*t-m*). This transformation is accompanied by an approximately 3% volume expansion which can produce cracks in the bulk of the material and eventually catastrophic failure (Garvie *et al.*, 1975). It has been reported that the discovery of adding CaO to stabilize cubic zirconia at room temperature

dates back to the beginning of the 20th century (Ruff, 1929). Ever since, the ceramic engineering community has been researching the possibilities of adding different oxides as MgO, La_2O_3 and Y_2O_3 to stabilize *t* and *c* phases of zirconia at room temperatures. ***Partial stabilization*** by 2-5 Mol% of yttrium oxide, formally known as yttria-stabilized tetragonal zirconia polycrystals (Y-TZP), is commonly used in the dental field and will be referred to as (partially stabilized zirconia, PSZ) in this series of studies. On the other hand, ***full stabilization*** by <8 Mol% yttrium oxide is known as fully stabilized zirconia (FSZ) (Goff *et al.*, 1999), and will be referred as such in the following studies as well.

The metastable tetragonal phase that results from the addition of yttria oxides to zirconia, is the toughest and most desired form. As a crack propagates towards the core of the material, tensile stresses develop around the tip of the crack, transforming the tetragonal particles to monoclinic. Monoclinic particles are larger in size, and that is accompanied by a compressive stress that opposes the crack tip and prevents its propagation, thus increases its localized fracture toughness (Figure 1). The transformation toughening phenomena increases the zirconia's flexural and tensile fracture resistance. However, excessive grinding, temperature changes and stresses may exceed the compressive strengths around the crack tip, and the crack will propagate towards the core of the material leading to complete failure of the zirconia. Therefore, the transformation toughening phenomena may be beneficial to the strength of zirconia at first, but as the fatiguing forces and stresses in moist environments increase, the challenges of zirconia strength becomes questionable. Yet the definitive answer awaits quantitative clinical assessment.
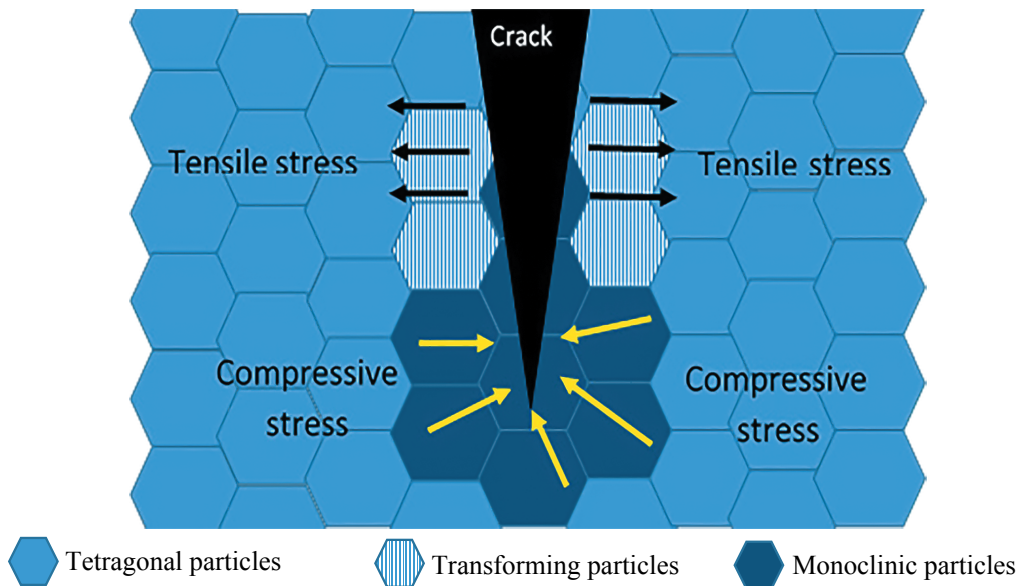

Figure 1: Schematic illustration of the transformation toughening phenomenon.

2.3.2. Physical properties

Owing to the transformation toughening phenomena, zirconia ceramics are considered the strongest and toughest among other present dental ceramics. Table 1 compares some of the properties of the most used ceramic materials in fixed prosthodontics. The flexural strength of zirconia can range from 800 to 1500 MPa (Tinschert *et al.,* 2000; Aboushelib *et al.,* 2008) in its partially stabilized form, as the fully stabilized form has been reported to possess lower flexural strengths of around 600 MPa. The fracture toughness of zirconia has also been reported to be high ranging from 6.3 to 11.5 MPa m$^{1/2}$ (Tinschert *et al.,* 2007; Aboushelib *et al.,* 2008). As for other properties such as chemical solubility, zirconia has been reported to be very stable (Piconi & Maccauro, 1999), which is considered important to withstand the different environmental changes in the oral cavity. Zirconia is also considered to have a low thermal conductivity, protecting the pulp from temperature changes in the mouth. The documented *in vitro* physical properties in the literature of zirconia are indeed impressive for a dental ceramic, with clinical studies awaits conclusions.

Table 1: Properties of zirconia in comparison to other ceramic materials used in fixed prosthetic dentistry.

Material	Flexural Strength (MPa)	Elastic modulus (GPa)	Hardness (VHN)	Reference
Feldspathic porcelain (Vita VMK 68)	83	57	703	(Tinschert *et al.,* 2000)
Leucite reinforced glass ceramic (Empress 2)	283	96	550	(Aboushelib *et al.,* 2007a)
Lithium disilicate (IPS e.max)	360	95	5800	(Ivoclar, Vivadent)
Alumina (Al2O3)	500	380	2200	(Piconi and Maccauro, 1999)
Zirconia (Y-TZP)	800-1500	210	1200	(Piconi and Maccauro, 1999)

2.3.3. Thermal degradation of zirconia

The excitement of the physical aforementioned properties of zirconia comes with a potential threat to the survival of this material. It was first reported by Kobayashi *et al.* that Y-TZP ceramics in a humid environment can suffer from a slow phase transformation from *t-m*, which can eventually lead to microcracking, dissipating the strength of zirconia (Kobayashi *et al.,* 1981). This negative phenomena was low-temperature degradation (LTD), which was best described by Chevalier of having the following features (Chevalier *et al.*, 1999):

- The transformation mainly occurs between temperatures of 200-300°C and is time dependent.

- The transformation is enhanced by water or water vapor.

- The transformation starts from the surface and proceeds towards the core of the material.

- The resistance to LTD is enhanced by smaller grain size and more stabilizing (yttria) content.

There have been many proposed theories explaining LTD. Lange *et al.,* described it as the reaction between H_2O and Y_2O_3 forming $Y(OH)_3$ depleting the stabilizer and triggering the transformation (Lange *et al.,* 1986). However, this theory has been somewhat rejected, as internal stresses leading to this transformation has been demonstrated, which leads us to the other two theories, one by Yoshimura *et al.,* where they proposed that the chemisorption of water can lead to stresses as a result of OH^- at the surface of the zirconia (Yoshimura *et al.,* 1989), and the other by Sato and Shimada, where their interpretation was that chemisorption of water forms Zr-OH at the surface, and the accumulated strain energy can lead to *t-m* transformation (Sato & Shimada, 1985). However, Guo questioned these theories and proposed that LTD should occur according to the following steps: (1) the chemical adsorption of H2O on the surface, (2) the reaction of H_2O with O^{2-} on the surface to form the OH^- ions, (3) the penetration of the OH^- ions into the inner part by the grain boundary diffusion, (4) the annihilation of the oxygen vacancies by the OH^- ions, consequently the OH^- ions are impregnated into the ZrO_2 lattice, (5) when the oxygen-vacancy concentration is reduced to a critical magnitude where the maintenance of the tetragonal phase is impossible, a tetragonal to monoclinic transformation occurs, further degradation can expand along the grain boundaries and the cracks (Guo,1999). A sophisticated study (Chevalier *et al.*, 1999), observed the *t-m* transformation, artificially aged zirconia in water and steam at 70 to 130°C, by XRD and optical interferometer techniques and fitted by the Mehl-Avrami-Johnson law. Chevalier concluded that each zirconia ceramic is unique in its susceptibility to LTD as each zirconia ceramic has different microstructure (density, grain size and yttrium content) and that nucleation and growth to be the key mechanism for *t-m* transformation. The nucleation and growth of a tetragonal grain can cause internal shear strains that can lead to the up-lift of that grain, transforming it to a larger monoclinic grain developing internal stresses which eventually leads to a cascade of events affecting the neighboring grains, microcracking and allowing water to penetrate towards the core of the material.

Newer more recent theories have emerged since Chevalier's theory, challenging the latter theory. Munoz-Tabares *et al.* in their work evaluated the subsurface microstructure and the nanoindentation behavior of hydrothermal degraded 3Y-TZP and concluded that monoclinic in-depth distribution follows a non-lineal gradient. Also, the thickness of the

transformation layer is larger than the thickness of the layer in which microcracks are detected. Grain boundary microcracks, which are predominantly parallel to the surface, are formed by shear deformation of the first martensitic plates produced in a grain partially transformed, which generate local tensile stresses at grain boundaries. The orientation of these microcracks is not favorable for water penetrating further into the material through the microcracks network. Monoclinic phase propagation (and subsequent microcracking) during degradation is assisted by stress-induced transformation mechanisms, where water is necessary to activate these mechanisms (Munoz-Tabares *et al.*, 2011) (Figure. 2).

The impact of LTD on the femoral heads maybe different from that on dental zirconia restorations as zirconias from different manufacturers behave differently to LTD depending on its microstructure. Further research is required to properly comprehend LTD and dental zirconia restorations.
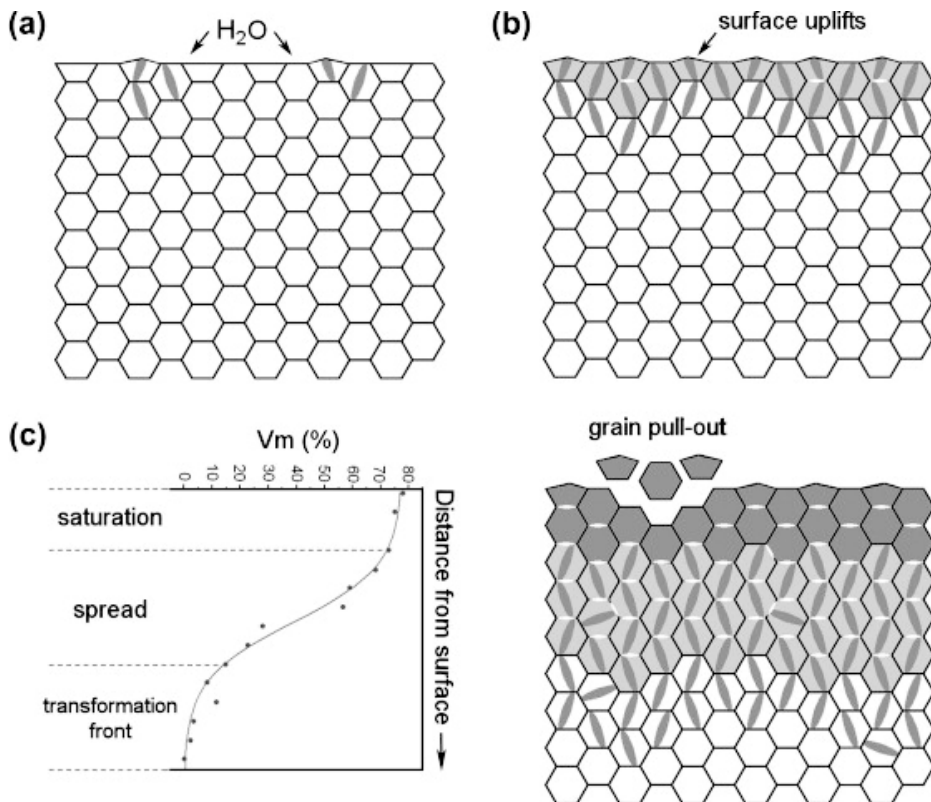
Figure 2: Micro-mechanism proposed for hydrothermal degradation. (a) Water adsorption on surface, destabilization of tetragonal phase and the subsequent transformation to monoclinic phase in preferential nucleation superficial points as pores or cubic grains. (b) Shear strain produced by formation of the martensite plates in a partially transformed grain is accommodated by grain boundary microcracking. (c) Once microcracking releases the constraint by decohesion of partially transformed grains, the rate of monoclinic phase propagation increases drastically until saturation. Reprinted, Munoz-Tabares et al., Acta Materialia. 2011; 59:473-84.

2.4.   **Zirconia applications in dentistry**

Zirconia ceramics was first introduced to the dental field in the early 1990's. The ability to highly refine and control zirconia powders, and the introduction of CAD/ CAM technology played a major role. Now, zirconia is considered the most interesting polycrystalline ceramic available in dentistry today due to the transformation toughening phenomena (Kelly & Benetti, 2011). The use of zirconia has rapidly increased in many dental applications, such as:

- *Implants:* The first reported use of zirconia in dentistry was by Cranin *et al.,* determining their biocompatibility in the oral cavity. Histological examinations revealed fibrointegration, indicating its possible use (Cranin *et al.,* 1975). It was till the beginning of the 90's, when Akagawa *et al.* started experimenting the use of zirconia as implants in animals (Akagawa *et al.,* 1993). It was followed by many *in vitro* and *in vivo* research proving the success of osteointegration, cell metabolism, collagen fiber orientation around the implant necks and soft tissue response, all in comparison to titanium implants. (Kohal *et al.,* 2004; Olivia *et al.,* 2007; Tete *et al.,* 2009). The use of zirconia implants is still premature, and yet to replace titanium implants.

- *Implant abutments:* Zirconia abutments can be custom milled by CAD/CAM technology in the laboratory and then inserted at the implant-abutment interface by a titanium screw. Or it can come as an 'all in-one' with the implant body and the abutment in one piece. The main advocate for the use of zirconia abutments was that its non-metallic appearance can enhance better color matching in the esthetic zone, especially now with the increased use of all-ceramic crowns, and the fact that the greyish hue of titanium abutment may show through the peri-implant tissues giving an unpleasing appearance (Yildirim *et al.,* 2000). Some studies have reported that the plaque accumulation around zirconia is less compared to that of titanium (Scarano *et al.,* 2004). The short term reported clinical trials have indicated that zirconia abutments could function without fracture (Nakamura *et al.*, 2010; Guess *et al.*, 2012). However, some in vitro studies have proven titanium abutments to have preferable fracture resistance than zirconia abutments. Att *et al.*, reported in a well-planned study after fatiguing the zirconia and titanium abutments in water, that titanium abutments had a better fracture resistance (Att *et al.*, 2009). Proper designing of the abutment along with controlled occlusion and final restoration should be planned thoroughly.

- *Root canal posts:* Also introduced in the beginning of the 90's, the white color of zirconia and its strength were suggested as an alternative to metal posts. Only some short-term clinical studies have confirmed its success (Kakehashi *et*

al., 1998). Most of the failures that were reported in retrospective studies were to loss of retention or extraction of the tooth (Paul & Werder, 2004; Bateli *et al.,* 2010). Zirconia posts are sensitive to fitting, which may require adjustments prior to cementing, and such adjustments may induce transformations within the zirconia leading to microcracks and eventually fracture. The increased stiffness and concentration of forces within the root, has been a main concern for zirconia application as root canal posts.

