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Effect of pH Fluctuations in Saliva on Low-Temperature Degradation of Dental Monolithic Zirconia Restorations.

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by

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This is to certify that we have read the thesis **Effect of pH Fluctuations in Saliva on Low-Temperature Degradation of Dental Monolithic Zirconia Restorations.**submitted by **Ender AKAN**, and it has been judged to be successful, in scope and in quality, at the defense exam and accepted by our jury as a MASTER'S THESIS.

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Effect of pH Fluctuations in Saliva on Low-Temperature Degradation of Dental Monolithic Zirconia Restorations.

Abstract

Monolithic zirconia restorations are known for their excellent mechanical properties, biocompatibility, and aesthetics. However, they are susceptible to a phenomenon called low-temperature degradation (LTD). LTD refers to the degradation of zirconia in the presence of water or water vapor at temperatures below 100 degrees Celsius. It involves a phase transformation from the metastable tetragonal phase to the more stable monoclinic phase. This phase transformation can lead to microcracks and dimensional changes in the zirconia, compromising its mechanical strength and long-term stability. Saliva is a complex fluid that contains electrolytes, enzymes, proteins, and bacteria. The pH of saliva can vary depending on various factors, such as diet, oral hygiene, and systemic conditions. Saliva can provide a moist environment for zirconia restorations, allowing water absorption and subsequent phase transformation. Additionally, the ions present in saliva, such as hydroxyl ions (OH-) and hydrogen ions (H+), can influence the pH of the surrounding environment and affect the kinetics of the phase transformation.

The study aims to provide valuable insights into the role of pH fluctuations in saliva and its influence on the long-term stability and performance of zirconia restorations, ultimately contributing to the development of improved dental materials and treatment protocols.

20x20 mm cylinder-shaped blocks were fabricated by CAD/CAM from a pre-sintered 5Y-TZP block (ZenostarT; Wieland Dental). SiC papers (600 and 1200-grit) were used to smooth the sidewalls of the cylindrical shape. 1.65 mm thick slices (discs) were obtained by cutting under water cooling with diamond blades (ISOMET 1000, Buehler).

The artificial saliva Fusayama-Meyer (pH 5.8) was prepared and divided into three groups. To create different acidic saliva media, pH 1.2 (group 1) and pH 2.5 (group 2),

hydrochloric acid (HCl), which is the main component of gastric acid, was used. The Fusayama solution with a neutral pH level of 5.8 (group 3) was kept as the control group. Microhardness, XRD and SEM analyses were performed.

Keywords: Zirconia, Saliava, LTD (Low Temperature Degredation)

Tükürükteki pH Dalgalanmalarının Dental Monolitik Zirkonya Restorasyonlarının Düşük Sıcaklıkta Bozulmasına Etkisi.

Öz

Monolitik zirkonyum restorasyonlar, mükemmel mekanik özellikleri, biyouyumluluk ve estetiği ile bilinir. Ancak, düşük sıcaklık bozulmasına (LTD) eğilimlidirler. LTD, su veya su buharı varlığında 100 santigrat derecenin altındaki sıcaklıklarda zirkonyumun bozulmasına karşılık gelir. Metastabil tetragonal fazdan daha kararlı monoklinik faza bir faz dönüşümünü içerir. Bu faz dönüşümü, zirkonyumda mikro çatlaklara ve boyutsal değişikliklere neden olabilir, bu da mekanik mukavemetini ve uzun vadeli stabilitesini tehlikeye atabilir.

Tükürük, elektrolitler, enzimler, proteinler ve bakteriler içeren karmaşık bir sıvıdır. Tükürük pH'ı, diyet, oral hijyen ve sistemik koşullar gibi çeşitli faktörlere bağlı olarak değişebilir. Tükürük, zirkonyum restorasyonlar için nemli bir ortam sağlayabilir, su emilimine ve ardından faz dönüşümüne izin verebilir. Ek olarak, tükürükte bulunan iyonlar, örneğin hidroksil iyonları (OH-) ve hidrojen iyonları (H+), çevredeki ortamın pH'ını etkileyebilir ve faz dönüşümünün kinetiklerini etkileyebilir.

Bu çalışma, tükürük pH dalgalanmalarının rolü ve zirkonyum restorasyonların uzun vadeli stabilitesi ve performansı üzerindeki etkisine dair değerli bilgiler sunmayı amaçlamaktadır. Bu, nihayetinde geliştirilmiş dental malzemeler ve tedavi protokollerinin geliştirilmesine katkı sağlayacaktır.

20x20 mm silindir şeklindeki bloklar, bir ön sinterlenmiş 5Y-TZP bloktan (ZenostarT; Wieland Dental) CAD/CAM ile üretilmiştir. SiC kağıtları (600 ve 1200 grit) silindirik

şeklin yan duvarlarını düzeltmek için kullanılmıştır. 1.65 mm kalınlığındaki dilimler (diskler), elmas bıçaklar (ISOMET 1000, Buehler) ile su soğutma altında kesilerek elde edilmiştir.

Yapay tükürük Fusayama-Meyer (pH 5.8) hazırlandı ve üç gruba ayrıldı. Farklı asidik tükürük ortamları oluşturmak için pH 1.2 (grup 1) ve pH 2.5 (grup 2), mide asidinin ana bileşeni olan hidroklorik asit (HCl) kullanılmıştır. Fusayama çözeltisi, nötr bir pH seviyesi olan 5.8 (grup 3) kontrol grubu olarak tutuldu. Mikrosertlik, XRD ve SEM analizleri yapılmıştır..

Anahtar Kelimeler: Zirkonyum, Tükürük, LTD (Düşük Sıcaklık Bozulması)

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List of Abbreviations

CAD	Computer-aided Deesign
CAM	Computer-aided Manufacturing
ASTM	American Society for Testing and Materials,
ISO	International Standards Organization
SEM	Scanning Electron Microscopy
STL	Standard Triangle Language
YSZ	Yttria stabilized zirconia
CIP	Cold isostatic press
HIP	Hot isostatic press
LTD	Low temperature degradation
PVA	Polyvinyl alcohol
XRD	X-ray diffraction
TGA	Thermal gravimetry analysis
TZP	Tetragonal zirconia polycrystals

List of Symbols

°	Degree
°C	Celsius degree
μm	Micro meter
rpm	Revolutions per minute
%	Percent
t	Tetragonal phase
m	Monoclinic phase

Chapter 1

Introduction

Dental ceramics are the leading restorative materials used in dentistry due to their aesthetic and biocompatible properties. Despite their superior mechanical properties, metal-ceramic restorations have disadvantages such as the reflection of metal color in the gums, the possibility of allergies, corrosion, and lack of light transmission in the anterior region.

The increasing aesthetic concerns and technological developments have led to the search for different restorative systems that are tooth-colored, biocompatible, and provide the superior mechanical properties of a metal substructure as an alternative to metal-backed ceramic restorations that have been used for a long time. Researchers have tried to strengthen the substructure of the restoration by using different materials. Ceramic substructures have begun to be strengthened with different techniques such as the distribution of aluminum with controlled crystallization, glass infiltration, and the use of leucite or lithium disilicate crystals. However, only single crowns and three-member fixed restorations in the anterior region have been successful with the ceramics produced using these methods.

Zirconium oxide (zirconia) ceramics have been increasingly used in dentistry because they are more aesthetic, biocompatible, and have superior mechanical properties than ceramic restorations with metal substructures. Zirconium oxide ceramics allow excellent aesthetic results to be obtained in restorations in the anterior region because they transmit light in a similar way to natural teeth. Additionally, zirconium oxide ceramics are resistant to corrosion, making them more durable and reliable than ceramic restorations with metal substructures.

Zirconia was used as substructure material because its optical properties are still not sufficient compared to the ceramic material such as lithium disilicate or feldspathic ceramics. However, chipping of the veneering ceramics was occured by time and it results as clinicle failure. In order to overcoma this failure, monolithic zircona introduced. Optical properties were improved and it could be used without veneering ceramics. Mono layer zirconia restorations without vennering cermics appeared new phenomen, zirconia are in contact with oral envirement. Monolithic zirconia now exposed to hard conditions of oral enviroment such as pH fluctations, cheewing cycles, thermal changes.

The study will involve conducting controlled laboratory experiments to simulate the oral environment and replicate pH fluctuations in saliva. Zirconia specimens will be exposed to different pH levels, including acidic and alkaline conditions, to evaluate their impact on low-temperature degradation. The data obtained from the experiments will be analyzed and compared to determine the influence of pH fluctuations on low-temperature degradation. Statistical analysis may be performed to identify significant differences and correlations between pH levels and degradation parameters. The findings may contribute to the development of guidelines or recommendations for dental professionals regarding oral hygiene practices, patient education, and material selection to minimize the impact of pH fluctuations on the longevity and performance of zirconia restorations.

Chapter 2

Literature Review

2.1 Dental Ceramics

Dental ceramics are the leading restorative materials used in dentistry due to their aesthetic and biocompatible properties. Dental ceramics typically contain silicon. Silicon exists in the form of silica (silicon dioxide) and its derivatives. Silicates have a silicon tetrahedron structure. Large oxygen atoms act as a matrix, surrounding them with more covalent bonds. These strong bonds give ceramics properties such as stability, hardness, resistance to heat and chemicals. However, this structure also causes undesirable properties such as low thermal and electrical conductivity and brittleness.