- *Orthodontic brackets:* Introduced in the 90's as well, for achieving a better esthetic outcome, yet no clear advantage for its use has been proven in any study. There has been no clinical study in the literature proving its advantageous implication in the orthodontic field.

- *Substructure for fixed dental restorations:* Zirconia ceramics can be milled as a monolithic restoration or as a bilayered structure made of a milled substructure and either a manually layered, hot pressed or a CAM designed veneering ceramic bonded to the coping. The zirconia ceramic can be milled either; in its pre-sintered stage as in Katana (Noritake, Japan) or partially sintered state as in IPS e.max ZirCAD (Ivoclar Vivadent) or fully sintered as in Kavo Everest ZH Blanks (Kavo Dental). The pre-sintered stage milling method is most probably preferred than the fully sintered as less robust machining is required, faster time and less cost. In addition, the surface flaws that may be incorporated to the fully sintered zirconia can affect its long-term strength.

One of the major concerns for use of zirconia in fixed prosthodontics is the need to adjust the zirconia coping or monolithic crown, as grinding induces flaws and microcracks, which can decrease the fracture resistance of the material (Kosmac *et al.,* 2000; Curtis *et al.,* 2006). Therefore, it has been recommended to avoid grinding zirconia. However, minor adjustments should be done with great care utilizing burs designated for zirconia adjustment, keeping in mind bur efficiency, speed and cooling. If there is a need to make any major occlusal adjustments remaking the crown is recommended.

Air-particle abrasion has been recommended for the treatment of restorations' interior surfaces as some studies have reported its benefits (Kern & Wegner, 1998). This topic has been an area of interest and research as air-particle abrasion can increase surface roughness and enhance the bond strength between the zirconia and the luting cement (Derand & Derand, 2000). It may also lead to surface phase transformation enhancing the zirconia's strength on one hand, and if not executed properly can induce microcracks and weaken the zirconia on the other. Many factors play a role such as; particle size, shape, blasting pressure, distance and time (Heikkinen *et al.,* 2007). Depending on the methodology used in different studies with the considerable variable factors, it can be

concluded from the literature that some studies favored air-particle abrasion (Kosmac *et al.,* 1999; Papanagiotou *et al.,* 2006; Karakoca & Yilmaz, 2009), enhancing the zirconia's strength. While others confirmed in their reports that the larger air abrading particle size decreased the surface roughness and had no effect on the strength (Curtis *et al.,* 2006). Therefore it can be suggested, that air-particle abrasion will incorporate stress on the surface tetragonal particles causing phase transformation. It may result in increasing the initial strength of zirconia, but as the restorations are fatigued in moist oral environments, microcracks may propagate.

The amount of randomized long term clinical trials supporting layered zirconias success rates are rather vague. But, one conclusion seems to be agreed upon, that the chipping of the veneering porcelain seems to plague all of these studies (Della Bona & Kelly, 2008). There have been many attempts to explain this issue such as unsupported porcelain, non-anatomic substructure design, weaker porcelain, mismatch of thermal conductivity and porcelain bonding. Kelly & Benetti described chipping as being the cause of residual stresses within the porcelain due to rapid cooling (Kelly & Benetti, 2011). Indeed, it has been agreed upon that thermal stresses due to lack of compatibility between the coefficient of thermal expansion of the zirconia core and the veneering ceramic is the main cause of the ceramic chipping (Tholey *et al.*, 2011; Choi *et al.*, 2011; Choi *et al.*, 2011; Stawarczyk *et al.*, 2012). Reducing these stresses can be possible by using a veneering ceramic with a coefficient of thermal expansion as close as possible to that of the zirconia core (Tholey *et al.*, 2011; Hallmann *et al.*, 2014), in addition to slow heating as well as slow cooling rate during the veneering process have been shown to reduce the incidence of chipping (Tan *et al.*, 2012).

Other problem that has been reported is prosthesis fracture at the connector area. A minimum of 4 mm connector diameter is currently recommended for fixed dental prostheses in the posterior region (Larsson *et al.,* 2007). As for marginal adaptation, it has been reported (Coli & Karlsoon, 2004; Att *et al.,* 2009; Gonzalo *et al.,* 2009) that fitting of zirconia restorations has been below the tolerated limit of 120 µm (Belser *et al.,* 1985).

2.5. Optical properties of teeth and indirect restorations

One of the greatest challenges in restorative dentistry is the ability of any type of restoration to mimic the appearance of natural tooth. Therefore, knowledge of the optical behavior of the teeth and restorative material is of utmost importance.

The major components of esthetic tooth appearance are:

- *Color*: described as being three-dimensional, Munsell was the first who put color into perceptual uniform and independent dimensions represented

by Hue, Value and Chroma (Kuehni, 2002). The International Commission on Illumination (CIE) described the conversion of the spectrophotometric measurements to three-color parameters (CIE L* a* b*) where L* refers to the lightness, a* redness to greenness and b* yellowness to blueness. Also, it pointed out the requirements to know the spectrum of light from the illuminant and how that light is transmitted or reflected from the object, and the human's ability to recognize hue, value and chroma (Johnston, 2009). The color receptors in the retina of the eye translate to the brain the color of an object. If the light is completely absorbed by the object, the object will appear black, and if the light is completely reflected by the object, it appears white.

- *Fluorescence*: is the phenomenon in which the light energy is absorbed by the material at a shorter wavelength and reflected with a wavelength spectrum longer than the incident light. In such case, the tooth actually becomes a lighting source (McLaren, 1997).

- *Opalescence*: is the scattering of the shorter wavelengths of light as it transmits through an object giving a bluish appearance under reflected light, and a brown-red appearance under transmitted light (McLaren, 1997).

- *Translucency*: the ability of a layer of colored substance to allow the appearance of an underlying background to show through (Johnston *et al.,* 1995).

The optical behavior of any material is dependent on many factors (Halliday & Resnick, 1993):

i) Light refraction: which means change in the direction of the light wave due to change in the transmission medium.

ii) Light dispersion: a wavelength-dependent refractive index, causes different colors to refract at different angles, splitting white light into a rainbow.

iii) Light transmission: is the fraction of incident light at a specified wavelength that passes through a sample.

iv) Light absorption: is the way in which the energy of the wavelengths is taken up by matter.

In dental ceramics, the amount of light that is absorbed, transmitted through, and/or reflected depends on the crystalline content, chemical nature, and particle size. If the particle size is larger than the incident wavelength (0.2 μm) then the light is reflected. A transmitting medium can be classified into three categories: (a) Transparent; which allows light passage without modification in its path, (b) Translucent; which allows light passage with modification to its path and (c) Opaque; where the light is absorbed and or

reflect, but not transmitted through. Translucency is affected by the presence or absence of color, thickness of the material, and surface texture. It has been reported as the shade of the restoration is darker, more light is absorbed and less transmitted, thus increasing the opacity of the restoration (Brodbelt *et al.,* 1980). The opacity of any given restoration increases as the thickness of the restoration increases (Ahmed, 2000). A restoration will also become more opaque when its surface roughness increases, as more light is diffusely reflected and the color tends to be more luminous (Villarroel *et al.*, 2011).

There have been many devices used in research to determine the translucency of a given material such as:

- *Spectrophotometer*: measures either the amount of light reflected from a sample object or the amount of light that is absorbed by the sample object. It can operate two different measuring geometries of specular component excluded (SCE), which excludes the specular component of light, and specular component included (SCI) which includes the specular component of light (ASTM E805-06, 2006). The difference between the SCE and SCI reflectance (ΔE*SCE-SCI) gives estimation about the surface gloss (Kress-Rogers & Brimelow, 2001).

- *Spectroradiometer:* which measures the spectral energy (power distribution) of a source. Their units are expressed by luminance (cd/m^2) and illuminance (lux) for spectral radiance and irradiance, respectively (Paravina & Powers, 2004). Spectrophotometric and spectroradiometric measurements have been compared and appear to be similar and highly correlated (Lim *et al.,* 2010).

- *Colorimeter:* provides the capability for measuring the colors of a number points along a line on the surface of an object. Colorimeters are useful to quantify color differences between two tested specimens with convenience and simplicity (Paravina & Powers, 2004).

The main concern in using any of the mentioned devices for determining or comparing the color and/or translucency of specimens is accuracy and repeatability. The accuracy of the device maybe conducted by comparing a test specimen to a reference specimen which parameters are to be correct, and precision is assessed by having the ability to repeat the measures of the same specimen, concluding the same results (Johnston, 2009).

Translucency values are either expressed as translucency parameter (TP) or contrast ratio (CR). TP is the color difference between a uniform thickness of a specimen over a white and black background, and is considered as a common visual assessment of translucency (Johnston *et al.,* 1995). The TP values of 2 or below can block out a black background (Chaiyabutr *et al.,* 2011), and as the TP value increases the translucency

increases as well. CR is the ratio of the reflectance of a specimen over a black backing to that over a white backing of a known reflectance (Miyagawa *et al.,* 1981). The CR value of 0 is considered to be transparent while CR of 1 is opaque (Powers, 1978).

Perception of translucency, as perception of color, is a subjective matter. Many factors as age, eye-fatigue, lighting and experience play a role in perception. There have not been many studies on translucency perception. Liu *et al.,* evaluated the relationship between instrumental measurements and subjective visual assessment of differences in dental porcelain translucency and concluded that 50% of the study population perceived a 0.06 CR difference in translucency (Liu *et al.*, 2010).

It is worth mentioning an important phenomenon when discussing translucent material, which is 'edge-loss effect'. It can be defined as the light that is scattered to the edges of a sampled material without being absorbed (Bolt *et al.,* 1994). As mentioned, it is a phenomena that is related to translucent material, so the chances of edge-loss effecting the measurements of translucency in zirconia specimens is minimum.

2.5.1. Translucency of natural teeth

It is important to understand the optical properties of natural teeth, as it is the base to any clinical shade matching, and the esthetic properties of any given restorative material is judged upon its resemblance to natural tooth structure. When light strikes a tooth, the light is either (Jahangiri *et al.,* 2002):

- Transmitted through the tooth.

- Diffusely reflected (light reflectance in all directions as a result of surface roughness).

- Specular reflected (light reflection from a smooth surface at a definite angle).

- Light is absorbed and scattered within the tooth structure.

Determining the translucency of natural teeth is somewhat challenging. As the spectrophotometers and colorimeters are designed to measure flat surfaces, tooth structure is not flat and may have different anomalies resulting in a wide variation of translucency and color values, as evident within the studies in the literature (Joiner, 2004).

It may be considered, that dentin represents the color of the tooth allowing 52.6% light transmittance. While the enamel is considered as the color modifier, allowing 70.1% light transmittance (Magne, 1996). It has been reported that the TP of enamel at 1 mm thickness is 18.7, and CR is 0.55. Meanwhile, TP of dentin at 1 mm thickness is 16.4 and CR is 0.60 (Yu *et al.*, 2009).

2.5.2. Translucency of ceramic restorations

One of the important factors to consider when reviewing the literature to determine the translucencies of certain ceramic systems is thickness. It is well established that the translucency of certain restorative material decrease as the thickness increases, as the transmitting light is challenged to find its way through a thicker material compared to a thinner, and different thicknesses are required within a restoration depending on anatomy and preparation. Other factors including the methodology and devices used for measurement must be translated carefully. Indirect restorations made from feldspathic porcelain, Empress and IPS e.max, will be discussed briefly. Different types of restorations have different reactions to light and therefore have different degree of translucency.

- *Feldspathic porcelain:* primarily composed of silica (SiO_2) and alumina (Al_2O_3), with an amorphous structure and a refractive index similar to that of enamel and dentin (1.54), feldspathic porcelain is still considered the best ceramic to mimic the optical properties of the natural dentition (Kelly, 2008). The TP of feldspathic porcelain at 1 mm thickness is approximately 16.8 and CR value is in the range of 0.60-0.78 (Antonson & Anusavice, 2000).

- *Pressable ceramics:*
    - IPS Empress Esthetic (Ivoclar Vivadent) is a pressable leucite-reinforced ceramic, which belongs to the aluminosilicate glass ceramic family (Kelly, 2008). Leucite is added for strength improvement, and also due to its refractive index which is similar to that of feldspathic glass, giving it relatively high translucency to become a popular selection for esthetic restorations only. The CR of Empress at 1 mm thickness is reported to be 0.64 and the TP around 18.4 (Bagis & Turgut, 2013).

    - IPS e.max (Ivoclar Vivadent) composed primarily of a modified lithium disilicate glass ceramic. With mechanical properties higher than Empress and optical properties that can mimic natural dentition, IPS e.max material can either be used as a full crown, inlay, onlay, or veneer (Heintze *et al.,* 2008). IPS e.max has a well-arranged shades coordinated with each other, also of different translucency and/or opacity. Its translucent ingots have been used for the esthetic zones, and its opaque ingots are mainly used as cores to block out dark underlying abutments. IPS emax's CR at 1 mm thickness is 0.78, and its TP is 17.8 (Wang *et al.,* 2013). The translucency of IPS e.max is less than that of IPS Empress.

2.5.3. Translucency of zirconia

It is arguably one of the most challenging characteristics of zirconia restorations yet to be improved, and has been the focus of many manufacturers to produce zirconia

restorations that can be successfully used in esthetic zones. The very low translucency of zirconia is attributed to many factors such as: a high refractive index (2.1-2.2), particle size that is considered to be larger than the incident wavelength of light, low absorption coefficient and high opacity in the visible and infrared spectrum (Pecho *et al.,* 2012).

Advocates for all-ceramic restorations see the immediate advantage of zirconia being white in comparison to metal-based restorations, and the absence of the metal collar that can show through the gingiva "black line" (Christensen, 2007). Zirconia core systems have a CR of 1 (opaque) (Heffernan *et al.,* 2002; Chen *et al.,* 2008; Baldissara *et al.,* 2010), which is an advantage for masking underlying dark abutments, but can be rather challenging to produce optical properties through the veneering porcelain to mimic natural dentition. One phenomenon that can affect the optical properties of teeth, porcelain fused to metal, or zirconia, is the 'double layer effect' that was described by O'Brien. The fact that the light can transmit through a translucent surface (enamel or feldspathic porcelain) and then is diffusely reflected by the inner dentin, underlying opaque layer or core has a big influence on the apparent color of the tooth or restoration (O'Brien, 1985).

As mentioned, chipping of the veneering porcelain was a major problem that led to the perception of monolithic zirconia restoration owing to its desirable mechanical properties, biocompatibility and less manufacturing time and cost. Nevertheless the esthetic challenges have become even more evident, as the opacity of monolithic zirconia restoration is inevitable.

Increasing sintering temperatures can lead to larger zirconia grain size (Denry & Kelly, 2014), as zirconia particles increase in size, translucency can be decreased as more light is reflected. On the other hand, translucency is enhanced through less grain boundaries (Denry & Kelly, 2014). Staining, glazing, and polishing zirconia surfaces have all been advocated to enhance monolithic zirconia's appearance. The longevity of such stains, glazes and surface polishability are questionable.

Increasing yttrium content to more than 8 mol% achieves full stabilization of the zirconia (Goff *et al.*, 1999). This means that more cubic phase can be noticed, which can improve the optical properties of zirconia making it more translucent. Conversely this may lead to a definite effect on zirconia's strength.

Lava zirconia (3M ESPE) is a zirconia brand that is frequently used for research purposes. The CR of Lava zirconia (3M ESPE) at 1 mm thickness is 0.92, and its TP is 10.8 (Wang *et al.,* 2013). 3M ESPE later introduced Lava Plus (3M ESPE) and reported its CR to be 0.90 and its TP to be 13.8. Table 2 Compares the TP and CR values of the mentioned all-ceramic systems to enamel and dentin.

Table 2: Contrast ratio of and translucency parameter values of some brands of dental ceramics compared to enamel and dentin.

	Enamel	Dentin	IPS Empress	IPS e. max	Lava zirconia	Lava zirconia PLUS
Contrast Ratio	0.55	0.60	0.64	0.78	0.92	0.90
Translucency Parameter	18.7	16.4	18.4	17.8	10.8	13.8

2.6. Light curing properties, light irradiance, and radiant exposure through zirconia

Curing light transmittance through zirconia restorations can be a concern due to material's inherent opacity. Light curing lamps that have been used for photo initiation of the polymerization process are:

- *Quartz-tungsten-halogen (QTH) lamps:* which have a quartz bulb with a tungsten filament that emits both white and ultraviolet light which must be filtered to provide a violet-blue wavelength (about 400 to 500 nm) and suppress heat generated from the bulb. They must be calibrated at all times, as the bulbs irradiance diminishes with time.

- *Plasma arc curing (PAC) lamps:* ionized xenon gas produces a plasma with white light that must be filtered resulting in a high irradiance blue light.

- *Argon laser lamps:* which have been used to emit a single wavelength of around 490 nm, and are considered the highest irradiance of all lamps.

- *Light-emitting diode (LED) lamps:* not requiring a filter, as these lamps produce light only in the blue spectrum (440 to 480 nm) and are considered to have low irradiance, thus newer versions have two or more LED units to increase their irradiance and extend their range of wavelength.

These curing lamps deliver a wide range of spectral emission and irradiance level (Rueggeberg, 2011), which can affect the polymerization process. LED curing lamps have become the golden standard for the photopolymerization of the resin-based material (Jandt & Mills, 2013).

It is worth mentioning that efforts have been proposed to utilize the correct measurement units in reporting's of radiometric quantities used in dental photo-initiated polymerization systems. Therefore, when discussing light, there are two main components; a radiometric component (measure the electromagnetic radiation), and a photometric component (which is the measurement of light that is detected by the eye) (Kirkpatrick, 2005). When photo-polymerized systems are evaluated, it is the radiometric component that

is relevant and not the photometric. This is important to understand the curing kinetics of the polymer systems, in addition to providing an effective method of communication between researchers and clinicians. Therefore, the following radiometric terms will be used in this project: **Irradiance,** which is power (mW) multiplied by area (cm^2). **Radiant exposure,** which is (irradiance × time) (J/cm^2). The common term known to the dental community 'light intensity' should be avoided due to the mentioned reasons.

Any photo-polymerized system contains a photo-initiator such as camphorquinone (CQ) that has highest absorption at around 470 nm (Jandt & Mills, 2013), and that most LED units produce a spectral emission within that range to optimize photo-initiation. Other photo-initiators such as Ivocerin and TPO (2,4,6-trimethylbenzoyl-dphenyl-phosphine oxide) are sensitive to different wavelengths, thus the spectral emission of the curing lamp must be within their range to ensure optimal absorption of light and initiation.

Main points to focus on when it comes to understanding light curing and photo-initiation are:

- Light cure output, which is the average irradiance over an incident area (mW/cm^2).

- Whether the light beam has a uniform output, as the light tip has so called 'hot and cold spots' (Price *et al.*, 2014), emitting irradiance either very high or very low which may result in some areas of the resin receiving an inadequate amount of energy when light curing.

- The diameter of the beam and the effect of distance, as the irradiance is highest at the tip and declines rapidly as drifting away from the tip (Price *et al.*, 2010). It is important to know the irradiance at the tip and at certain relevant distances, which is currently being provided by some manufacturers.

- Radiant exposure (J/cm^2), in photo-polymerized systems represents the minimum amount of energy required for polymerization, and will be discussed in further detail in 'cement polymerization'. Some manufacturers mention the minimum amount of radiant exposure for polymerization. For instance, if the amount of radiant exposure is 16 J/cm^2, that would require a curing time of 20 secs with a curing light irradiance of 800 mW/cm^2 (irradiance × time), or a curing time of 40 secs with a minimum irradiance of 400 mW/cm^2. However, the international standard organization (ISO) has recommended that minimum amount of irradiance for polymerization is 300 mW/cm^2 for a 1.5 mm thickness of a resin-based material (ISO, 1999). It is important to know all these factors and their relation to one another to achieve optimal polymerization.

To conclude, light irradiance and radiant exposure can be influenced by the thickness of the ceramic restoration, the degree of ceramic translucency, and ceramic shade as the curing light beam must be able to transmit through the indirect restoration reaching the resin based cement. Kilinc *et al.,* reported that the ceramic thickness has more effect on polymerization than the shade, and that 3 mm thickness was the critical threshold (Kilnic *et al.,* 2011).

2.7.   Resin cement polymerization

Resin based cements are favored for adhesive cementation. The polymerization process is chemical, light, or dual-cured. Bonding to zirconia restorations has been a topic of interest for many *in vitro* studies, which is not the focus of this project. Conventional cements, like resin modified glass ionomer and zinc phosphate may still be used but with extra care, as long as the abutment preparation enforces adequate retention. A recent review reported that loss of retention of fixed dental prostheses was frequently associated with conventional cements compared to those luted with resin cements (Le *et al.*, 2015), which emphasis critically reviewing each case scenario before luting. In cases where proper retentive preparations are not possible, resin based cement are required. When talking about resin cements, and the possible limitations of being underexposed underneath a ceramic restoration, one way to overcome this problem would be to combine chemical curing and light curing components in the same resin (dual-cure resin cements), which is highly recommended for cementing zirconia restorations. As for (light-cured only) resin cements, they provide the advantage of having an extended working time, and curing upon demand, in addition to a stable color improvement. They are mostly indicated for cementing translucent thin ceramic restorations as veneers, where light is not attenuated through the restoration thus affecting the curability of the light-cured resin cement (Chan & Boyer, 1989). Therefore, there is no 'all purpose' cement, and the selection of a resin-based cement should be based on its intended use, as not all resin cements polymerize adequately in every clinical situation (Caughman *et al.,* 2001).

2.7.1. Dual-cure resin cements

Dual-cure resin cements are composed of two pastes, one containing benzoyl peroxide and the other an aromatic tertiary amine accelerator (Anusavice, 2013). The mixing and handling time is fairly extensive, and setting is very slow in its 'self-cure' form. However, the setting time can be accelerated upon exposure to light that is absorbed by the amine/CQ combination triggering polymerization. As an advantage for these cements, inadequate light exposure can be of less importance, as the optimum cure can be secured through the chemical component, when compared to the light-curable resin cements. One drawback may be the presence of aromatic amine accelerators which can

effect color stability, but not as severe as self-cure cements. They are mainly indicated to cement restorations of relative bulk and opacity that can attenuate light penetration. Yet, certain amount of light irradiance is required to initiate the polymerization process, otherwise the self-curing polymerization can be too extensive and affect bonding strengths. In addition, underexposure can lead to a lower level of monomer conversion, which can further lead to residual monomer leakage that has been reported to be harmful (Ferracane & Cordon, 1990).

2.7.2. Degree of conversion (DC)

The DC is a measure of the percentage of carbon-carbon double bonds that have been converted to single bonds to form a polymeric resin (Anusavice, 2013). There has been no report of a clinically relevant DC, but the higher the percentage the better the resin performance (e.g. resistance to wear, strength, resistance to water sorption, and microleakage). A range of 50-75% of polymerized methacrylate groups is typical of a bis-GMA-based composite resin conversion (Ruyter & Øysæd, 1987). However, this does not mean that the 30-40% of the monomer molecules are left in the resin, as one of the methacrylate can form a pendant group that is covalently bonded to the polymer structure.

Evaluation of DC of resin based systems, have been reported through measurements of the surface hardness of the composite resin as in Vickers hardness test, as lower microhardness can be in direct relation to incomplete polymerization of the resin composite. Although, the most reliable measurement of DC has been through infrared analysis (Rueggeberg *et al.*, 1990; Imazato *et al.*, 2001). The methodology of conversion analysis by infrared methods relies upon calculation of the ratio of the aliphatic carbon-to-carbon ($C = C$) absorption at 1640 cm^{-1} to the aromatic $C = C$ absorption at 1608 cm^{-1}. Other methods such as differential thermal analysis (DTA) have also been reported to successfully measure the DC (McCabe, 1985). Analyzing the DC gives an important estimate of the resin based systems' performance, allowing researchers to determine factors that can affect the DC and how a specific type of resin based material performs in a certain given situation to conclude with accuracy a clinical recommendation.

Many factors affect the degree of monomer to polymer conversion, such as the composition of the resin, the concentration of the sensitizer, initiator, inhibitor, and most importantly the transmission of light through the material. As mentioned earlier, the light transmission depends on the light curing units' irradiance, also the nature of the material that the light must penetrate as the light can be reflected, absorbed, or scattered before reaching the resin based material. Tezvergil-Mutluay *et al.,* investigated the DC of multiple dual-cure luting cements that where irradiated through various restorative material and dentin. They concluded that DC was different amongst the different cements, and that

the restorative material significantly influenced the DC of the luting cement underneath (Tezvergil-Mutluay *et al.,* 2007). The DC has also been evaluated underneath different ceramic restorations of various thickness and shade (Barghi & McAlister, 2003; Lee *et al.,* 2011; Kilinc *et al.,* 2011) and reported that thicker restorations with higher chroma (saturation) values had less DC. As for the curing lights' radiant exposure, Komori *et al.* evaluated the effect of different radiant exposures (10, 20, and 30 J/cm^2) on the DC of dual-cured cements, and concluded that a radiant exposure of 10 J/cm^2 had a significant reduction in the DC. Nowadays, and to accommodate the high esthetics demand, dual-cure cements come in various shades. It was reported that the shade of the dual-cure cement had no effect on the DC (Passos *et al.,* 2013).

2.8. Zirconia and oral environment challenges

Many challenges have arisen after placing zirconia restorations in the oral cavity, questioning its long-term performance. Some complications emerged, and requirements for handling technical and clinical problems were investigated. It has been discussed previously the susceptibility to LTD, as studies have proven zirconia's vulnerability to moist environment (Chevalier, 2006). Also, the veneering porcelain chipping (the most common causes of failure) has been identified due to residual stresses, and the solution of slow cooling in the restoration fabrication process has been recommended (Kelly & Benetti, 2011). These problems were lately discovered, and whether this material was introduced prematurely without proper research, exposes the deficiencies and lack of research in providing solid evidence of material's success before being recommended for clinical use in humans.

With the recognition that zirconia cores had close to no reported failures, the elimination of the veneering porcelain and fabricating a crown made of monolithic zirconia made common sense. In its stained and glazed forms, monolithic zirconia restorations have been placed in large numbers mainly in the posterior region. As many reasons may be the cause of this transition, it is important not to fall under a manufacturer driven industry where clinicians are considered as beta testers for their products. Up to this date (2015), there has been no clinical study proving monolithic zirconia's success rate and many properties need to be critically evaluated.

However, the oral cavity is a harsh environment, as its aqueous state can threaten LTD, in addition to the fluctuant pH ranging from 1 to 10 (Esquivel-Upshaw *et al.,* 2013), with mostly being on the acidic side especially with today's beverages and gastric related issues. Apart from that, is the substantial temperature range (0-67°C) that the oral cavity experiences and the fact that higher temperatures can increase the kinetics of any reaction between the restoration surface and the liquids present. Combining all of the mentioned

conditions along with occlusal stresses may enhance dissolution and degradation of the zirconia restoration.

Dental erosion (corrosion) by definition is "the loss of tooth structure due to non-bacterial chemical causes" (Sapp *et al.*, 1997). The erosive acids can be of intrinsic origin as in stomach acid, or extrinsic as in acidic beverages and food. Intrinsic causes of erosion are mainly represented by gastric acid that fluxes into the oral cavity. It can be part of a disease condition such as gastroesophageal reflux disease (GERD), eating disorder, chronic alcoholism, and pregnancy. GERD is a common disease affecting up to 65% of the western population (Moazzez & Bartlett, 2014). Gastric acid is mainly composed of hydrochloric acid (HCl) and has a pH less than 2 that is below the critical pH of enamel (5.5), and with high titratable acidity it can cause severe erosive damage to the tooth structure (Figure 3).

Figure 3: A patient with gastroesophageal reflux disease. Multiple signs of erosion including loss of anatomy of the posterior teeth and 'cupping', the amalgam restorations 'standing tall', and complete loss of enamel on the palatal surface of the anteriors.

As a consequence to erosively induced loss of tooth structure, loss of vertical dimension is inevitable in some circumstances. The rehabilitation of such cases is challenging, as the clinician must follow an appropriate and stringent treatment plan. It requires the knowledge of material properties of direct and or indirect restorations that are to be placed and how these restorations can perform in such cases. Attin and Wegehaupt in their review on the impact of erosive conditions on tooth-colored restorative material discussed about many studies recommending the use of ceramics in the restoration of the worn dentition, and also pointed out the fact that no clinical follow-up studies have been reported (Attin & Wegehaupt, 2014). It is well known that hydrofluoric acid and

acidulated phosphate fluorides (APFs) are able to etch the surface of feldspathic and leucite reinforced glass ceramics (Anusavice, 1992) revealing the vulnerability of glass ceramics to corrosive acid degradation. Milleding *et al.,* also reported upon exposing different ceramic systems to a corrosive acid, that all the ceramic material displayed an increase in surface roughness compared to the baseline condition (Milleding *et al.,* 1999). In another study, the ion dissolution from glass and all crystalline ceramics was investigated under an *in vitro* corrosion of 4% acetic acid at 80°C for 18 hrs, and concluded that large numbers of inorganic elements leached out from the ceramics and that none of the studied ceramics were chemically inert in an aqueous environment (Milleding *et al.,* 2002). On the other hand, another study has determined with immersing leucite-based feldspathic for 24 hrs in simulated vomit (pH of 3.8) that the corrosive acid had no effect on the surface roughness of the ceramic (Matsou *et al.,* 2010).