The composition of dental ceramics is mainly composed of feldspar (K_2O Al_2O_3 $6SiO_2$), kaolin (Al_2O_3 SiO_2 H_2O) and quartz (SiO_2). Feldspar is a mixture of potassium alumina silicate and sodium alumina silicate. It is the main structure that gives porcelain a natural translucency and is present at a minimum of 60%. It melts at temperatures of 1250-1500 °C and turns into glass, helping to bond the structure together with quartz and kaolin. Kaolin is a molecule with an aluminum silicate hydrate structure, known as china clay. It is present at 1-5% and is very resistant to heat. Due to its adhesive property, it helps the porcelain to stay together and be easily shaped before firing. However, it is used in small amounts because it is opaque view. Quartz has a silica structure and is present in the matrix at 10-30%, acting as a filler. It provides stability to the mass by preventing shrinkage that may occur as a result of the firing process. Since it has a high melting point, it helps the restoration to maintain its shape at high temperatures. It gives the material a transparent properties (1,2,3).

In addition to these three main ingredients, porcelain composition may also contain glass modifiers, intermediate oxides, various color pigments, opacifiers, or agents that

enhance the fluorescence property. High-temperature metal oxides of elements such as titanium, magnesium, iron, cobalt, copper, and nickel are added to give color to porcelain. Thus, porcelain color pigments are obtained. In particular, opacifiers are also added to porcelain in metal-supported porcelain restorations to give naturalness to porcelain. Of the opacifier agents obtained from metal oxides, cerium oxide, titanium oxide, and zirconium oxide are the most commonly used (4,5)

2.1.1 Reinforced Dental Ceramics

Ceramics are strong in compression, but weak in tension. This is because ceramics are brittle. Various methods have been developed to strengthen ceramics.

Ceramic strengthening methods: (6,7,8,9)

1. Strengthening ceramics with core material
    a. Reinforcement with metal core
    b. Reinforcement with zirconia core
2. Strengthening of ceramics by controlled crystallization of glass
3. Reinforcement of ceramic by glass infiltration
4. Reinforcement of ceramics by surface treatments
    a. Rapid cooling, tempering,
    b. Surface ion-exchange

Reinforcement with a core material such as metal or zirconia is a method used to achieve durable and aesthetic results, often combining the advantages of different materials. In this process, ceramics and core material are typically brought together. Ceramics are brittle materials prone to cracking. Therefore, a core substructure is used to enhance the durability of ceramics. Metal alloys are more resistant to tensile forces,

so a metal layer or frame is often created underneath ceramics. The metal core enhances the tensile strength of ceramics, preventing crack formation.This way, ceramic-covered dental restorations can be successfully completed, both aesthetically and functionally.

Metal-ceramic restorations, while successfully utilized, have aesthetic drawbacks due to their interference with light transmission. Additionally, coloration and corrosion resulting from the ionization of ions in the gum tissue are among the other disadvantages of metal core. To overcome these disadvantages associated with metals, the use of zirconia as a core material is recommended. Zirconia, while having weaker optical properties, offers excellent mechanical properties. Utilizing zirconia as a core material with veneering ceramic has enabled the production of aesthetically successful restorations.

Ceramic reinforcement through controlled crystallization of glass involves transforming glass into glass-ceramic by means of the lost wax technique and applying a heat treatment. In this process, nuclei form within the glass matrix, and crystalline growth occurs around these nuclei. As a result, controlled crystal size is achieved instead of an amorphous structure, leading to the formation of homogeneous, non-porous, and uniformly sized microstructures with high durability.

Glass Infiltration for Ceramic Reinforcement; when a durable crystalline material is added to a glassy phase, the strength and resistance of the glass increase. These crystals include leucite, lithium disilicate, alumina, magnesium alumina spinel, and zirconia. Cracks cannot propagate as easily through these particles in the glass matrix. The level of durability depends on the type, size, volume, interparticle gaps, and thermal expansion coefficient of the crystals.

Reinforcement of ceramics also achieved by creating compressive stresses on the surface, thus preventing tensile stresses within. Thermal tempering is based on the principle of cooling under pressure immediately after porcelain is removed from the furnace. Ion-exchange is a method for creating compressive stresses on the porcelain surface. Larger alkali ions replace smaller ions. As the temperature rises, larger ions diffuse and settle on the surface of the ceramic or glass through diffusion. During the process, the ceramic is immersed in a molten salt bath. During cooling, the larger ions

create compression on the porcelain surface, reducing the effect of tensile forces on microcracks. The compressive stresses generated on the porcelain surface prevent the formation of microcracks and strengthen the porcelain.

Classification of Dental Ceramics According to Their Content

A. Glass - Matrix Ceramics
    1. Feldspathic

    2. Synthetic
        a. Leucite
        b. Lithium disilicate and derivatives
        c. Fluorapatite

    3. Glass infiltration
        a. Alumina
        b. Allumina and magnesia
        c. Allumina and zirconia

B. Polycrystalline Ceramics
    1. Allumina
    2. Zirconia
    3. Allumina and zirconia

C. Resin – Matrix Ceramics
    1. Resin nanoceramic
    2. Glass ceramic in a resin matrix
    3. Zirconia in a resin matrix

Zirconium was first discovered in Sri Lanka in 1789. Zirconium (Zr), with an atomic number of 40 and an atomic weight of 91.22, is a chemical element belonging to the metals group in the periodic table and has a silver-white color at room temperature . The density of zirconium is 6.49 g/cm^3, its melting point is 1855°C, and its boiling point is 4409°C. This element is not found in nature in its pure form; it forms silicate oxides (ZrO_2 X SiO_2) or free oxides (ZrO_2) compounds (10).

Zirconia was first used as a biomedical material in orthopedics, but its usage significantly decreased due to fractures occurring in these prostheses. In dentistry, zirconia was introduced in the 1990s and its usage became widespread with the development of CAD/CAM systems. Zirconia is used in dentistry for various materials such as final restoration and/or core material in crown and bridge restorations, implants and implant abutments, non-metallic retainers, cutting and surgical burs, and orthodontic brackets (11,12).

Zirconia (ZrO2) is a polymorphic material and zirconium oxide crystals can be found in three different phases (Figure 1) (10,13):

(i) cubic phase: in the form of a square-shaped flat prism,

(ii) tetragonal phase: in the form of a rectangular-shaped flat prism,

(iii) monoclinic phase: in the form of a deformed prism with parallel faces.

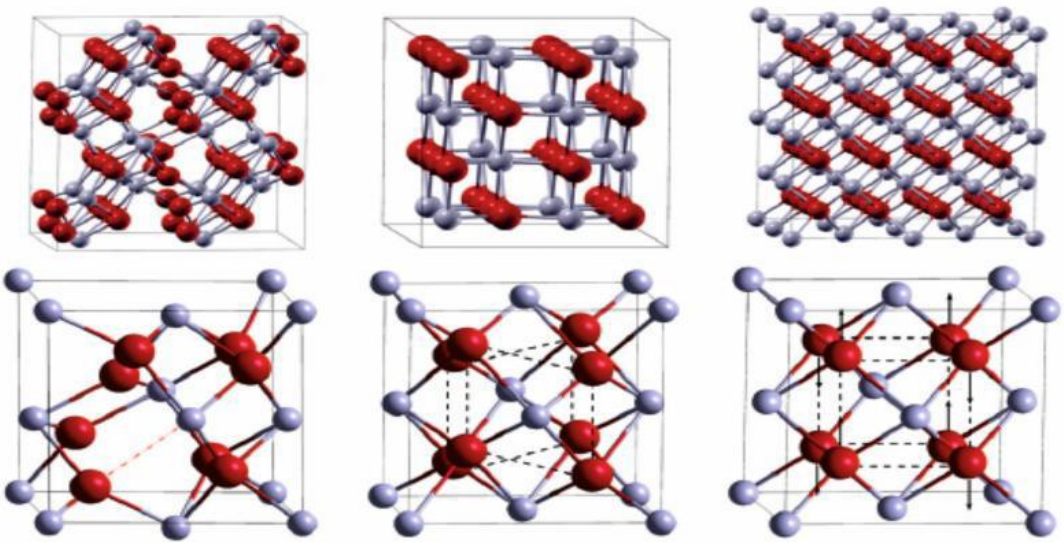


Figure 1: Monoclinic phase 1170°C < Tetragonal phase 2370°C < Cubic phase

Zirconium oxide crystals are found in the cubic phase between temperatures of 1170°C and 2370°C, with a melting point of 2680°C, and they are stable and possess average mechanical properties. The tetragonal phase is stable between 1170°C and 2370°C and exhibits superior mechanical properties. The monoclinic phase is stable between room temperature and 1170°C, showing lower mechanical properties, which may lead to a decrease in cohesion and density between ceramic particles.

Pure zirconium oxide exists in the monoclinic phase at room temperature. This structure is stable up to 1170°C, transitioning to the tetragonal form above this temperature and to the cubic form above 2370°C. During the cooling process, a tetragonal-to-monoclinic phase transformation occurs at 1070°C, accompanied by a volume increase of 3-5% . Although the compressive forces resulting from this volume increase enhance zirconium's resistance, if this phase transformation is not controlled, it can lead to fractures in zirconia. Therefore, zirconia needs to remain stable under normal conditions. Various oxides such as magnesium oxide (MgO), yttrium oxide (Y2O3), calcium oxide (CaO), and cerium oxide (Ce2O3) can be added to stabilize zirconia in the tetragonal or cubic phase under normal conditions. Adding stabilizer oxides results in a multiphase material at room temperature. The formation of alloys of pure zirconia with stabilizing oxides such as CaO, MgO, Y2O3, or CeO2 stabilizes zirconia in the tetragonal phase at room temperature, controls the transformation from the stress-generating tetragonal phase to the monoclinic phase, effectively prevents crack formation, and ensures high hardness. By adding these stabilizers to zirconia, when the temperature is raised above 1000°C, zirconia transitions from the monoclinic phase to the tetragonal phase, and upon returning to room temperature, partially stabilized zirconia (PSZ: Partially Stabilized Zirconia), a mixture of cubic and tetragonal phases, is obtained, thus preventing uncontrolled phase transformation (14,15).