It is important when reviewing the literature for the effects of corrosive acids on ceramic restorations, that there are many variables to be considered in the methodology of such study. Factors such as the chemical composition of the corrosive acid, its concentration and pH, the exposure time and temperature and the composition and microstructure of the ceramic evaluated, all have an influence on the reported results. The ISO standard 6872 for dental ceramics recommends the use of 4% acetic (which has a pH of 2.4) at 80°C for 16 hrs, as a corrosive environment (ISO, 1995). Some studies have modified that recommendation in efforts to mimic a closer *in vivo* resemblance. Hunt and McIntyre have reported their efforts in developing an *in vitro* model that can replicate dental erosion (Hunt & McIntyre, 1992). Their erosive agent was simulated by 0.06 M HCl (0.113% solution in deionized distal water) with a pH of 1.2. Whether it will ever be possible to mimic the oral environment is still controversial, yet many of these studies have shown the vulnerability of ceramic material to a corrosive acid attack.

3. AIMS OF THE THESIS

The research presented in this thesis is based on the working hypothesis that monolithic zirconia exhibits acceptable optical and mechanical characteristics to be used as a full contour restorative material.

Accordingly, the following aims were established to:

1. Evaluate the effect of zirconia thickness on the surface gloss and translucency values, in addition to determining light attenuation through the specimens by measuring irradiance and radiant exposure values (Study I).

2. Study the effect of light attenuation irradiated through variable zirconia thicknesses on the degree of conversion of dual-cure cements (Study II).

3. Evaluate the effect of staining and sintering on the optical and mechanical properties of partial and fully stabilized monolithic zirconia (Study III).

4. Determine the effect of corrosive (gastric) acid on the surface topography and optical properties of monolithic zirconia (Study IV).

4.   MATERIALS AND METHODS

4.1.   Materials

4.1.1. Yttria tetragonal stabilized zirconia

The monolithic zirconia materials that were used in the experimental studies are listed in Table 3. In study IV, the zirconia specimens were compared to IPS e.maxCAD (Ivoclar Vivadent AG; Schaan, Liechtenstein) of the following composition: SiO_2 in addition to Li_2O, K_2O, MgO, Al_2O_3, P_2O_5 and other oxides.

Table 3: The monolithic zirconia materials used in the experimental studies.

Brand name	Manufacturer	Composition
Partially stabilized zirconia (PSZ)		
Prettau Zirconia	Zirkonzahn, Taufers, Italy	4%–6% Y_2O_3, <1% Al_2O_3, max. 0.02% SiO_2, max. 0.01% Fe_2O_3, max. 0.04% Na_2O
Bruxzir Zirconia	Glidewell Laboratories, Irvine, USA	4.1% Y_2O_3, 4.0% HfO_2, 0.34% Al_2O_3, <0.01 SiO_2, Fe_2O_3, Na_2O, and balance ZrO_2
Wieland Zenostar Translucent	Ivoclar Vivadent, Principality of Liechtenstein	Unknown
Katana High Translucent	Kurary Noritake INC, Noritake, Japan	(ZrO_2 + HfO_2 + Y_2O_3) > 99.0 %, yttrium oxide (Y_2O_3) > 4.5 – <= 6.0 %, hafnium oxide (HfO_2) <= 5.0 %, other oxides <= 1.0 %
Fully stabilized zirconia (FSZ)		
Prettau Anterior	Zirkonzahn, Taufers, Italy	<12% Y_2O_3, <1% Al_2O_3, max. 0.02% SiO_2, max. 0.01% Fe_2O_3, max. 0.04% Na_2O
Control (PSZ)		
ICE Zircon	Zirkonzahn, Taufers, Italy	4%–6% Y_2O_3, <1% Al_2O_3, max. 0.02% SiO_2, max. 0.01% Fe_2O_3, max. 0.04% Na_2O

4.1.2. Dual-cure resin cements

The dual-cure resin cements used in study II are listed in Table 4.

Table 4: Dual-cure resin cements and their chemical compositions.

Brand	Shade	Manufacturer	Filler vol.%	Chemical Composition
RelyX Ultimate	Translucent	3M-ESPE, St. Paul, MN	43	Base: Methacrylate monomers, radiopaque silanated fillers, initiator components, stabilizers and rheological additives. Catalyst Paste: Methacrylate monomers, radiopaque alkaline (basic) fillers, initiator components, stabilizers, pigments, rheological additives, fluorescence dye, dark cure activator for Scotchbond Universal adhesive.
Variolink II	Translucent (low viscosity)	IVOCLAR, Vivadent, Lichtenstein	43.6	Base: Bis-GMA* (10-25%), urethane dimethacrylate (2.5-10%), TEGDMA (2.5-10%), inorganic filler, ytterbium trifluoride, initiator, stabilizer. Catalyst: Bis-GMA (50-100%), UDMA** (2.5-10%), TEGDMA*** (2.5-10%), inorganic filler, ytterbium trifluoride, benzoyl peroxide (<2.5%), stabilizer.

* Bis-GMA: Bisphenol-A-glycidyl dimethacrylate.
** UDMA: Urethane dimethacrylate.
*** TEGDMA: Triethylene glycol dimethacrylate

4.1.3. Acid-free water-base coloring liquid

In study III, the partially and fully stabilized zirconia (Prettau® and Prettau® Anterior, Zirkonzahn, Italy) were colored (stained) using a water-base and acid-free coloring liquid shade A2 (Color liquid Prettau® Anterior Aquarell; Zirkonzahn, Taufers, Italy).

4.2. Methods

4.2.1. Fabrication of test specimens

The number of groups, specimens (n) and thicknesses are listed in Table 5.

Table 5: Groups, number of specimens and thicknesses used for each study.

Study	Number of groups	Number of specimens (n)	Thicknesses (mm)
I*	6	n= 180 (5/subgroup)	0.50, 0.70, 1.00, 1.20, 1.50, 2.00
II*	5	n=60 (3/subgroup)	0.50, 1.00, 1.50, 2.00
III**	3	n=90 (15/subgroup)	1.20
IV*	6	n=30 (5/subgroup)	1.00

* Square-shaped specimens
** Disc-shaped specimens

4.2.1.1. *Preparation of square-shaped specimens for optical properties measurement (Study I, II and IV)*

The pre-sintered stage machinable aforementioned zirconia materials (Table 3) were cut into square-shaped specimens (10×10 mm) using a cutting device (Struers Secotom-50, Copenhagen, Denmark) (Figure 5) With shrinkage percentage taken into consideration, each specimen was sequentially ground (dry) to the specific thickness using silicon carbide grinding paper (FEPA #1200, 2400 and 4000) (Struers LaboPol 21, Struers A/S, Rodovre, Denmark). The final thicknesses after sintering where 0.50, 0.70, 1.00, 1.20, 1.50 and 2.00 mm (±0.01mm), where measured using a digital caliper (Mitutoyo Corporation, Kanagawa, Japan).
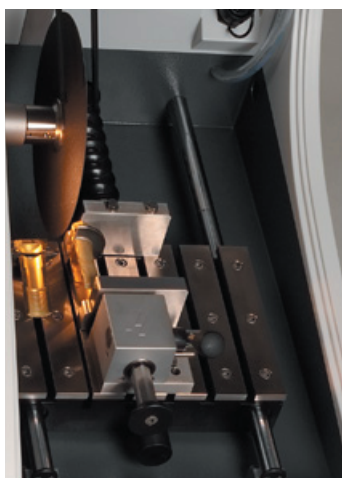

Figure 5: Cutting the specimens by (Struers Secotom-50, Copenhagen, Denmark).

4.2.1.2. *Preparation of disc-shaped specimens for optical properties and bi-axial flexural strength measurements, and specimen coloring (staining) (Study III)*

The pre-sintered stage partially stabilized zirconia (Prettau®) and fully stabilized zirconia (Prettau® Anterior) blocks were milled (Milling unit M5, Zirkonzahn, Taufers, Italy) into 20 mm diameter cylinders, and then cut with same aforementioned cutting device to a 1.80 mm thickness. Each specimen was sequentially grounded to a 1.50 mm thickness (±0.01mm) using silicon carbide grinding paper (FEPA #1200, 2400 and 4000).

For the stained group, staining was done using shade A2 Color Liquid Prettau® Anterior Aquarell (Zirkonzahn, Taufers, Italy). A touchup brush was used to apply two coats of the liquid stain. The specimens were placed for 20 minutes under an infrared drying lamp, Zirkonlamp 250 (Zirkonzahn, Taufers, Italy), following manufacturer's instructions.

4.2.2. Sintering conditions (Study I–IV)

All specimens were sintered according to the manufacturers' instructions using the designated furnace for each brand of zirconia. The sintering temperatures for each brand are listed in Table 6. The holding time was 2 hrs for all brands.

Table 6: Sintering temperatures of the tested zirconia brands.

Brand name	Sintering temperature
Prettau® Zirconia	1600°C
Prettau® Anterior	1500°C
Bruxzir Zirconia	1530°C
Wieland Zenostar Translucent	1450°C
ICE Zircon	1500°C
Katana high translucency block	1500°C

4.2.3. Specimen finishing/polishing and cleaning (Study I–IV)

The specimens for all test groups were polished using diamond polishers (Zircpol Plus and Zircoshine Plus, Diatech, Switzerland) followed by a polishing paste (Zircon-Brite, Dental Ventures of America Inc., Corona, CA). The polishing process was completed by one operator, under constant pressure and a standard time in a single directed motion. The specimens were cleaned ultrasonically in distilled water for 10 mins before testing (Quantrex 90, L&R Ultrasonics Manufacturing Co., Kearny, NJ) and subsequently air-dried for 20 secs.

4.2.4. Optical properties measurement (Study I, III and IV)

The optical measurements of surface gloss, translucency parameter (TP) and contrast ratio (CR) were determined using a reflection spectrophotometer (CM-700d, Konica Minolta Sensing Inc., Tokyo, Japan) according to the CIE 1976 L*a*b* color scale relative to the CIE standard illuminant D65 (as defined by the International Commission on Illumination) which corresponds to "average" daylight (including ultraviolet wavelength region with a correlated color temperature of 6504K). The degree of angle illumination was set to 8° viewing angle. All specimens were viewed through a 3 mm aperture, and the spectrophotometer was calibrated using a standard illuminant over a white background (CIE L*=98.1, a*= -0.5 and b*=2.8), and a black background (CIE L*=4.7, a*= -0.1 and b*=0.0). A total of 5 measurements of the polished surface of each specimen over a white and black background were done to determine the following:

4.2.4.1. Surface gloss

The spectrophotometer provides virtually simultaneous specular component included (SCI) and specular component excluded (SCE) measurements. The difference between

the two (ΔE*SCE-SCI) can give an estimation of the surface gloss of a material (Kress-Rogers & Brimelow, 2001). Differences in surface gloss (ΔE*SCE-SCI) values were calculated by the following equation:

$$\Delta E*SCE\text{-}SCI = [(\Delta L*SCE\text{-}SCI)^2 + (\Delta a* SCE\text{-}SCI)^2 + (\Delta b* SCE\text{-}SCI)^2]^{1/2}$$

4.2.4.2. Translucency parameter (TP)

The color difference of each specimen was measured over a black background (b) and a white background (w), and the TP values were then measured using the following equation:

$$TP = [(Lb* - Lw*)^2 + (ab* - aw*)^2 + (bb* - bw*)^2]^{1/2}$$

L* refers to the lightness, a* to redness to greenness, and b* to yellowness to blueness.

4.2.4.3. Contrast ratio (CR)

The ratio of illuminance (Y) for each specimen was measured over a white background (Yw) and over a black backing (Yb), the CR values were determined with the following equation:

$$CR = Yb/Yw$$

4.2.5. Light cure irradiance and radiant exposure quantification (Study I and II)

The light cure irradiance (mW/cm^2) and radiant exposure (J/cm^2) were quantified through each specimen at the selected thicknesses. A LED light-curing unit of 1200 mW/cm^2 irradiance and wavelength range 430–480 nm (Elipar S10, 3M ESPE, St. Paul, MN) was utilized with light-curing times of 10 secs (Study I), 20 and 40 secs (Study II). The irradiance and radiant exposure measurements were evaluated by MARC® Resin Calibrator (BlueLight analytics Inc., Halifax, Canada) using the 'bottom surface' side of the device. A custom jig was used to hold the light-curing unit for stability and placement accuracy. Plastic rings with a 10 mm opening of the corresponding thicknesses were used to measure the light irradiance and radiant exposure values before placement of the specimens. Then the irradiance and radiant exposure was determined through each specimen.

4.2.6. Fourier transform infrared spectroscopy analysis (Study II)

The DC of two dual-cure cements (Table 4) were monitored by fourier transform infrared spectroscopy (FTIR) (Frontier; Perkin Elmer, Beaconsfield Bucks, UK) with a universal Attenuated Total Reflectance (ATR) sampling accessory. The cements were mixed according to manufacturer's instructions and placed on the crystal which had two 40 μm thick shims on each side, then covered by a Mylar strip and a pressure arm was

swung over to the top of the specimen and the node was rotated until a load of 12 N was indicated by the force gauge, thus ensuring proper thickness of the cement for each tested specimen. To serve as a control the DC was measured for each cement before placement of zirconia specimen. The cement was cured using the aforementioned light-curing unit through the selected zirconia thicknesses of each group (Table 5) and cured for 20 secs for the RelyX Ultimate and 40 secs for the Variolink II (manufacturers' instructions).

After curing, the specimen was shielded from ambient light. The infrared spectra was recorded for each experimental condition (zirconia brand, thickness and resin cement brand) continuously from the bottom of the specimen at every 5.2 secs for 15 mins at a rate of 16 scans/spectrum at 4 cm^{-1} resolution, using reaction kinetics software (TimeBase V4, Perkin Elmer, UK). Since the resin cement presented the aliphatic bonds of the methacrylate functional group and the aromatic vinyl bonds of bisphenol, the DC was calculated from the aliphatic C=C peak at 1638 cm^{-1} and normalized against the aromatic C=C peak at 1608 cm^{-1} (Ruyter & Svendsen, 1978; Rueggeberg *et al.,* 1990) according to the formula:

DC (%) = $(1-C/U) \times 100$,

Where C and U are the normalized absorption peak heights (1638 and 1608 cm^{-1}) for the cured and uncured materials, respectively. A new mix of cement was placed under each specimen for a total of five measurements.

4.2.7. Bi-axial flexural strength (Study III)

Bi-axial flexural strength values were determined in accordance with the ISO Standard 6872. The thickness and diameter of the sintered disks were confirmed with a digital caliber before the fracture test. The specimens were tested dry at room temperature with a universal testing machine (Model LRX, Lloyd Instruments Ltd, Fareham, UK) where they rested on three symmetrically based steel balls and the load was applied to the center of the top surface by the piston (diameter 1.60 mm) until fracture occurred (Figure 6). The cross-head speed of the piston was 1.0 mm/min. Results were recorded with Nexygen software (Lloyd Instruments Ltd, Fareham, UK). The biaxial flexural strength was calculated as:

$S = -0.2387P(X - Y)/d^2$

S: biaxial flexural strength (MPa); P: fracture load (N); d: specimen disk thickness at fracture origin (mm).