In dentistry, zirconia is commonly used in the form of yttrium-stabilized tetragonal polycrystalline zirconia (Y-TZP), partially stabilized zirconia polycrystal with magnesium (Mg-PSZ), and zirconia toughened alumina (ZTA). In addition to these, research has begun on the use of cerium-stabilized polycrystalline zirconia (Ce-TZP) in recent years. Although Ce-TZP has higher fracture toughness values compared to Y-TZP (Ce-TZP=19 MPa > Y-TZP=5-10 MPa), its lower flexural strength and harder

nature have limited its widespread use in dentistry (45). While Mg-PSZ has shown successful results as a biomaterial, its usage has decreased due to its porous structure, making it more susceptible to erosion compared to Y-TZP, as well as its extremely high sintering temperature (approximately 1800°C) and the complex production methods requiring precise techniques.

Y-TZP, formed by adding 2-3 mol% of Y2O3 (yttrium oxide) to pure zirconia, is widely used in dentistry due to its superior mechanical properties. Y-TZP has a fracture toughness of 5-10 MPa and a flexural strength ranging from 900 to 1400 MPa. In addition to these positive mechanical properties, Y-TZP is biocompatible, exhibits low bacterial adhesion, allows cementation with both conventional and adhesive cements, and has low thermal conductivity. However, the main disadvantages of Y-TZP restorations include their opaque appearance, which may not meet aesthetic expectations adequately, the potential negative impact of surface treatments on the mechanical properties of Y-TZP, and the need for more tooth preparation when used in conjunction with superstructure ceramics (16,17).

When an external force, such as abrasion or high forces, is applied to partially stabilized zirconia (PSZ), the tetragonal phase particles begin to transform into the monoclinic phase. This transformation results in a volume increase in the relevant region of the ceramic, creating compressive forces around it. Consequently, the compressive stresses localized at the crack tips prevent the propagation of micro-cracks within the material. This physical phenomenon is called "transformation toughening" (also known as phase transformation toughening) (Figure 2). Due to this physical property, zirconia achieves significantly high fracture toughness and flexural strength values (18).

The spontaneous transition of zirconia from the tetragonal phase to the monoclinic phase implies the loss of the material's semi-stable property over time. This condition was first described by Kobayashi (19) and is known as "low-temperature degradation" (LTD), also referred to as zirconia aging. It has been

determined that for this phase transformation to occur, the material must be exposed to a critical temperature range of 200-300°C.

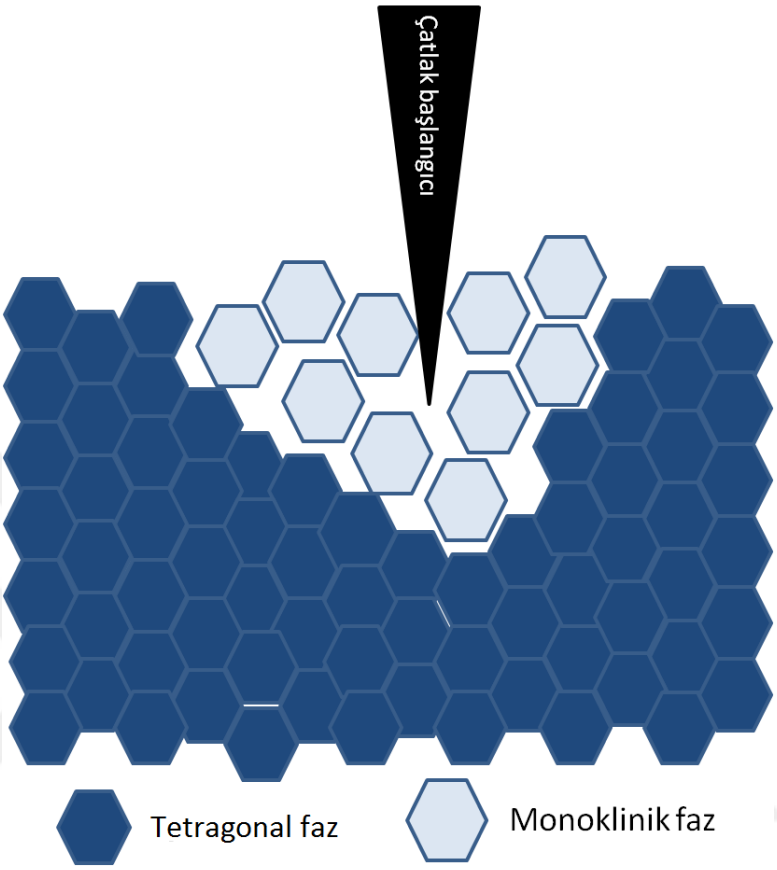


Figure 2: Transformation Toughening (Phase Transformation Hardening)

Low-temperature degradation primarily initiates on the surface of polycrystalline zirconia and then progresses into the material. The transformation of a crystal induces stress formation around the crystals and micro-cracks, leading to volume expansion. The presence of moisture in the environment increases the extent of phase transformation. Water absorption causes surface degradation first, followed by phase transformation. It is known that there is an increase in crystal dimensions during phase transformation. This expansion during the transition to the monoclinic phase is reported to be due to the formation of Zr-OH or Y-OH after the absorption of H2O on the surface. This phase transformation starts at the grain boundaries on the surface, increasing the volume of adjacent grains and facilitating the penetration of water into deeper regions, thus promoting the propagation of micro-cracks. These micro-cracks formed as a result of the transformation reverse the positive expectations in the long

term. Additionally, the micro-cracks resulting from the transformation lead to an increase in surface roughness. Any factor that can disrupt the stability of zirconia in the tetragonal phase initiates low-temperature degradation. The degree of low-temperature degradation varies among tetragonal zirconia polycrystals (TZP) because aging behavior depends on various factors such as stress formation, yttrium concentration and distribution, grain size, crack population, etc. (20,21,22).

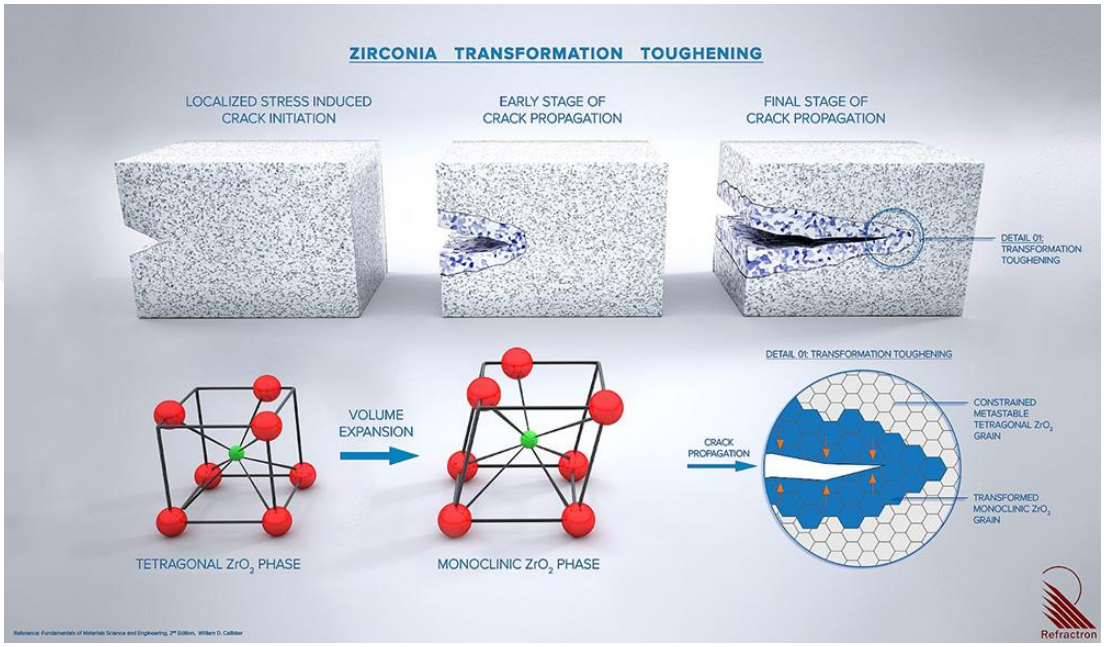


Figure 3: Zirconia Transformation Toughening

Y-TZP-based all-ceramic systems can be successfully used in posterior regions where chewing forces are high due to their high mechanical properties. However, due to its opaque nature, Y-TZP may not meet aesthetic expectations adequately as it cannot provide natural light reflection and diffusion. In Y-TZP-based restorations, sufficient thickness of the veneering porcelain is required to mask the opaque color of Y-TZP. To achieve this, more tooth preparation is necessary, which can lead to tooth sensitivity or even pulp perforation in teeth with large pulp chambers. The fracture strength of all-ceramic systems should be evaluated not only with a strong core material but also with an aesthetic brittle veneering ceramic. Moreover, layered systems have disadvantages such as having a multi-step production process, low fracture strength of

the veneering ceramic, and weak bonding mechanism between the core and veneering (23).