$X = (1+ v)\ln (B/C)^2 + [(1-v)/2](B/C)^2$

$Y = (1+ v)\ln (A/C)^2 + [(1-v)/2](A/C)^2$

v: Poisson's coefficient (ceramic = 0.25, ISO 6872); A: radius of support circle (mm); B: radius of loaded area (mm); C: radius of specimen disk (mm).
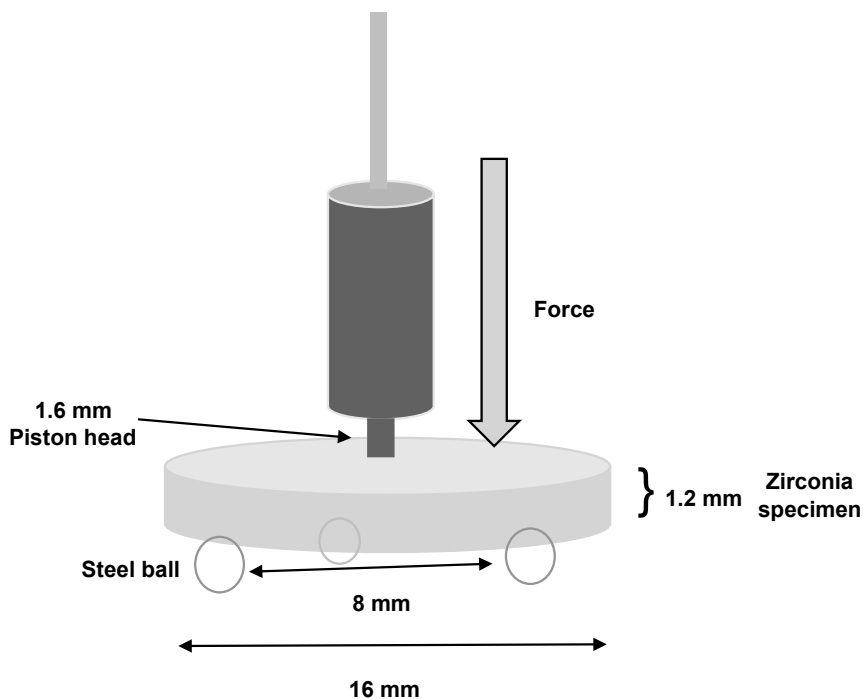

Figure 6: A schematic illustration of the bi-axial flexural strength test. The specimen (16 mm diameter) rested on three symmetrically based balls (8 mm apart) and the load (F) was applied to the center of the top surface by the piston (diameter 1.60 mm) until fracture occurred.

4.2.8. Specimen immersion in diluted hydrochloric acid (Study IV)

Simulation of gastric acid was done in accordance with Hunt and McIntyre's method of preparing a corrosive acid causing erosion to enamel similar to *in vivo* conditions (Hunt & McIntyre, 1992). Hydrochloric acid (HCl) 0.06 M (0.113% solution in deionized water, pH 1.2) was prepared. The pH was monitored every 24 hrs and each specimen was immersed, polished surface facing up, in 5 ml of the simulated acid for 96 hrs in a 37°C incubator (Termaks, Bergen, Norway).

4.2.9. Surface topography

4.2.9.1. Scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX) (Study III and IV)

The surfaces of the specimens were characterized using field-emission scanning electron microscopy (FE-SEM) (Leo Gemini 1530; Zeiss, Oberkochen, Germany) coupled

with energy dispersive x-ray spectroscopy (EDX, UltraDry Silicon Drift Detector, Thermo Scientific, Madison, WI, US). Specimens were mounted on a metal stub and approximately 20 nm of gold or carbon layer was applied to the substrates using a sputter coater (Temcarb TB500, Emscope Laboratories Ltd., Ashford, United Kingdom) and secondary electron images were taken. The machine was operated at 15 kV energy, an aperture size of 30 μm and the surface was viewed for visual examination at 1000x, 5000x and 15000x for any morphological changes to the specimen surface before and after acid immersion. The variation of the elemental composition at the surface before and after acid immersion was determined by EDX and was represented by atom % of each element.

4.2.9.2. Roughness measurement

A spinning disk confocal microscope with a white light source (COM, μSurf explorer, NanoFocus, Oberhausen, Germany) was used to determine S_a (defined as the arithmetic mean of the absolute values of the surface departures above and below the mean plane within the sampling area and is measured in micrometers. Sullivan *et al.,* 2000) and S_q (defined as the root-mean-square value of surface asperity departures from the reference datum within the sampling area. Dong *et al.,* 1994) surface parameters before and after acid immersion. S_a/S_q values according to DIN EN ISO 4287 were measured at 100x magnification. In calculation of the S_a/S_q values a Gaussian filter (ISO 11562) was used. At 100x magnification, the vertical resolution of the lens is 2 nm and the numerical aperture 0.8–0.95 for a measurement area of 160–158 μm. For the measurements done with the 100x lens, the cutoff wavelength of 80 μm was used. At least 5 readings per substrate were made at different random areas. The mean value was calculated and quantitatively expressed as a numerical value (in micrometers).

4.3. Statistical analysis

Statistical analysis was performed with Statistical Package for the Social Sciences (Version 22.0; SPSS. Inc, Chicago, Illinois). The distribution of data was normal, which was determined by the Kolmogorov-Smirnov test. Studies (I, II and IV) were analyzed using one- or two-way analysis of variance (ANOVA) followed by Tukey's post-hoc test for pairwise comparisons. In study III, the data were analyzed using multivariate analysis of variance (MANOVA) followed by Tukey's post-hoc test. Differences were considered significant at 95% confidence level for all studies.

In study I, the independent variables were zirconia brand and thickness, and dependent variables were TP, CR, and irradiance. Measurement of correlation between TP, CR, and irradiance was performed using the Pearson Correlation test. In study II, the

independent variables were zirconia brand and thickness, and the dependent variable was the cement type. In study III, the independent variable was the zirconia type and the dependent variables were staining, type of furnace, surface gloss, TP and CR. In study IV, surface roughness, TP and surface gloss as dependent variables and specimen brand as independent variable.

5. RESULTS

5.1. Optical properties (Study I, III and IV)

5.1.1. Surface gloss

In study I, polishing resulted in significant enhancement in surface gloss (ΔE*SCE-SCI) of all zirconia brands both against black and white background ($p<0.05$). The thickness of the specimens had no significance ($p>0.05$) on the surface gloss. The ranking of the materials from the highest surface gloss to the lowest was as follow: Prettau Anterior=Bruxzir > Katana> Prettau>Zenostar ($p<0.05$) (Figure 7).
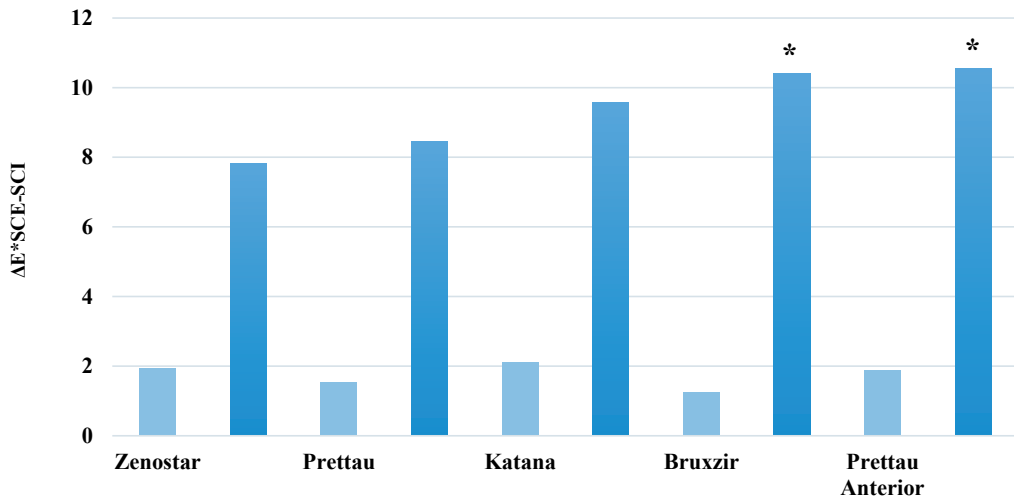

Figure 7: Surface gloss of the tested specimens at 1.00 mm thickness before and after polishing. Surface gloss was enhanced regardless of the brand or background ($p<0.05$). (*) indicates no statistical significance (ANOVA, post hoc Tukey's HSD test, $p>0.05$.

In study (III), the effect of staining and sintering in vacuum furnace on surface gloss (ΔE*SCE-SCI) of the partially (Prettau) and fully (Prettau Anterior) stabilized zirconia was determined. It was found that the staining increased the surface gloss of FSZ ($p<0.05$), but had no effect on PSZ ($p>0.05$). Type of sintering had no effect on either of the zirconia types ($p>0.05$) (Table 7).

Table 7: Surface gloss values of full and partially stabilized zirconia before and after staining or sintering under vacuum.

Group	Mean ± SD	Statistical difference*
FSZ	7.88 ± 0.67	a
PSZ vacuum	8.02 ± 0.07	a, b
FSZ vacuum	8.09 ± 0.17	a, b
PSZ	8.66 ± 0.14	b, c
FSZ stained	9.28 ± 0.22	c
PSZ stained	9.35 ± 0.88	c

* Same letter indicates no statistical difference (p>0.05).

Acid immersion had no effect on surface gloss of Katana or Bruxzir specimens (p>0.05), while the surface gloss enhanced significantly for Zenostar, Prettau Anterior and IPS e.max (p<0.05). (Study IV)

5.1.2. Translucency parameter (TP)

Study I showed that the increasing thickness decreased the TP values of all specimens significantly (p<0.05). Polishing the specimens had no effect on TP values, nor did the white or black evaluation background (p>0.05). Ranking of the materials from the most to the least translucent was as follow: Prettau Anterior> Katana> Zenostar> ICE Zircon=Prettau=Bruxzir (p<0.05) (Figure 8).

*ICE zircon was considered as a control.

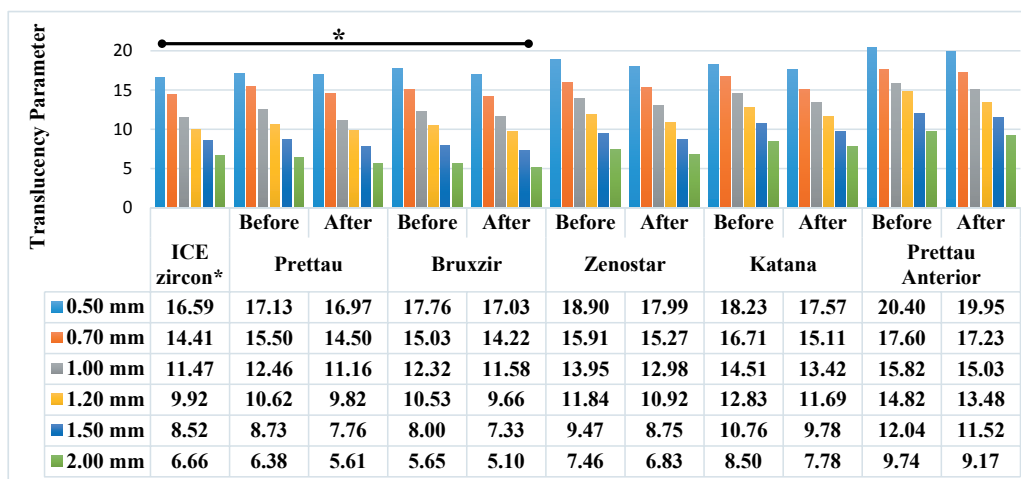|	ICE zircon*	Before Prettau	After Prettau	Before Bruxzir	After Bruxzir	Before Zenostar	After Zenostar	Before Katana	After Katana	Before Prettau Anterior	After Prettau Anterior
0.50 mm	16.59	17.13	16.97	17.76	17.03	18.90	17.99	18.23	17.57	20.40	19.95
0.70 mm	14.41	15.50	14.50	15.03	14.22	15.91	15.27	16.71	15.11	17.60	17.23
1.00 mm	11.47	12.46	11.16	12.32	11.58	13.95	12.98	14.51	13.42	15.82	15.03
1.20 mm	9.92	10.62	9.82	10.53	9.66	11.84	10.92	12.83	11.69	14.82	13.48
1.50 mm	8.52	8.73	7.76	8.00	7.33	9.47	8.75	10.76	9.78	12.04	11.52
2.00 mm	6.66	6.38	5.61	5.65	5.10	7.46	6.83	8.50	7.78	9.74	9.17

Figure 8: Translucency parameter (TP) values of the tested specimens before and after polishing on a white background. The TP values decreased as the thickness increased (p<0.05). There was no difference in TP values before and after polishing (p>0.05). (*) indicate no statistically significant differences among the groups (ANOVA, post hoc evaluation with Tukey's HSD test, p>0.05).

In study III, the TP values for FSZ (Prettau Anterior) where significantly higher than PSZ (Prettau) (p<0.05) regardless of the staining or the type of sintering used. For Prettau, staining had no significant effect (p>0.05), while vacuum sintering improved the TP values (p<0.05). In case of FSZ, staining decreased the TP values significantly (p<0.05), but sintering in a vacuum furnace had no effect (p>0.05) (Table 8).

Table 8: Translucency parameter values of partially (Prettau) and fully (Prettau Anterior) stabilized zirconia before and after staining or sintering in vacuum conditions.

Groups	Mean ± SD	Statistical difference*
PSZ stained	9.48 ± 0.62	a
PSZ	9.82 ± 0.08	a
PSZ vacuum	10.77 ± 0.11	b
FSZ stained	12.09 ± 0.43	c
FSZ vacuum	12.79 ± 0.49	c, d
FSZ	13.46 ± 0.16	d

* Same letter indicates no statistical difference (p>0.05).

In study IV, the TP values increased after acid immersion for Prettau, Zenostar and IPS e.max (p<0.05), with no significant effect on the other specimens (Katana, Bruxzir and Prettau Anterior) p>0.05.

5.1.3. Contrast ratio

The CR of the specimens in study I was brand and thickness dependent: the CR values increased as the thickness increased (p<0.05). The ranking of the brands from the most translucent (lowest CR values) to the least translucent (highest CR values) was as follow: Prettau Anterior> Katana> Zenostar=Prettau=ICE Zircon> Bruxzir (p<0.05).

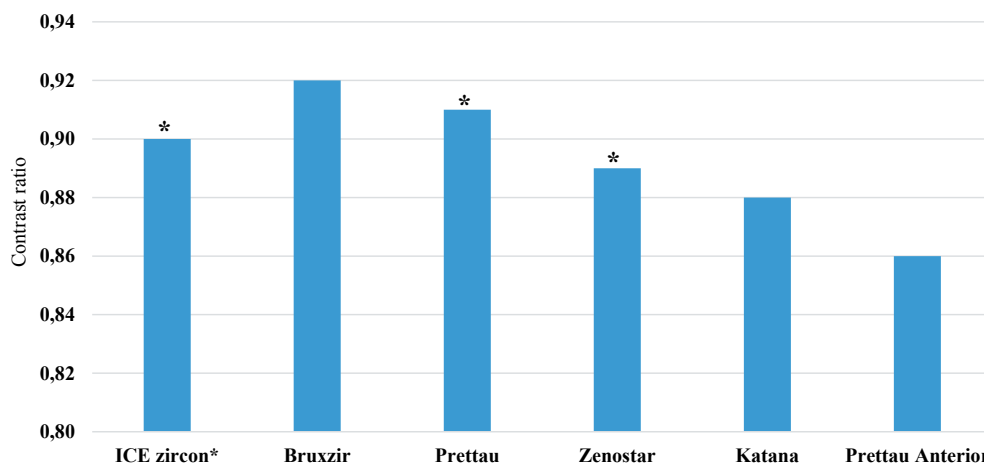*Ice zircon was considered as a control.