To overcome these disadvantages of layered systems, monobloc materials produced with CAD/CAM systems have been developed. Monoblock restorations made with lithium disilicate reinforced glass ceramics have been reported to yield more successful results than restorations made with layering technique. However, the lack of bridge indications in the posterior region for lithium disilicate reinforced glass ceramics has led to the development of fully contoured monolithic zirconia restorations for posterior use (24,25).

Monolithic zirconia restorations prepared in anatomical form are characterized by high fracture strength as they do not contain veneering porcelain. The most significant disadvantage of zirconia restorations is their inability to provide sufficient aesthetic properties due to their opaque structure. To address this issue, various modifications have been made in the production and sintering of Y-TZP to develop more advanced optical properties of translucent zirconia (26).

Improvements in the optical properties of monolithic zirconia are achieved through microstructural modifications such as reducing alumina content, increasing density, reducing grain size, adding cubic zirconia, and reducing the proportion of structural defects. The grain size is the most important factor affecting the translucency of polycrystalline ceramics. In the past, attempts were made to increase the grain size of polycrystalline ceramics during sintering to obtain highly translucent materials. Having larger grain particles in the material resulted in fewer grain boundaries and therefore less scattering of light entering the material. However, for Y-TZP, using larger grain sizes negatively affects both mechanical properties and the stability of the tetragonal phase, so increasing the translucency of zirconia by increasing the grain size is not achievable (27,28,29).

Characteristics of Monolithic Zirconia:

Exceptional Strength: Monolithic zirconia restorations are known for their remarkable mechanical strength and durability. They can withstand the forces of chewing and grinding, making them suitable for both anterior and posterior teeth.

Biocompatibility: Zirconia is biocompatible and well-tolerated by the human body, making it safe for use in dental applications, including implants.

Aesthetics: Advances in zirconia processing techniques have led to highly translucent and aesthetically pleasing options. Monolithic zirconia can mimic the appearance of natural teeth, providing a natural, tooth-like appearance.

Minimal Tooth Removal: Monolithic zirconia restorations often require less tooth structure removal compared to traditional materials, preserving more of the patient's natural tooth. Resistance to Wear and Corrosion: Monolithic zirconia is highly resistant to wear, corrosion, and staining, ensuring long-lasting performance.

Applications of Monolithic Zirconia in Dentistry:

Dental Crowns: Monolithic zirconia crowns are used to restore damaged or decayed teeth. They are particularly favored for posterior teeth due to their exceptional strength.

Dental Bridges: Monolithic zirconia bridges are a popular choice for replacing missing teeth, providing both strength and aesthetics.

Implant-Supported Restorations: Zirconia is used in implant-supported crowns and bridges, ensuring stability and long-term success.

Veneers: Thin monolithic zirconia veneers can improve the appearance of discolored, misshapen, or damaged teeth while maintaining a natural look.

Advantages of Monolithic Zirconia:

Strength and Durability: Monolithic zirconia is highly resistant to fractures and chipping, ensuring the longevity of restorations.

Aesthetics: It offers excellent aesthetic outcomes, making it suitable for both anterior and posterior teeth.

Biocompatibility: Monolithic zirconia is well-tolerated by the body, reducing the risk of adverse reactions.

Minimal Tooth Reduction: The conservative nature of monolithic zirconia preparations helps preserve more natural tooth structure.

Stain Resistance: Monolithic zirconia resists staining and discoloration, ensuring a lasting, attractive appearance.

Considerations and Limitations:

Cost: Monolithic zirconia restorations can be more expensive than some alternative materials, which may affect treatment planning and patient choices.

Brittleness: While zirconia is exceptionally strong, it can still be brittle under extreme conditions or impact.

Processing Complexity: Fabricating monolithic zirconia restorations requires specialized equipment and expertise.

In oral cavity the pH of saliva is constantly changing depending on the food taken, saliva content and stomach activity. The pH may vary due to the consumption of acidic foods and beverages, and to the bacteria metabolism than can result in organic acid formation (30). Theocharidou et al. assumed that the effect of acidic pH can cause significant corrosion of ceramic surfaces (31). Factors that could disrupt the stability of zirconia in tetragonal phase initiate low temperature degradation. LTD and ageing behaviour depends on stresses, yttrium concentration and distribution, grain size, crack population (30,31).

Gastric acid is a colourless, acidic, digestive fluid and it is an acid solution with a pH of 1 to 2, consisting mainly of hydrochloric acid (HCl) (around 0.5%, or 5000 parts per million), and large quantities of potassium chloride (KCl) and sodium chloride (NaCl) and Ph of the oral cavity can decrease because of gastroesophageal reflux disease (GERD). In GERD, the esophageal pH is less than 4 in 60 minutes per day and it reaches pH 1.0 at least 10 minutes of that (33). According to a systematic review

(32) the median prevalence of dental erosions (DE) in GERD patients was 24%, with a large range (5–47.5%), and the median prevalence of GERD in DE adults patients was 32.5% (range: 21–83%) and in paediatric population 17% (range: 14–87%). Theocharidou et al. assumed that the effect of acidic pH can cause significant corrosion of ceramic surfaces (30).

This in-vitro study aimed to investigate the impact of acidic saliva on 5Y-TZP using as a dental restorative material in terms of low-temperature degradation and elemental release.

This study was based on the hypothesis that different acidic values of saliva could accelerate the aging of Y-TZP

Chapter 3

Materials and Methods

Specimen preparation

20x20 mm cylinder shaped blocks were fabricated by CAD/CAM from 5Y-TZP pre-sinterize block (ZenostarT; Wieland Dental). SiC papers (600 and 1200-grit) were used to smoothing the sidewalls of the cylindrical shape. 1.65 mm thick slices (discs) were obtained by cutting under water-cooling with diamond blades (ISOMET 1000, Buehler). Again specimens were polished on both sides with SiC paper (1200-grit), and sinterized according to the manufacturer's instructions (final dimensions: 15 mm Ø and 1.2 ± 0.2 mm in thickness). Specimens were randomly divided to three grup.

Figure 4 : ZenostarT; Wieland Dental

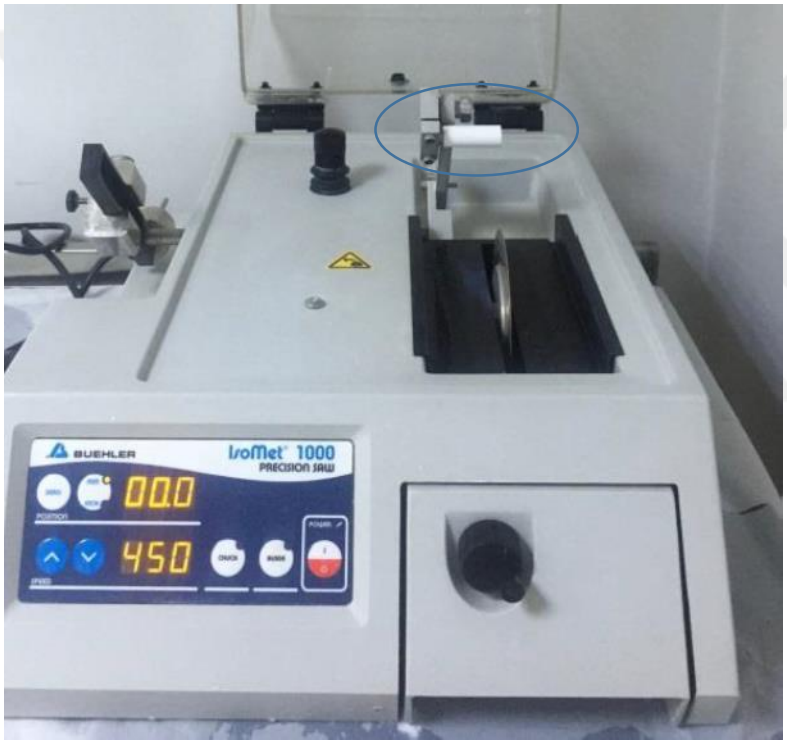


Figure 5:1.65 mm thick slices (discs) were obtained by cutting under water-cooling with diamond blades (ISOMET 1000, Buehler).

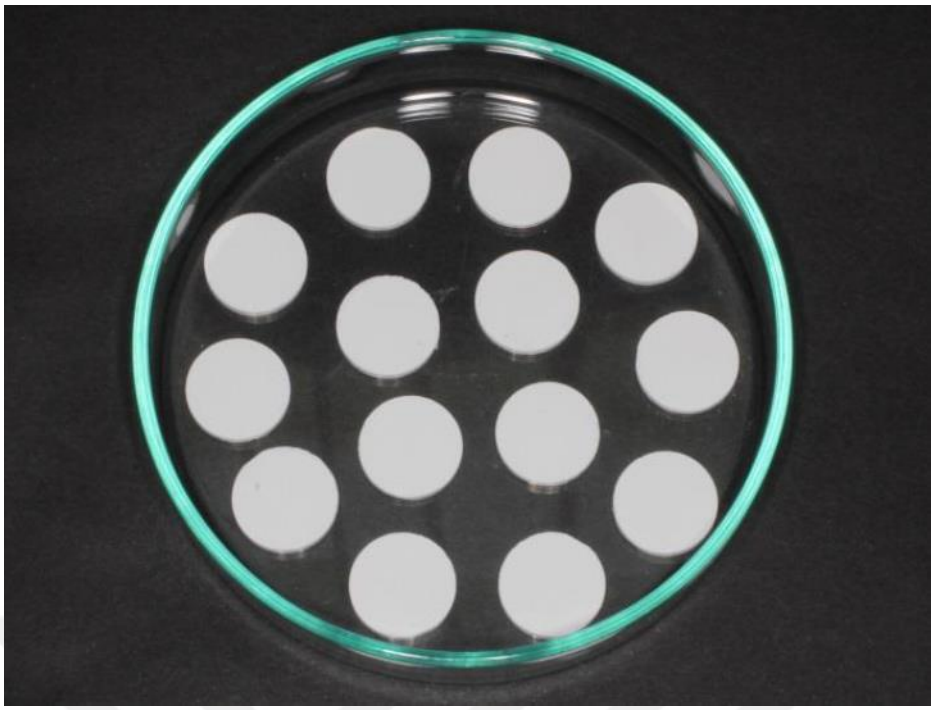


Figure 6: Speciemens after sinterization

Table 1: chemical composition of Y-TZP (ZenostarT; Wieland Dental)

Y-TZP	
Zirconium oxide (ZrO_2+HfO_2+Y_2O_3)	$\geq$ 99%
Yttrium oxide	4,5<->6%
Hafnium oxide, HfO_2	$\leq$ 5%
Aluminum oxide + other oxide	$\leq$ 1.0

Table 2: materials properties of Y-TZP (ZenostarT; Wieland Dental)

Properties	MO/T
Chemical solubility	< 100 µg/cm²
Flexural strength	≥ 900 MPa
CTE value (100 – 500 °C) [10-6/K]	10.5 ± 0.5
Composition	Zirconium oxide (ZrO_2 + HfO_2 + Y_2O_3) ≥ 99.0% Yttrium oxide (Y_2O_3) > 4.5 – ≤ 6.0% Hafnium oxide (HfO_2) ≤ 5.0 % Aluminum oxide ≤ 1.0%

Preparation of artificial saliva

The artificial saliva Fusayama-Meyer (pH 5.8) was prepared with the compounds listed in Table 3. It was divided into three group. In order to obtain different acidic saliva media pH1.2 (group 1) and pH 2.5 (group 2), hydrochloric acid (HCl), which is the main component of gastric acid was used. Neutral pH level of Fusayama solution pH 5.8 (group 3) kept to use as control group.

Table 3: Composition of artificial saliva Fusayama-Meyer used in this study

Components Concentration: g/l	
Potassium chloride (KCl)	0.4
Sodium chloride (NaCl)	0.4
Calcium chloride dihydrate (CaCl2·2H2O)	0.795
Monosodium phosphate dihydrate (NaH2PO4·2H2O)	0.0016
Sodium sulfide nonahydrate (Na2S·9H2O)	0.69
Urea	1

Each specimen was immersed, polished surface facing up, in 5ml of the different acidic aqueous media prepared with pH 1.2, 2.5 and 5.8 which is the neutral pH of Fusayama-Meyer in a 37 °C incubator to simulate oral temperature and the pH was monitored every 24h. It has been mentioned in a previous study that esophageal pH is reaches pH 1.0 at least 10 minutes per day at gastroesophageal reflux disease (33). Based on this knowledge 60 hours immersion period was calculated to represent one year exposure of restoration to acidic saliva.

Vickers hardness

Before and after immersion, each specimen's micro-hardness was determined with a micro-hardness tester (Isoscan HV2, LTF Spa, Antegnate, Bergamo, Italy) using a Vickers diamond indenter. Three indentations were made equally placed over a circle, each being no closer than 0.5 mm to the adjacent indentation using a 1000 g load with a 15 s well time. The two diagonal lengths of each indentation were measured by a 40× magnification built-in scale microscope, and were converted into a micro-hardness value (VHN) using the following equation: HV = 1.854 P/d2, where HV is micro-hardness in kg/mm2, P is the load in kgf and d is the average length of the diagonals in mm. For a given specimen, the five hardness values for each surface were averaged and reported as a single value.

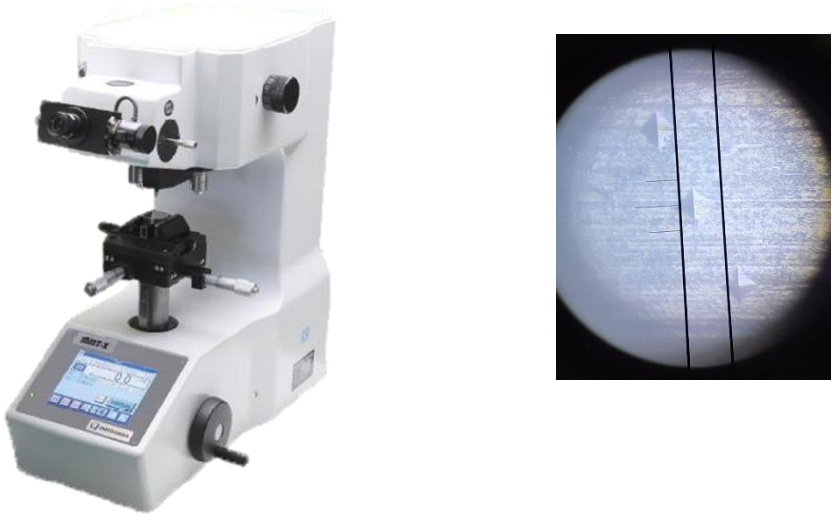


Figure 7: Vickers hardness, Isoscan HV2, LTF Spa, Antegnate, Bergamo, Italy

Monoclinic phase determination, X-ray diffraction (XRD) analysis

In order to evaluate t-m phase transition one specimen of each group was characterized by X-ray diffraction before and after immersion and incubation (XRD, Panalytical, Emperian with Kα: Cu as incident radiation and Ni filter). The equipment was operated at 40 kV and 45 mA and the scanning was performed with a step of 0.04° and 2 s per step in the range 2θ between, 10 - 80°. The specimens were studied and analyzed in steel sample holders. The set of divergence, receiving and scattering slits were 1°, 0.2°, 1° and in this study no monochromator was used. For the pattern analysis, "High Score" program was used for all specimen phase determinations.

Figure 8: Panalytical Empyrean XRD.

Inductively coupled plasma mass spectrometry

Inductive Common Plasma Mass Spectrophotometry (ICP-MS) analysis were made by Agilent 7800 model instrument. The saliva solutions used in the degradation tests were analyzed for the determination of Y and Zr molar concentrations. 1ml samples were diluted 50 ml with ultrapure water. ICP-MS instrument was calibrated by standard Y and Zr solutions with 5 different concentrations; 100 ppb, 1 ppm, 2 ppm , 5 ppm and,10 ppm, respectively. Accuracy and resolution of instrument evaluated from standard solutions. The diluted samples were fed to ionization chamber with argon gas and ions were detected with mass spectrophotometry (MS) detector.

Figure 9: Inductively Coupled Plasma Mass Spectrometry (ICP-MS) Agilent Technologies, Tokyo, Japan

ICP-MS parameter	Value
RF power	1500 W
RF matching	1.67 V
S/C temperature	2 ºC
Sample Depth	8.1 mm
Carrier gas flow rate	0.85 L/min
Make up gas flow rate	0.21 L/min
Nebulizer Pump flow rate	0.10 rps

Biaxial Flexural Strength Testing

Thirty specimens of each group were subjected to a biaxial flexural strength test (ISO 6872 standard) using a universal testing device which was MTS trademark, Criterion model 20KN load cell equipped system. Each disc specimen was placed centrally on three hardened steel balls (with the diameter of 3mm, positioned 120° apart on a support circle with a diameter of 11mm). The specimen was loaded with a flat punch (diameter 1.5mm and length 1mm) at a cross head speed of 1mm/min until failure occurred. The test was performed for each sample five times and recorded biaxial

flexural strength (MPa) that was calculated using the following equations (1)–(3) according to the ISO 6872 standard,

equations (1)–(3) according to the ISO 6872 standard,

$$S = -0{,}2387\,\frac{\mathrm{P(X-Y)}}{d^2} \qquad \text{(Equ. 1)}$$

Where S is the maximum tensile stress in Pascals, P the total load causing fracture in Newtons and d is the specimen thick- ness at fracture origin in millimetres. X and Y were determined

as follows:

$$X = (1+v)\ln\left(\frac{r_2}{r_3}\right)^2 + \left[\frac{(1-v)}{2}\right]\left(\frac{r_2}{r_3}\right)^2 \qquad \text{(Equ. 2)}$$

$$Y = (1+v)\left[1+\ln\left(\frac{r_2}{r_3}\right)^2\right] + (1-v)\left(\frac{r_2}{r_3}\right)^2 \qquad \text{(Equ. 3)}$$

in which: v is Poisson's ratio. If the value for the ceramic concerned is not known, a Poisson's ratio = 0.25 is used; r_1 the radius of support circle, in millimetres; r_2 the radius of loaded area, in millimetres; r_3 the radius of specimen, in millimetres; d is the specimen thickness at fracture origin, in millimetres. the radius of support circle, in millimetres; r_2 the radius of loaded area, in millimetres; r_3 the radius of specimen, in millimetres; d is the specimen thickness at fracture origin, in millimetres.