Figure 9: Contrast ratio of tested specimens at 1.00 mm thickness. Contrast ratio of 1 is opaque. The contrast ratio increased as the thickness increased ($p < 0.05$). (*) indicates no significant difference among the groups (ANOVA, post hoc evaluation with Tukey's HSD test, $p > 0.05$).

According to study III the CR values of the materials can be ranked to the following order from the most to the least translucent: Prettau Anterior= Prettau Anterior vacuum sintered> Prettau Anterior stained> Prettau vacuum sintered> Prettau> Prettau stained, $p < 0.05$

5.2. Light cure irradiance and radiant exposure (Study I and II)

In study I the amount of light irradiance and radiant exposure decreased significantly ($p < 0.05$) as the thickness of the specimens increased regardless of the brand of zirconia. When comparing irradiance and radiant exposure values among the brands, Bruxzir showed the lowest values, while Prettau Anterior and Katana showed the highest values. The ranking of the brands from the highest irradiance and radiant exposure values to the least was as follow: Prettau Anterior=Katana> ICE Zircon=Zenostar> Prettau>Bruxzir ($p < 0.05$). The mean values ($\pm$SD) of irradiance for all groups are shown in Table 9.

Table 9: Mean ($\pm$SD) value of the irradiance (mW/cm^2) level according to the zirconia brand at variable thickness.

Thickness	ICE Zircon*	Zenostar	Bruxzir	Prettau	Katana	Prettau Anterior
0.50 mm	726 (6)	664 (2.9)	564 (15.1)	672 (17.4)	820 (7.4)	831 (2)
0.70 mm	645 (5.2)	636 (3.2)	421 (3.9)	606 (10.4)	721 (8.3)	716 (5.6)
1.00 mm	536 (10.3)	572 (11.8)	305 (10.2)	467 (8.5)	617 (11)	620 (7.8)
1.20 mm	452 (6.9)	521 (12.1)	229 (9.1)	414 (10.4)	572 (20.6)	566 (1.4)
1.50 mm	419 (5.6)	410 (1.5)	165 (4)	315 (3)	473 (12.6)	478 (10)
2.00 mm	352 (5)	360 (7.5)	103 (3.1)	255 (5.3)	381 (9.8)	400 (2.2)

*ICE zircon was considered as a control.

In study II four thicknesses, rather than the six used in study I, were evaluated. The curing times used were 20 and 40 secs according to the manufacturer's recommendation. The radiant exposure values for the mentioned curing times are presented in Tables 10 and 11.

Table 10: The total radiant exposure (J/cm^2) through the specimens at 20 secs curing time.

Thickness	ICE Zircon	Zenostar	Bruxzir	Katana	Prettau Anterior
0.50 mm	15	13	12	17	17
1.00 mm	11	12	6	13	13
1.50 mm	9	8	4	10	10
2.00 mm	7	7	2	8	8

Table 11: The total radiant exposure (J/cm^2) through the specimens at 40 secs curing time.

Thickness	ICE Zircon	Zenostar	Bruxzir	Katana	Prettau Anterior
0.50 mm	29	27	23	33	33
1.00 mm	21	23	12	25	25
1.50 mm	18	16	7	19	19
2.00 mm	14	14	4	15	16

5.3. Degree of conversion (Study II)

The DC was 63.10% for RelyX Ultimate and 66.02% for Variolink II dual-cure cements with no specimen attenuating the light. The DC was significantly affected by zirconia brand, zirconia thickness and cement type (p<0.001). The DC decreased significantly as the thickness of the specimen increased (P<0.001) Figures 10, 11. The ranking of the specimens from highest DC to lowest for any given cement was: Katana=Prettau Anterior>Zenostar>Bruxzir>ICE Zircon.
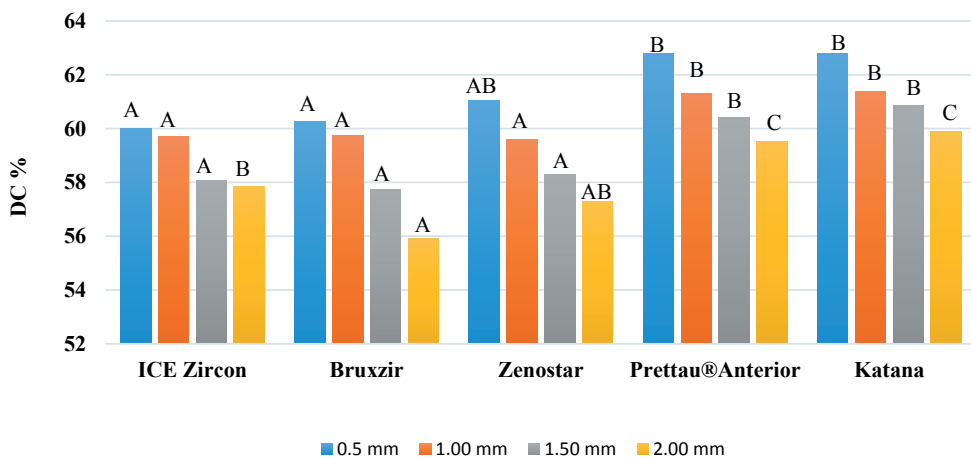
Figure 10: Mean degree of conversion of RelyX Ultimate cement after 20 secs curing time underneath the specimens with increasing thickness. Different letters indicate significant differences within the same thickness (p<0.05).
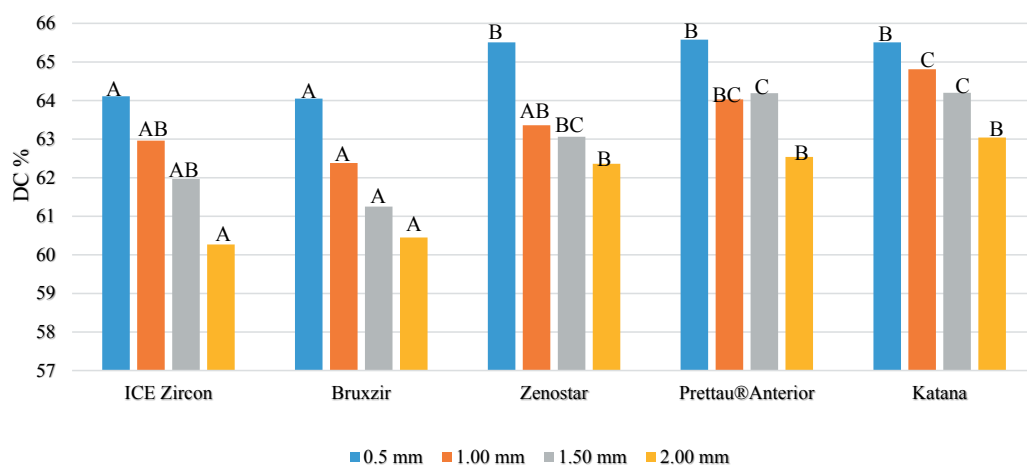
Figure 11: Mean degree of conversion of Variolink II cement after 40 secs curing time underneath the specimens with increasing thickness. Different letters indicate significantly different mean values within the same thickness ($p<0.05$).

5.4.   Bi-axial flexural strength (Study III)

The bi-axial flexural strength of PSZ was significantly higher than FSZ ($p<0.05$) (Table 12). Staining increased the bi-axial flexural strength of FSZ zirconia ($p<0.05$), but the type of sintering had no effect ($p>0.05$). Neither staining nor the type of sintering had an effect of the bi-axial flexural strength of the PSZ ($p>0.05$).

Table 12: Mean (±SD) bi-axial flexural strength values (MPa) of partially (Prettau) or fully (Prettau Anterior) stabilized zirconia before and after staining or sintering in vacuum conditions.

Group	Mean ± SD	Statistical difference*
FSZ	734 ± 129	a
FSZ vacuum	869 ± 114	a, b
FSZ stained	993 ± 83	b, c
PSZ stained	1026 ± 180	b, c
PSZ	1108 ± 201	c, d
PSZ vacuum	1237 ± 224	d

* Same letter indicates no statistical difference ($p>0.05$).

5.5.   Percentage of wieght loss (Study IV)

The zirconia brands showed a varying degree of weight loss in acid immersion (Study IV) with Prettau Anterior (FSZ) losing the most weight. Percentages of weight loss of the specimens after acid immersion are presented in Table 13. The pH of the HCl solution remained constant (pH=1.2) during the immersion. Percentage weight loss of lithium disilicate containing glass ceramic (IPS e.max) was about 3 times higher than that of any zirconia specimen.

Table 13: Percentage of weight loss specimens after acid emersion.

Groups	Weight loss %
Prettau	0.96%
Bruxzir	0.56%
Katana	0.70%
Prettau Anterior	1.40%
Zenostar	0.70%
Emax	3.05%

5.6. Surface characterization

5.6.1. Scanning electron microscopy (Study III and IV)

In Study III, the SEM evaluation indicated differences in grain morphology between FSZ and PSZ, with no differences between the sintering methods (regular furnace versus vacuum furnace). FSZ displayed some minor cracks on the grains, while PSZ demonstrated a smoother grain surface (Figure 12).
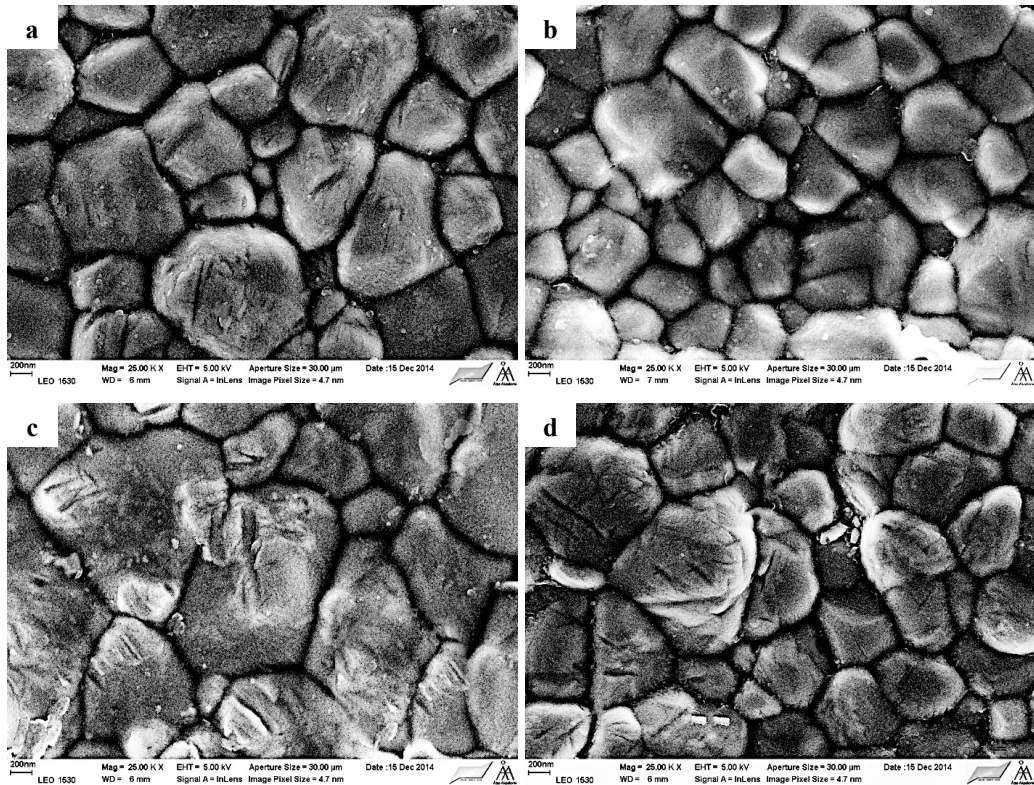
Figure 12. Scanning electron micrographs of partially and fully stabilized monolithic zirconia sintered in regular and vacuum furnaces. (a) Prettau after regular sintering, (b), Prettau after vacuum sintering, (c) Prettau Anterior after regular sintering, and (d) Prettau Anterior after vacuum sintering.

In study IV, the SEM evaluation indicated some areas of possible degradation after acidic challenge for Bruxzir, while other specimens showed bead-like shapes that were determined to be different oxides of Al, Ca, K, and Fe via EDX spectroscopy. Scratches from the polishing procedure were evident on all specimen, the outline of these scratches seemed to be less sharp after acid immersion (Figure 13).
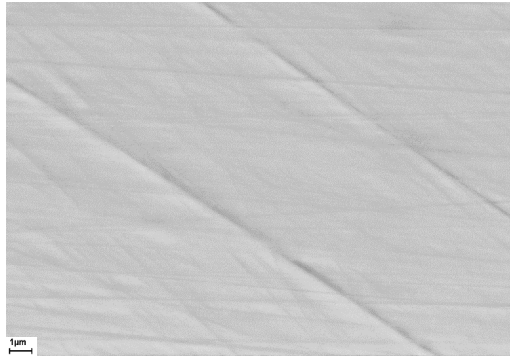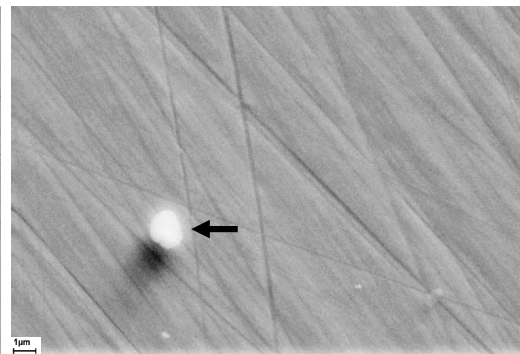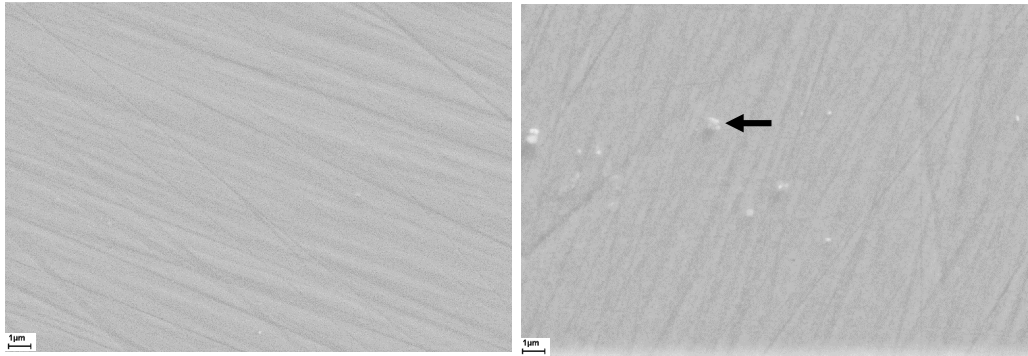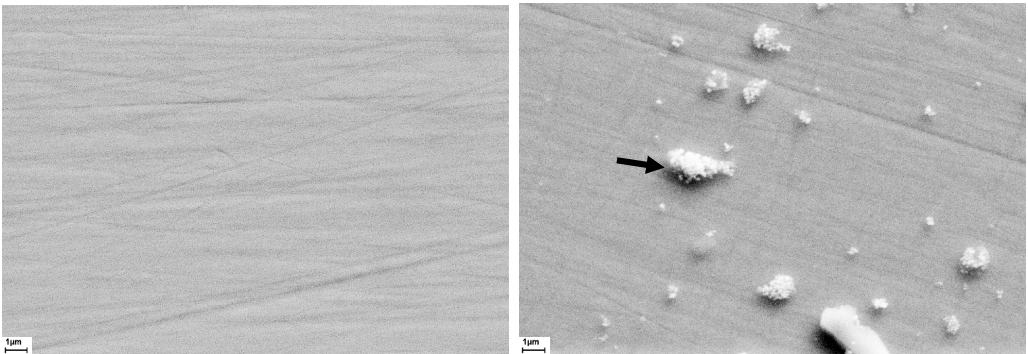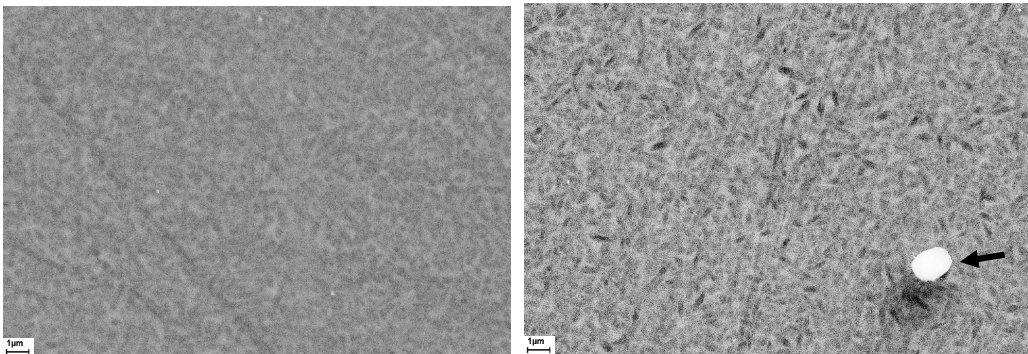