Scanning Electron Microscopy

The sample surfaces of the dental ceramics were observed using a scanning electron microscope (SEM) Carl Zeiss trademark, 300VP model (from Germany) operated at 15.0 kV. Low vacuum values were used for all analysis and Back Scattering Detector (BSD) system used for observation of different phase formation on the surface of samples. A thin layer of gold was coated on the surface of the sample by using an automatic sputter coater (Emitech K550X) to reduce the extent of sample arcing during SEM observation.

Contact Angle

Bioline Scintific AB company, Theta Attention model surface tension and contact angle measurement system were used for measuring surface wettability properties of samples. All test were performed under same conditions; 20 °C and pure water was dropped the surface of the samples. Contact angle changes were measured video camera system and recorded for 15 sec. Average contact angel was evaluated from system and recorded as images depend to time fragments.

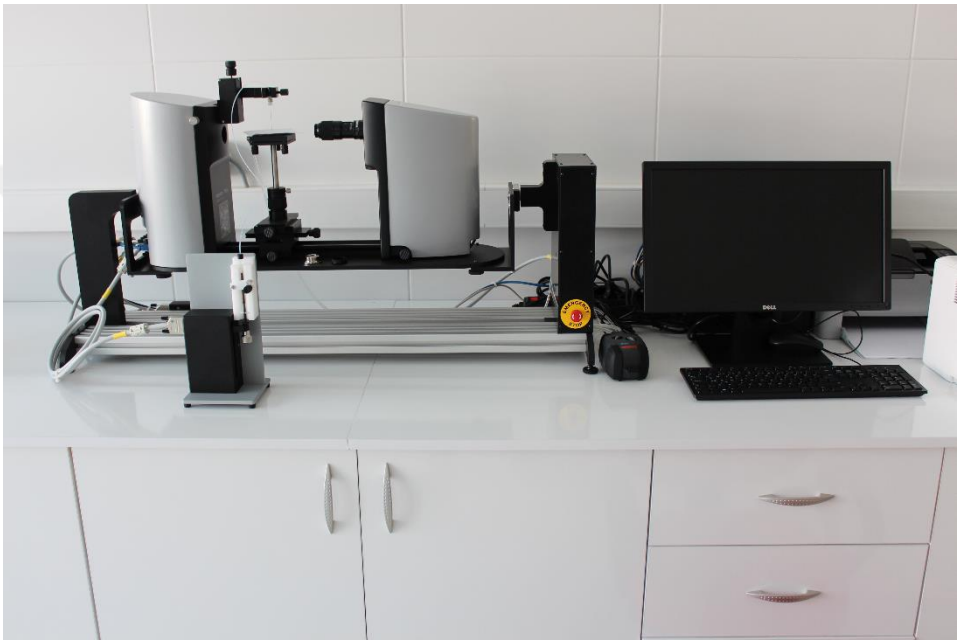


Figure 10: Contact angle measurements, Attension Theta

Statistical analyses

All statistical analyses were performed with the Statistical Package for Social Sciences (SPSS 21.0 Windows, SPSS Inc., Chicago, IL, USA). Normal distribution of the data was verified with the Kolmogorov-Smirnov test. For comparison between groups, One-Way ANOVA and Tukey test for multiple comparisons were used. Statistical significance was determined at a probability value of $p<0.05$.

Chapter 4

Results

The results of hardness were given at table 4. It was observed that decreasing the pH in artificial saliva decreased the surface hardness of monolithic zirconia samples.

Table 4: Results of Vickers hardness test

	Mean	SD	p	1/2	1/3	2/3
Group 1	1452,71	94,34	0,044	0,327	0,035	0,46
Group 2	1374,02	117,04				
Group 3	1308,97	128,67				

According to the X-Ray diffraction analysis, it was determined that there was a shift between groups in the relevant peaks in the crystal phases. It was observed that this shift was greater in the group where the pH was 1.2. Figure 11 shows the shifts in the crystal peak of groups.

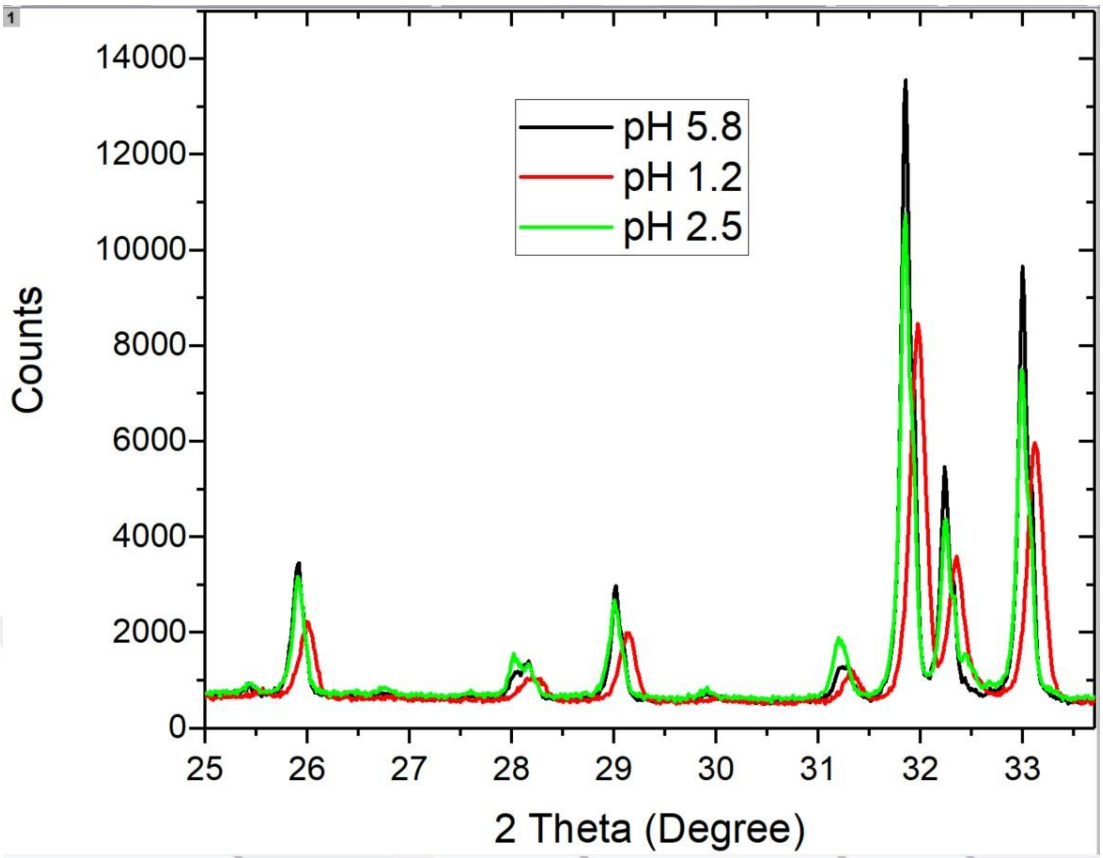


Figure 11: the shifts in the crystal peak of groups.

According to Inductively Coupled Plasma Mass Spectrometry (ICP-MS) analysis It was observed that as the pH level in the groups decreased, the amount of yttrium and zirconia released into artificial saliva increased.

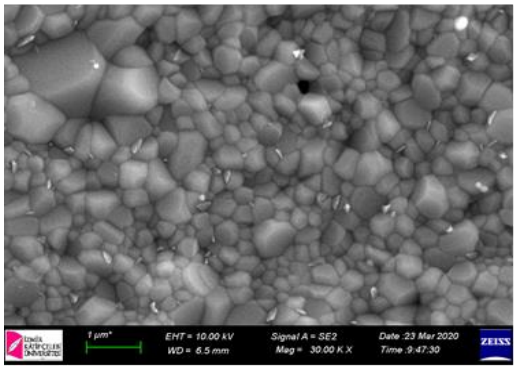
Table 5: Results of Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

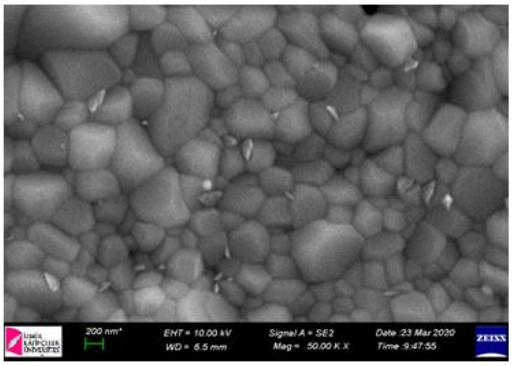
Sample				
	Data File	NK_0.d	NK_2_5.d	NK_1_2.d
	Acq. Date-Time	26.04.2021	26.04.2021	26.04.2021
	Type	Sample	Sample	Sample
	Level			
	Sample Name	NK_0	NK_2_5	NK_1_2
	Total Dil.	1	1	1
	Comment			
89 Y [He]	Conc. [ppb]	0,33	2,20	34,26
90 Zr [He]	Conc. [ppb]	1,32	2,21	5,89

According to scanning electron microscopy results, it was observed that the surface of the samples kept in a low pH environment was defective.

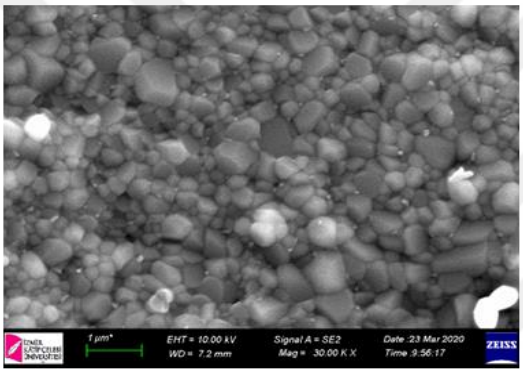
Figure 12: SAM images of groups.

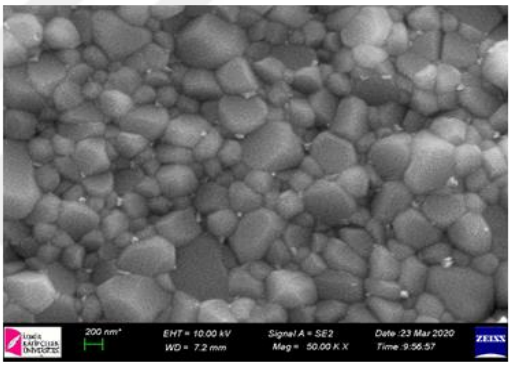
Group 1



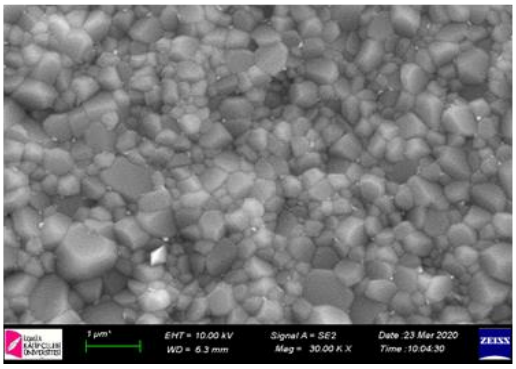


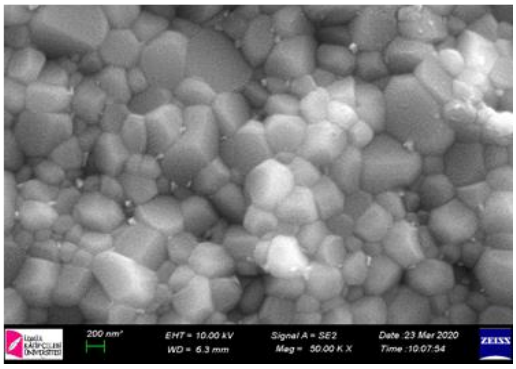
Group 2





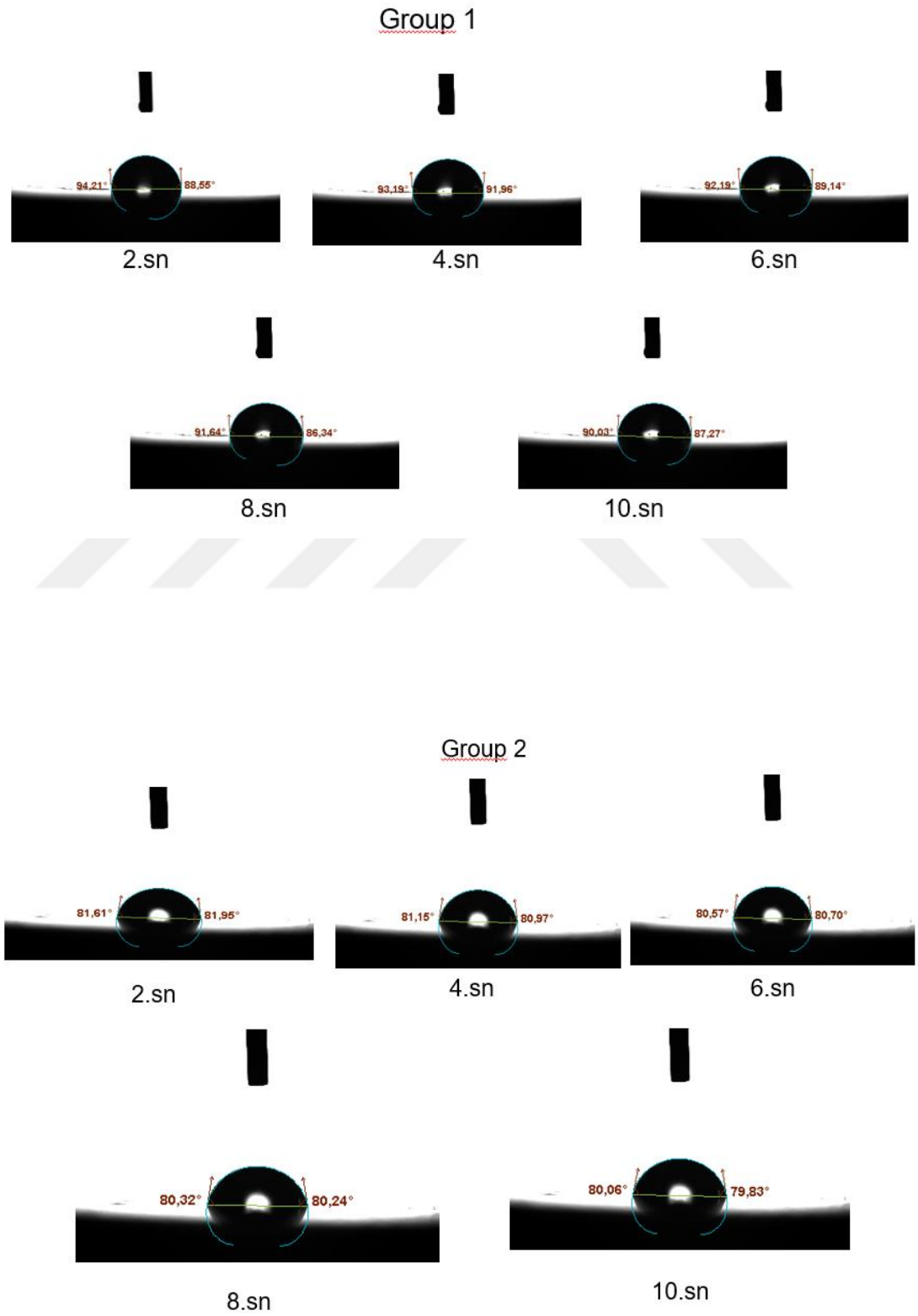
Group 3



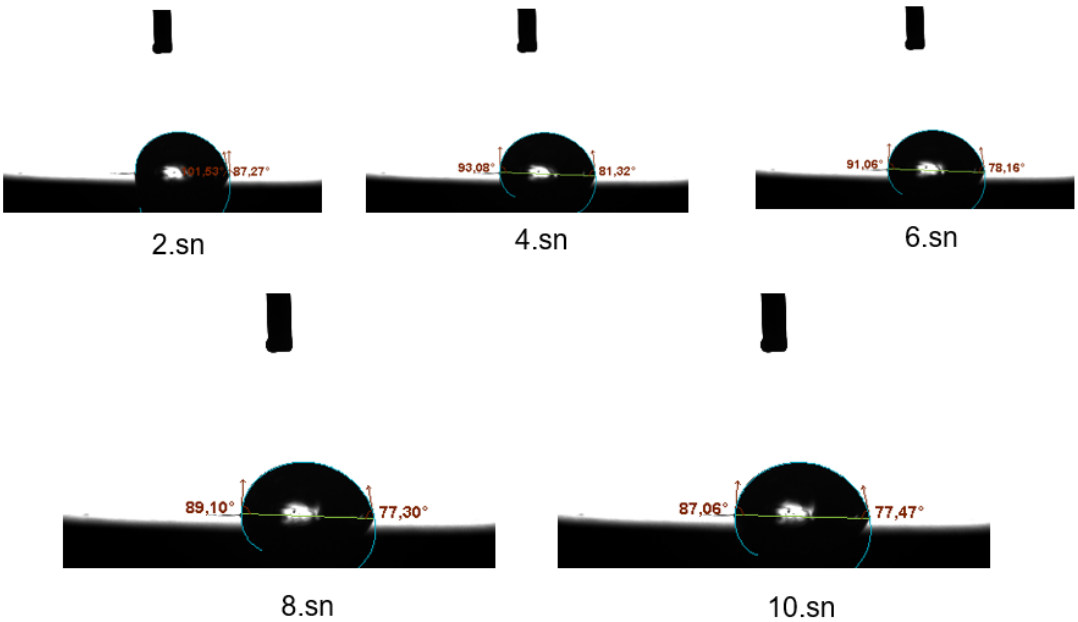


When the contact angle measurement results were examined, it was seen that the contact angle was lower and the wettability was higher in group 3. This revealed that the surface was rougher for the group.

Figure 13 :Contact angle results



Group 3



2.sn 4.sn 6.sn

8.sn 10.sn

When examined in terms of biaxial fracture strength, it was found to be 285.314 megapascals in Group One samples, 308.55 megapascals in Group 2 and 364.321 megapascals in Group 3.

Chapter 5

Discussion

Nowadays, with the increasing aesthetic expectations of patients, the use of full ceramics has become popular even in the posterior region due to their optical, mechanical and physical properties as well as their positive biocompatibility. Thanks to the developments in CAD/CAM technology, the production of substructure, superstructure and monolithic restorations from ceramic materials can be successfully done.