Bruxzir
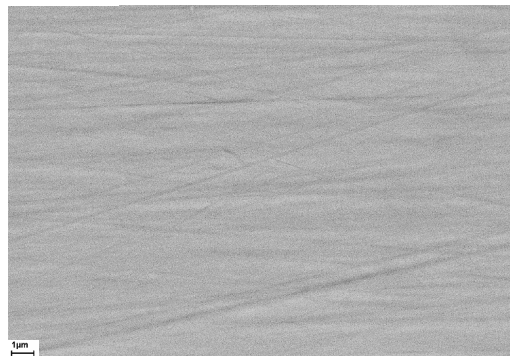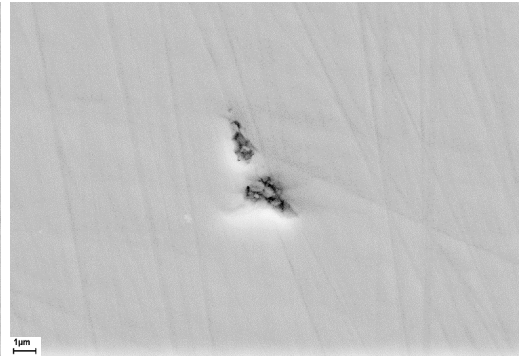
Prettau
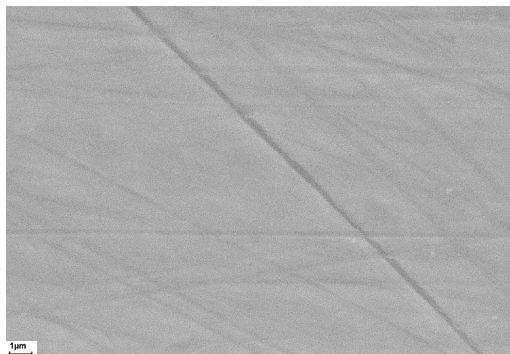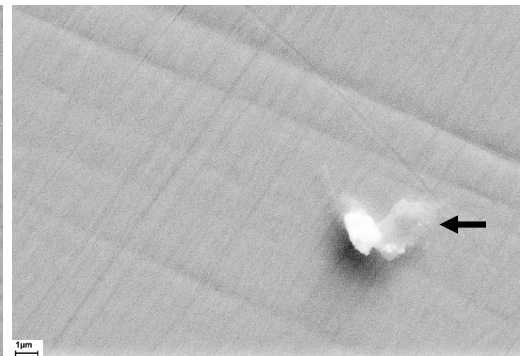
Katana

Zenostar

Prettau Anterior

IPS e.max

Figure 13: Scanning electron micrographs (Signal A= SE2, 5000x) of the investigated specimens. Left images show the surfaces before and right images show the surfaces after acid immersion. Arrow indicates 'bead-like' shape that were determined to be different oxides of Al, Ca, K, and Fe via EDX spectroscopy.

5.6.2. Energy dispersive x-ray spectroscopy (Study IV)

Ranges of surface elements (atom %) of zirconia specimens before acid immersion were Zr (22.7-26.8%), O (70.6-75.2%), Y (1.6-1.7%) and Hf (0.3-0.7%). Yttria atom % of Prettau Anterior (FSZ) was 3.1%. Surface elements (atom %) of zirconia specimens after acid immersion comparing two areas (1: bead-like shapes; 2: normal surface) are presented in Table 14. IPS e.maxCAD surface elements (atom %) before and after is presented Table 15.

Table 14: Surface elements (atom %) of monolithic zirconia materials after acid immersion.

Elements	Prettau (atom %)		Zenostar (atom %)		Bruxzir (atom %)		Katana (atom %)		Prettau Anterior (atom %)	
	1	2	1	2	1	2	1	2	1	2
Zr	19.3	29.5	20.0	28.5	16.7	27.9	13.2	29.3	18.9	21.6
O	80.7	70.5	80.0	71.4	44.6	72.0	78.7	70.6	79.5	61.9
N	--	--	--	--	38.6	--	--	--	--	16.3
Al	--	--	--	--	--	--	0.2	--	1.2	--
Ca	--	--	--	--	--	--	7.9	--	--	--
Fe	--	--	--	--	--	--	--	--	0.5	--

1: Bead-like area.
2: Normal area.

Table 15: Surface elements (atom %) IPS e.maxCAD after acid immersion.

	(Atom %)						
	Si	O	Mg	Al	P	K	Ca
1	26.1	73.7	--	1.5	1.2	1.0	0.4
2	22.4	69.6	0.1	1.3	1.1	1.3	--

1: Bead-like area.
2: Normal area.

5.6.3. Surface roughness (Study IV)

The S_a and S_q of the different specimens are listed in Table 16. S_a and S_q values for Prettau Anterior, Zenostar and IPS e.max were significantly lower ($p<0.05$) after acid immersion. There was no significant difference of S_a and S_q values for Katana, Prettau and Bruxzir after acid immersion.

Table 16: Mean values and standard deviation (SD) of S_a and S_q (µm) measurements before and after acid immersion.

Groups	S_a		S_q	
	Before	After	Before	After
Prettau	0.009 (0.002)	0.008 (0.001)	0.011 (0.001)	0.010 (0.001)
Bruxzir	0.009 (0.003)	0.008 (0.002)	0.011 (0.002)	0.008 (0.001)
Katana	0.009 (0.001)	0.008 (0.001)	0.014 (0.002)	0.012 (0.003)
Prettau Anterior	0.013 (0.002)	0.008 (0.002)*	0.021 (0.004)	0.011 (0.003)*
Zenostar	0.012 (0.001)	0.007 (0.002)*	0.015 (0.002)	0.012 (0.004)*
Emax	0.014 (0.002)	0.012 (0.001)*	0.022 (0.003)	0.017 (0.002)*

S_a is the arithmetic mean of the absolute values of the surface departures calculated from a mean plane.
S_q is the root-mean-square value of surface asperity departures from the reference datum within the sampling area.
*Indicates significantly lower S_a/S_q after acid immersion i.e. reduced surface roughness after acid immersion, post-hoc Tukey's HSD ($p < 0.05$).

6.   DISCUSSION

6.1.   General Discussion

The aims of the presented *in vitro* studies were to evaluate the optical and mechanical properties of different monolithic zirconia materials with varying thicknesses and different stability levels. Staining and sintering under vacuum, in addition to zirconias exposure to an acidic environment were evaluated from an optical and mechanical perspective. Light irradiance and transmission of energy through the zirconia were quantified in order to distinguish the influence of zirconia brand or material thickness on the DC of dual-cure cements that have been increasingly used for bonding zirconia restorations. Exploring monolithic zirconia in the aforementioned studies was of interest as this material has gained much attention and demand as a restorative material in dentistry.

The focus on clinical significance was an important aspect considered in the methodology design of the studies, when possible. As in the first study, the thicknesses of the zirconia specimens where selected to fit any clinical scenario with a preparation design requiring a restoration thickness from 0.5 mm to 2.0 mm, with four other thicknesses in between. Thickness of the ceramic material has an effect on the optical behavior of the restoration (Antonson & Anusavice, 2000), as most of the studies reported in the literature use the thinnest thickness recommended by the manufacturer which promote high translucency values and have the least clinical significance, making it very misleading.

The inevitable very low translucency of zirconia raised a series of questions of light cure irradiance and radiant exposure attenuation through the material, which led to the methodology of study II where light irradiance and exposure were quantified through zirconia specimens of different thicknesses and brands. Then the DC of two dual-cure cements were determined through infrared spectroscopy, and resulted in DC values larger than 50%, which seems to be typical of Bis-GMA-based resin material (Ferracane & Greener, 1986), thus enforcing the use of a dual-cure cement system where the light can trigger the polymerization process and the chemical component can complement it to achieve a DC that can be acceptable clinically.

In study III, the optical and mechanical properties of zirconia were investigated from a different perspective. Most of the zirconia material that has been documented in the literature is PSZ. Recently, FSZ has been introduced in effort to enhance zirconia's optical properties (by the presence of the more translucent cubic phase grains). Indeed, the FSZ did differ from PSZ as staining increased its gloss and enhanced its strength, while sintering under vacuum had minimal effects on both properties.

Another aspect of optical behavior was evaluated in study IV, where the simulation of gastric acid was attempted to mimic the acidic oral conditions of GERD patient. As moist environments have been reported to trigger LTD (Kobayashi *et al.,* 1981), but no data was available on the influence of a corrosive acid on the surface topography of the zirconia which in turn can affect its optical properties. The exposed zirconia surface to the corrosive acid did indeed display some form of surface topography changes which was in accordance with previous reports on the impact of a corrosive acid on ceramics (Milleding *et al.,* 1999; Esquivel-Upshaw *et al.,* 2013) with the FSZ again indicating different behavior than the PSZ.

6.2. Optical properties

The optics and esthetics related to monolithic zirconia have been the most demanding property for the clinician, and the most challenging task for manufacturers. Exploring the optical properties of monolithic zirconia from different manufacturing companies of different thicknesses gave us an insight of how close can monolithic zirconia mimic the natural dentition. In study I, five brands of monolithic zirconia were compared in terms of surface gloss, TP and CR values using a reflection spectrophotometer which operates by lighting two xenon lamps in quick succession and can virtually determine SCE and SCI measurements providing gloss of the surface in an 8° angle. Indeed, polishing the zirconia surface increased surface gloss significantly regardless of the brand and thickness of the zirconia specimen. Though, it was interesting to observe that some brands displayed more polishability than others, which may indicate the differences in grain structure and processing methods amongst the zirconias tested, as the polishing method was attempted at the least variability possible. Zirconia brightness (represented in L* values) increased after polishing, as more light is reflected thus making it more luminous and lighter value. This was in disagreement with another study that concluded polishing the zirconias surface decreases its lightness (Kim *et al*., 2013). The results for gloss measurements relies on many factors such as the material tested, manually cutting the zirconia blocks for research purposes versus milling procedures with cutting burs used for crown fabrication, the finishing protocol followed and the device used for gloss measurement.

Light transmission through zirconia is restricted due to its grain size that is larger than the incident wavelength causing the light to be reflected. Zirconia is well known to be an opaque material, hence the porcelain layering. In zirconias monolithic form, the degree of translucency measured in TP and CR values was evaluated in this project to compare the translucency of different zirconia brands and to evaluate the effect of the zirconia thickness on the translucency values. The thickness of the zirconia had a significant effect decreasing its translucency, which was in agreement with other

studies that examined the relation between the restorative materials thickness and translucency (Myers *et al*., 1994; Rasetto *et al*., 2004; Chaiyabutr *et al*., 2011). With the findings of this project, it was able to compare the translucency of zirconia to that of enamel and dentin. The TP values of the tested zirconias at 1 mm thickness ranged between 11.2–15.3, whereas TP values of enamel and dentin at 1 mm thickness are 18.7 and 16.4 respectively.

Comparison was even further enhanced when the CR values were determined. The perception of translucency was not very clear with TP values as no study in the literature has confirmed what the translucency perception threshold is in TP values. While Liu et al., determined the translucency perception threshold in CR values to be 0.06 (Liu *et al.*, 2010). The most translucent of the tested zirconias at 1 mm thickness was Prettau Anterior at 0.86. The CR of dentin at 1 mm thickness is 0.55 (Yu *et al*., 2009). It is obvious from the difference being more than 0.06 that the most translucent of the tested zirconias is dentin, which contradicts the manufacturer's claims for producing 'translucent zirconia'. Zirconia has a long way of development before being able to mimic the translucency of natural tooth. On that note, monolithic zirconia material may be classified as a *semi-translucent* material, and due to the presence of more cubic form zirconia, FSZ are relatively more translucent than PSZ.

In study III, the TP, CR and surface gloss were evaluated based on the level of stabilization of the zirconia. Optical properties of FSZ (Prettau Anterior) and PSZ (Prettau) were compared after staining and under vacuum sintering. It is to my knowledge, that there has been no reported study in the literature to this date (2015) for such a comparison. Due to the increased cubic phase of FSZ, the results indicated a more translucent FSZ than PSZ regardless of staining or type of sintering. However, staining decreased the translucency of FSZ with no significant effect on PSZ. This was interesting to observe as a possible explanation can be owed to the larger grain size of the FSZ with larger boundaries can lead to increase up take of the coloring liquid. In addition, the chemical nature of the coloring liquid can absorb more light photons decreasing the amount of transmitted light and negatively affecting the translucency. However, the difference in translucency was statistically significant, but less than 0.06 CR value, which may make it difficult for the eye to perceive according to Liu *et al*.'s study (Liu *et al*., 2010). Due to the increased intake of the staining liquid and decreased translucency of the FSZ, its surface gloss on the other hand was enhanced significantly with no effect on the PSZ. A possible explanation can be the result of decreased light transmission and possibly more light is reflected from the surface, making it more luminous and glossy. It might be important to consider the concentration of the coloring liquid on optical properties, as higher concentrations have a lower value (darker) and a more yellow-red hue than the same coloring liquids at lower concentrations (Suttor *et al*., 2004). Sintering under vacuum did provide a statistically significant enhancement for PSZ with no effect on the

FSZ. There is no logical scientific explanation to this result, the difference was less than 0.06 CR value and again is mostly non detectable by the human eye.

In study IV, the optical properties were investigated under an acidic environment. It is known that patients suffering from GERD have an eroded tooth structure, and most of them have lost their vertical dimension of occlusion and require extensive restorative work. Considering monolithic zirconia restorations as a viable option for restoring a worn dentition with conservative tooth preparation and the possibility of bonding to tooth structure, it was interesting to observe the effect of the simulated gastric acid on the translucency and surface gloss of the tested zirconias. The impact of the corrosive acid on the optical properties of zirconia was rather different among the zirconia brands. A smoother surface after acid immersion enhanced the surface gloss as less light is diffusely reflected rendering the specimen shinier. Some specimens displayed an enhanced translucency parameter value after acid immersion. However, the difference is very small and it is most probably not detectable by the eye with minimum threat to its esthetic appearance. It was also interesting to observe that certain specimens (Bruxzir and Zenostar) displayed lower b* values (more yellow) after acid immersion, while Katana had higher b* values, indicating that zirconia from different manufacturers have different composition that react differently with an acidic challenge. As most monolithic zirconia crowns are stained and glazed, it would be rather interesting to further research the effect of an acidic environment on the stability of such stains and how the esthetic appearance of the restoration is affected.

6.3. Light cure irradiance and radiant exposure

With the increased use of resin-based cements for cementation of monolithic zirconia restorations, it was important to determine light transmission through zirconia, and if enough energy was reaching the resin-based cement. The first study clearly showed, that monolithic zirconia is semi-translucent, thus light can be attenuated upon transmission. Simply defined, light irradiance represents the amount of light taken up by the material which was important to determine as a value for the amount of light transmitting through the specimens. Radiant exposure is the mathematical product of the light irradiance (mW/cm^2) multiplied by the exposure duration in seconds and is most relevant to polymerization.

It has been determined that the thicker the restoration and the darker the shade the less light is transmitted through it (Meyers *et al*., 1994; Rasetto et al., 2004). Indeed, the results of studies I and II are in agreement with earlier studies (Peixoto *et al*., 2007; Pazin *et al*., 2008). The light irradiance and radiant exposure decreased significantly with the increasing thickness of the zirconia specimens. As another determination,

the amount of light irradiance and radiant exposure were significantly influenced by the brand of zirconia. According to ISO standards 10650: "polymerization lights with an intensity of 300 mW/cm^2 appear to effectively polymerize most resin-based composite materials when appropriate polymerization times are used" (ISO standards 10650, 1999). Rueggeberg and Caughman suggested that the necessary amount of light irradiance to initiate polymerization was 400 mW/cm^2 at 60 seconds (Rueggeberg & Caughman, 1993). As determined from the results in studies I and II, most of the specimens fell under the latter limit with thicknesses more than 1.50 mm. Bruxzir displayed irradiance levels lower than 400 mW/cm^2 at thicknesses over 0.70 mm, which requires to increase the amount of exposure time in order to provide a radiant exposure sufficient to achieve optimal polymerization. Based on the results from study I, the curing ability of resin-based cements was questioned, which proposed the idea for the methodology of study II.

6.4. Dual-cure resin cement polymerization

As conventional acid-base reaction, and autopolymerizing cements can be used for cementing monolithic zirconia restorations when proper tooth preparation supports retention, there are circumstances where a retentive tooth preparation are hard to achieve, and the crown must be cemented with a resin-based cement bonding the restoration to the tooth structure. It is obvious from the results of studies I and II that light is attenuated through monolithic zirconia and the polymerization process may be compromised as insufficient energy can reach the cement. As a result, dual-cure resin cements have been advocated for cementing monolithic zirconia restorations.

In study II, two dual-cure resin cements were used to determine the DC under monolithic zirconia at variable thicknesses and from different manufacturers. The DC decreased significantly as the thickness of the specimens increased and the DC was significantly different among the tested brands with Katana and Prettau Anterior displaying higher DC values than Prettau, Zenostar and Bruxzir. This was in direct relationship to the amount of irradiance and radiant exposure determined in studies I and II. As the results were significantly different, yet the lowest reported DC value was above 50%. It has been reported that Bis-GMA resin-based material produce a DC 50−75% after polymerization (Ferracane & Greener, 1986; Bayne, 2005), therefore the DC may be considered to be within acceptable limits. A possible explanation for this is that both cements (RelyX Ultimate and Variolink II) had camphorquinone (CQ) as a photo initiator which has an absorption peak at 470 nm (Leonard, 2003) and is in accordance with the wavelength of the light used (Elipar S10, 420−480 nm). In addition to the role of the chemical component which further enhances polymerization to a certain limit when light is attenuated. The efficiency of the chemical component may differ from one brand to

another (Rueggeberg & Caughman, 1993). This can provide possible explanation for the higher DC of Variolink II versus RelyX Ultimate. However, despite the statistical significance in DC, the clinical significance may be irrelevant.

The results of study II were in agreement with the concepts of other studies concluding that the DC of resin-based material can be affected by the light curing time and irradiance, restoration thickness, shade and translucency (Rueggeberg & Caughman, 1993; Sheila *et al.*, 2013).

6.5. Bi-axial flexural strength

In study III, the bi-axial flexural strength of the PSZ (Prettau) where yttria content is 4–6 mol% and FSZ (Prettau Anterior) where yttria content is around 12 mol%, were evaluated in accordance with the ISO Standard 6872 (ISO 6872, 1995) after coloring (staining) the zirconia and sintering under vacuum. The overall strength of PSZ was superior to FSZ, as the latter possess more cubic grains and thus is less stable than the dominant tetragonal phase of the PSZ. It is well accepted that failure to load testing of dental ceramics provide minimal clinical relevance as fatiguing under a moist environment with a million cycles may provide a closer clinical relevance of around 5 years (Studart *et al.*, 2007). Yet, it is important to apply load testing as it may give an insight on the original strength of the material.

It was interesting to investigate the behavior of the newly introduced FSZ at the time (2014), as there have been no studies reported on FSZ in the literature. Indeed, staining of the FSZ enhanced its strength significantly with no effect on PSZ. This is difficult to explain, possibilities may stem from the different microstructure, nature of grains and the high yttria content of the FSZ that may have reflected upon this behavior. Further research regarding the microstructure of the FSZ is needed to draw a definite explanation. The concentration of the coloring liquid can have a considerable effect on the strength of zirconia material. Certain metal-salts at high concentration have been reported to decrease the strength of zirconia (Shah *et al.*, 2008; Hjerppe *et al.*, 2008).

In regards to the effects of sintering under vacuum versus a regular furnace on the bi-axial flexural strength of zirconia, our results indicated minor enhancement in the strength for both types of zirconia, however the results were not statistically significant. Vacuum-based furnaces can provide an environment with no oxygen or other gases inhibiting surface oxidation, preserving the yttria and renders it more stable and strong. Also it may prevent heat transfer within the product through convection.

6.6. Effect of simulated gastric acid on monolithic zirconia

In regards to the corrosive acid concentration and immersion time, there is no clear consensus in the literature of the actual method of gastric acid simulation and the equivalent time to replicate an *in vivo* model. The ISO standard 6872 solubility test for dental ceramics advocates the use of a 4% acetic acid and a standard exposure time of 16 hours at 80°C (ISO 6872, 1995). The *in vivo* relevance of this time was determined to be equivalent to approximately 2 years based on the study by De Rijk *et al.*, that reported an immersion in artificial saliva at 22°C for 22 years would have been required to produce the same degree of dissolution as exposure to 4% acetic acid at 80°C for 168 hours (De Rijk *et al.*, 1985). The *in vitro* simulation of corrosive effects of acids on surface topography of dental ceramics mainly depends on the concentration of the acid, the time of immersion and the temperature. In the present study, a stronger acid (HCl, pH 1.2) based on Hunt and McIntyre's method rather than the ISO standard 6872 of 4 % acetic acid was used (Hunt & McIntyre, 1992), with increasing the immersion time to 96 hours at 37°C, may better simulate an *in vivo* relevance of approximately 10-12 years.

Indeed, after acid immersion all materials showed weight loss, which however was small, with the fully stabilized zirconia (Prettau Anterior) bearing the most % of weight loss. IPS e.max, having a different microstructure than zirconia, displayed around 3 times more % of weight loss than the zirconia specimens, which may indicate its increased vulnerability to a corrosive conditions.

The fact that SEM images indicated that Bruxzir displayed some areas of possible degradation bares two possible interpretation; Chevalier (2006) reported similar observations in particular femoral heads and owed these "crater-like" areas to monoclinic nuclei formed by aging of the material (Chevalier, 2006). Another possible interpretation can be simply a missed spot during the polishing process. In either case, these areas can lead to further damage to the surface and to the opposing dentition, which denotes the importance of careful polishing process. Other specimens displayed bead-like shapes on the corroded surface. EDX spectroscopy revealed that these areas were oxides of either Al, Ca, K or Fe that possibly formed as these alkali ions were leaching out of the zirconia or Si, Ca and Mg ions leaching out of the IPS e.max, indicating a possible corrosive effect by the acidic solution. Another noticeable finding was how Prettau Anterior (FSZ) showed multiple bead-like shapes distributed on its corroded surface compared to more single or isolated bead-like shapes on the other (PSZ) specimens, which may indicate the increased vulnerability of the FSZ to corrosive acids. Surface roughening, however minor it is, may lead to increase wear to the opposing dentition and increase bacterial adherence through mechanical entrapment (Elftonson *et al.*, 1996). Also, a positive correlation between plaque accumulation and surface roughness has been previously reported (Castellani *et al.*, 1996).

The surface elements determined by EDX spectroscopy represented by atom % displayed rather interesting results. Certain elements were present before acid immersion with no trace of them after acid immersion (yttria and hydrogen fluoride elements present on the zirconia surface before acid immersion had no trace after acid immersion). The opposite is also true, as traces of certain elements were evident after acid immersion. Presence of certain elements in the bead-like shapes more than on the normal surface of the specimen may indicate the leaching process of this element out of the specimen. This confirms that a significant ion interaction occurs between the specimen surface and the acidic solution, which agrees with the findings of other studies (Milleding *et al.,* 2002; Kukiattrakoon *et al.,* 2010; Esquivel-Upshaw *et al.*, 2013)

6.7.   Strengths and weaknesses of the study

The comprehensive studies encompassed into this thesis focused on comparing the optical and mechanical properties of the major brands of monolithic zirconia in the market as of 2014. Concluding that monolithic zirconia is a semi-translucent material gives a better insight to the restorative dentist aiding in material selection. The evaluation of the recently introduced FSZ with comparison to the more traditional PSZ, to my knowledge, has never been conducted in the literature. The evaluation and comparison of the tested zirconias to an acidic challenge has not been studied earlier as well.

The strive for an ideal *in vitro* experiment and its ability to extract clinical significance and recommendations comes with the bitter challenge of inevitable weaknesses and limitations. In study II, possible limitations may be the design of the tested specimens which are flat, allowing the light curing tip to be in close approximation to the surface, whereas in clinical situation the cusps dictate the placement of the tip further away from the cement and reducing the lights efficacy and may negatively affect DC. On the other hand, the DC in study II was determined at room temperatures (23°C), wherein the oral cavity higher temperatures (37°) can positively influence the DC (Olivera *et al*., 2012).

No thermocycling was executed on any of the specimens as moisture and temperature differences may have a significant impact on how zirconia behaves within these environments. The nature of the mechanical test was static and monotonic uniaxial loading and may have less clinical significance to a cyclic fatiguing test in a moist environment (Jung *et al.*, 2000), but the intentions were only to determine basic strength facts about the zirconia material and not to conclude any clinical recommendations. Another possible limitation is in study IV, where the quantification and measurement of the ions leaching from the specimens would have further supported the difference in weight loss after acid immersion, and acknowledging that limitation initiated another

study determining the amount of ions leaching from monolithic zirconia and the effect it may have on its physical properties.

6.8. Perspectives of future studies

Monolithic zirconia material indeed possesses many desirable properties rendering it a material of choice for many dentists. The premature selection of recent zirconia restorations still fall behind a lacking of solid scientific and clinical evidence of its success. As the monolithic zirconias' optical properties are far from being considered as a restoration to mimic the natural dentition, manufacturers are introducing the fully stabilized zirconia as a more translucent material. Further research on the microstructure, physical properties and optical properties are needed before any conclusions or recommendations of this fairly new type of zirconia can be made.

Zirconias' vulnerability to low temperature degradation seems to still haunt this material, and only properly designed *in vitro* studies that can mostly relate to a clinical scenario must be conducted, as the more definite conclusions from a long term randomized clinical trial is difficult and still lacking in the literature. Cyclic fatiguing in an aqueous environment with cycle numbers of around a million has been determined in the literature to closely resemble a clinical significance of 5 years. It is recommended that monolithic zirconia to be tested under such circumstances, as the reports of failure to load may give us an insight on the material itself with minimum clinical relevance.

It seems that monolithic zirconias' surface topography and optical properties are affected minimally by a corrosive acids. It would be interesting to determine the effect of a corrosive acid on the strength of zirconia, and how a corrosive acid can affect the stability of stains and glazes that are used with most monolithic zirconia restorations.

It is crucial that more *in vitro* and *in vivo* research is conducted on monolithic zirconia before the announcement of any clinical recommendations. The upcoming years will be interesting for following up on the development and performance of this material.

7. CONCLUSIONS

Based on the findings of the studies included in this thesis, the conclusions can be summarized as follow:

1. Monolithic zirconias of different manufacturers have different translucencies, which is furthermore influenced by the thickness of the material. FSZ are relatively more translucent than PSZ. Various zirconia brands have different surface gloss that can significantly increase with polishing but is not influenced by the thickness of the material. The optical properties of monolithic zirconia are far from mimicking the natural tooth structure. Light irradiance and radiant exposure are attenuated through monolithic zirconia and are brand and thickness dependent.

2. The degree of conversion of dual-cure cements decrease significantly underneath monolithic zirconia restorations, but seem to be within the accepted range of 50%. It is important to use a cement system that is not dependent on light-curing for zirconia restorations, since it is difficult for the clinician to estimate the effect of thickness and shade on transmitted light needed for curing the cement used.

3. Fully stabilized zirconia behaves differently than the traditional partially stabilized zirconia as staining enhances the FSZs strength with minimum effect on the PSZ. Sintering under vacuum has minimum effect on the optical and mechanical properties with either type of zirconia.

4. Monolithic zirconia restoration may show a sign of resistance to an acidic environment with minimal effect of the acid on zirconia's optical properties. Whether a smoother surface is in fact a sign of true corrosion resistance or is purely the result of an evenly progressive corrosive process is yet to be confirmed by further research, bearing in mind the threat of low temperature degradation in an aqueous environment regardless of its acidity still seems to haunt yttria stabilized zirconia.

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