After zirconia ceramics were introduced, they found a great use in dental practice. Since they are opaque and white in color, they were veneered with feldspathic porcelains and used as infrastructure material (34). The most common problem that causes clinical failure of these restorations is chipping in the veneer porcelain (35). To prevent these problems, monolithic zirconia crowns that are produced with CAD/CAM systems, can be used without applying veneering porcelain, and consist of a single material have been developed. Thanks to their superior mechanical properties that have developed in recent years, the clinical use and indication areas of monolithic zirconias have increased (36).

Monolithic zirconias have an aesthetic appearance close to the natural translucent appearance of teeth, thanks to their non-porous structure, high biocompatibility and advanced optical properties. For this reason, there is no need to coat veneer porcelain. However, its optical properties are still not good enough. Natural tooth color can only be achieved using special staining solutions. Studies have reported that the application of color solution does not affect the translucency property of the material (37). Since monolithic zirconia ceramics are more translucent than conventional zirconia ceramics, during their cementation with resin cement, light penetrates the cement better and polymerization is better (38). Matsuzaki et al. In a study they conducted using monolithic zirconia in different colors; They concluded that monolithic zirconia

showed higher translucency than conventional opaque zirconia and gave color values similar to porcelain, even though it did not contain veneer porcelain. Translucent zirconia is similar to conventional zirconia in terms of durability. Recently, multi-layered zirconia systems, which aim to combine the advantages of different generations of zirconia in a single structure and can imitate the color transitions in natural teeth, have been developed in order to achieve a better aesthetic appearance in dental restorations (39). Multilayered zirconia blocks have various color layers that reflect the decreasing translucency value, increasing chroma and opacity from the incisal region to the gingival region in natural teeth. Zirconia. Developments in the production of ceramics with a more translucent structure and polychromatic monolithic zirconia blocks with color transitions between enamel and dentin in the natural tooth structure seem very promising for restorations that combine mechanical and aesthetic properties (40).

Changes in the formulation and microstructure of monolithic zirconia restorations have resulted in the production of more translucent zirconia materials (41). While the first produced monolithic zirconias were in the structure of 3Y-TZP (3% mol Y_20_3), the new generation zirconias with more translucent properties are in the structure of 4Y-TZP (4% mol Y_20_3) or 5Y-TZP (5% mol Y_20_3).

The fact that zirconia may in a spontaneous transition from the tetragonal phase to the monoclinic phase means that the material loses its semi-stable feature over time. This phenomenon, also known as the ageing of zirconia. Low temperature degradation basically starts at the surface of y-tzp and then progresses into the material. Humidity in the environment will increase the amount of phase transformation. Chemisorption of OH- from water at the surface of zirconia grains to form Y(OH)3 and depletion of Yttrium. Water absorption first causes surface degradation and then phase transformation. Micro cracks that occur as a result of transformation also cause an increase in surface roughness (21).

The use of zirconia as a monolithic full-contour restoration, which was previously used as a framework, confronted the adverse conditions of the oral environment such as Wide temperature change (≈65°C) and pH (0,5 - 8) fluctuations, average cyclic loads of approximately 60 to 250 N during mastication and (≈500–800 N) during parafunctional behaviours such as clenching and grinding, in a moist environment. The

number of chewing cycles per day is approximately 800–1400 and the contact surface between opposing teeth (wear facets) are in the range of 1–4 mm^2.

Corrosive environments, apart from deteriorating the mechanical properties of the material, increase the plaque accumulation by increasing the surface roughness and may cause abrasions on the opposite tooth.

Gastric acid is a colourless, acidic, digestive fluid and it is an acid solution with a pH of 1 to 2, consisting mainly of hydrochloric acid (HCl) (around 0.5%, or 5000 parts per million), and large quantities of potassium chloride (KCl) and sodium chloride (NaCl). (5,8) and Ph of the oral cavity can decrease because of gastroesophageal reflux disease (GERD). In GERD, the esophageal pH is less than 4 in 60 minutes per day and it reaches pH 1.0 at least 10 minutes of that (7).

According to a systematic review (6) the median prevalence of dental erosions (DE) in GERD patients was 24%, with a large range (5–47.5%), and the median prevalence of GERD in DE adults patients was 32.5% (range: 21–83%) and in pediatric population 17% (range: 14–87%).

Currently, the chemical solubility of dental ceramics is measured by the standardized testing method International Standards Organization (ISO) 6872 “Ceramic materials,” which is an accelerated test that immerses specimens of known surface area in 4% acetic acid at 80 °C for 16 hours.

Zirconium dioxide (ZrO_2), zirconia, is a white crystalline oxide of zirconium. As a biomedical material, zirconia was first used in orthopedics. Later, the use of these prostheses as a result of fractures decreased significantly (T39). In dentistry, zirconia was introduced in the 1990s and its use has become widespread with the development of CAD / CAM systems (T40). Zirconia is used in dentistry as a final restoration and / or core material in crown and bridge restorations, as well as in the production of various materials such as implant and implant abutments, cutting and surgical burs and orthodontic brackets (1)

Zirconia (ZrO_2) is a polycrystalline ceramic and its crystals could be found in three different crystallographic phases, cubic (C), tetragonal (T), monoclinic (M) phases. Zirconia is in the monoclinic phase at room temperature. This structure is stable up to

117^0 C and when heated above this degree it changes to tetragonal form, and above 237^0 C to cubic form. During the cooling process, a tetragonal-monoclinic phase change occurs at 1070 ° C and causes, a 3-5% volume increase that produce stresses that causes crack formation. (T41) This offers reduced mechanical performance and may contribute to a reduction in the cohesion of the ceramic particles and hence the density. cubic phase-forming oxides (stabilizer) has been added in order to obtain stabilized zirconia; a mixture of polymorphs consist of cubic plus metastable tetragonal phase. Different oxides such as magnesium oxide (MgO), yttrium oxide (Y^2O^3), calcium oxide (CaO) and cerium oxide (Ce^2O^3) can be added to stabilize the zirconia in the tetragonal and/or cubic phase at room temperature. Although there are many types of zirconia-containing ceramic systems, Mostly yttrium cation-doped tetragonal zirconia polycrystals (3Y-TZP), magnesium cation-doped partially stabilized zirconia (Mg-PSZ) and zirconia-toughened alumina (ZTA), Ceria Stabilised Zirconia (Ce-TZP) are used in dentistry. Ce-TZP shows high toughness and resistance to low temperature degradation compared to Y-TZP. Although Mg-PSZ gives successful results as a biomaterial, its use has decreased reasons like its porosity that causes worn easily than Y-TZP. It requires difficult production methods that require precise technique. Sintering temperature is extremely (approximately 1800˚C).

Y-TZP can be produced by co-precipitation of Y_2O_3 with ZrO_2 salts or by coating ZrO_2 grains with Y_2O_3. The tetragonal particles provided by the addition of Y_2O_3 are sufficiently small and can therefore be kept in a metastable state at room temperature. This stability is due to the fact that the surface energy of the tetragonal phase is lower than the monoclinic phase and/or the constraint of the rigid matrix on tetragonal grains (1). When a crack propagates, locally the pressure of the rigid matrix on the partially stable tetragonal phase crystals is reduced. Transformation from T to M phase occurs around the crack tips. Due to this phase transformation, an increase in volume occurs. This volume increase generates the compressive stresses around crack edges and tips. Thus, the energy required for crack progress increases. The basis of the high strength of Y-TZP comes from this martensitic like transformation also called transformation toughening. However, as the amount of transformation to this monoclinic phase increases, the mechanical properties of the material are rapidly adversely affected.

Y-TZP is still opaque white material. Because of this feature, it does not resemble natural teeth, is veneered with a ceramic material with better optical properties. In clinical use, it was observed that there were chipping and fracture between the zirconia framework and veneering ceramics. Although the strength of zirconia is sufficient, weak bond strength to the veneering ceramic made the success of the system questionable. The chipping of veneering ceramics has been reported to be 2%-9% for single crowns after 2-3 years and 3%-36% for FDPs after 1-5 years.[Malkondu 11,12] The main reason for this problem is the absence of glassy phase in Y-TZP and the mismatch of thermal properties between veneering ceramic such as thermal expansion coefficient, thermal diffusivity. Inappropriate framework design, cooling rates and low flexural strength of veneering ceramic compared to the Y-TZP core are also reported as the causes of chipping.

In order to overcome this common complication, it was recommended to make a full-contour restoration of zirconia as monolithic. To improve the optical properties, some modifications, such as stabilizer oxide rates, the sintering temperature, fabrication processes and addition of colouring liquids, have been applied. The modification of Y-TZP may affect the mechanical properties and could promote the low-temperature degradation (LTD) (malkondu) and was first described by Kobayashi (T50).LTD is the spontaneous *t* - *m* transformation at surface take place in air or aqueous media at low-to moderate temperature, results decrease in strength and fracture toughness (9).

In oral cavity the pH of saliva is constantly changing depending on the food taken, saliva content and stomach activity. The pH may vary due to the consumption of acidic foods and beverages, and to the bacteria metabolism than can result in organic acid formation (4). Theocharidou et al. assumed that the effect of acidic pH can cause significant corrosion of ceramic surfaces (5). Factors that could disrupt the stability of zirconia in tetragonal phase initiate low temperature degradation. LTD and ageing behaviour depends on stresses, yttrium concentration and distribution, grain size, crack population.

This in-vitro study aimed to investigate the impact of acidic saliva on 5Y-TZP using as a dental restorative material in terms of low-temperature degradation and elemental release. Within the limitations of these studies, it can be said that pH changes cause damage to the surface of zirconia and than yttrium is released

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