



T.C.

YEDITEPE UNIVERSIRY

INSTITUTE OF HEALTH SCIENCES

DEPARTMENT OF PROSTHODONTICS

**IN- VITRO EVALUATION OF SHEAR BOND
STRENGTH OF THREE PRIMER/RESIN CEMENT
SYSTEMS TO MONOLITHIC ZIRCONIA**

MSc MASTER`S THESIS

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SUPERVISOR


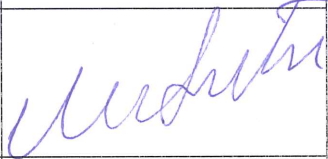
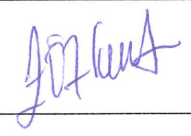
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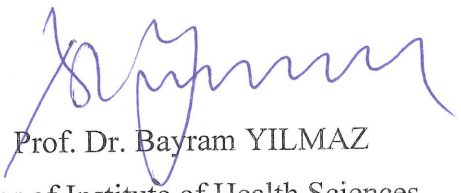
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APPROVAL

This thesis has been deemed by the jury in accordance with the relevant articles of Yeditepe University Graduate Education and Examinations Regulation and has been approved by Administrative Board of Institute with decision dated 12/10/2018..... and numbered 2018/17-02


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DECLARATION

I hereby declare that this thesis is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which has been accepted for the award of any other degree except where due acknowledgment has been made in the text.



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Dedication

This thesis and my study over the past two years of graduate training are dedicated to my family:

My most sincere gratitude and appreciation go to **my parents** for their patience, continuous encouragement and instilled the drive to keep learning and rising above every challenge over the past difficult years.

Special big thanks to my beloved husband **Tawfik AL-zwe**, you always believe in me. Words cannot express how grateful I am to you for all of the sacrifices that you have made on my behalf. Your prayer for me was what sustained me thus far. Your constant love and support have enabled me to successfully achieve all my goals.

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TABLE OF CONTENTS

	Page number
APPROVAL FORM	ii
DECLARATION	iii
DEDICATION	iv
ACKNOWLEDGMENT	v
TABLE OF CONTENTS	vi
LIST OF TABLES	ix
LIST OF FIGURES	x
LIST OF ABBREVIATIONS AND SYMBOLS	xii
ABSTRACT	xiv
ÖZET	xvi
1. Background and Aim	1
2. Introduction	3
2.1. Dental Ceramics	3
2.1.1. The History of Dental Ceramics.....	4
2.1.2 Properties of Dental Ceramics.....	6
2.1.3. The Classification of Dental Ceramic.....	6
2.1.3.1 Glass-Matrix Ceramics.....	8
2.1.3.1.1 Feldspathic Glass Ceramics.....	8
2.1.3.1.2 Synthetic Glass-matrix Ceramics.....	8
2.1.3.1.2.1 Leucite-Based.....	9
2.1.3.1.2.2 Lithium-Disilicate Glass Ceramic.....	9
2.1.3.1.2.3 Fluorapatite-Based.....	11
2.1.3.1.3 Glass-Infiltrated.....	11
2.1.3.1.3.1 In-Ceram Alumina (Glass-Infiltrated Alumina).....	11
2.1.3.1.3.2 In-Ceram Spinell (Glass-Infiltrated Magnesium Alumina).....	11
2.1.3.1.3.3 Alumina and Zirconia (In-Ceram Zirconia).....	12
2.1.3.2. Polycrystalline Ceramics.....	12
2.1.3.2.1 Alumina Procera (Pure Densely Sintered Alumina).....	12
2.1.3.2.2. Stabilized Zirconia.....	13
2.1.3.2.2.1 Yttrium-Oxide Partially Stabilized Zirconia (Y-PSZ).....	13
2.1.3.2.2.2 Ceria-Partially Stabilized Zirconia.....	16
2.1.3.2.3. Zirconia Toughened Alumina (ZTA).....	16

2.1.3.2.4 Alumina Toughened Zirconia (ATZ).....	17
2.1.3.3 Resin-Matrix Ceramics.....	17
2.1.3.3.1 Resin Nanoceramic.....	18
2.1.3.3.2. Glass Ceramic in a Resin Interpenetrating Matrix.....	18
2.1.3.3.3 Zirconia-Silica Ceramic in a Resin Interpenetrating Matrix.....	18
2.2. Polycrystalline Zirconia	18
2.2.1 History.....	18
2.2.2 Phases of Zirconia.....	19
2.2.3. Stabilized Zirconia.....	20
2.2.4 Transformation Toughening of Zirconia.....	21
2.2.5 Biological Characteristics of Zirconia.....	21
2.2.5.1 Biocompatibility and Degree of Toxicity.....	21
2.2.5.2 Radioactivity.....	22
2.2.6 Optical Characteristics.....	22
2.2.7 Aging of Zirconium.....	23
2.2.8 Manufacturing Procedures by Using CAD/CAM.....	23
2.2.8.1 Soft Machining.....	23
2.2.8.2 Hard Machining.....	24
2.2.9 Veneering of Zirconia Substructures.....	24
2.2.9.1 Slow Cooling Rate.....	25
2.2.9.2 Anatomical Framework Design.....	26
2.2.9.3 Thickness of Veneer.....	26
2.2.10 Full Anatomic Zirconia Restorations (Monolithic Zirconia).....	27
2.2.10.1 Monolithic Zirconia Properties.....	28
2.2.10.1.1 Wear Properties.....	28
2.2.10.1.2 Surface Roughness.....	29
2.2.10.1.3 Fracture Strength.....	29
2.2.10.1.4 Optical Properties.....	29
2.2.10.1.5 Marginal Fit.....	29
2.3. Adhesion in Dentistry	30
2.3.1. Classical Dental Ceramics Adhesion.....	30
2.3.2. Crystalline Dental Ceramics Adhesion.....	31
2.3.2.1. Luting Cements Mostly Used with Zirconia Ceramics.....	32
2.3.2.1.1. Composition of Resin Cements.....	32

2.3.2.1.2. Phosphate Monomer.....	33
2.4. Surface Conditioning to Improve Resin to Zirconia Adhesion.....	35
2.4.1. Surface Treatment Methods Causing Micromechanical Interlocking.....	35
2.4.1.1. Sandblasting.....	35
2.4.1.2. Hot Chemical Etching.....	36
2.4.1.3. Laser Treatment.....	36
2.4.1.4. Nano-Structured Alumina Coating.....	36
2.4.2 Surface Treatment Methods Causing Chemical Bonding and Micro-Mechanical Interlocking.....	37
2.4.2.1 Pyrochemical Silica Coating.....	37
2.4.2.2 Tribochemical Silica Coating.....	37
2.4.2.3 Selective Infiltration Etching (SIE).....	37
2.5. In Vitro Testing Methodology.....	38
2.5.1 Interfacial Degradation by Artificial Aging.....	38
2.5.1.1 Chemical Degradation.....	38
2.5.1.2 Thermal Degradation.....	38
2.5.1.3 Mechanical Degradation.....	39
2.5.2 Tests for Adhesion Measurement of Bond Strength.....	39
2.5.2.1 Shear Bond Strength Test.....	39
2.5.2.2 Tensile Bond Strength.....	40
2.5.2.3 Flexural Bond Strength Test.....	40
3. Materials and Methods	41
3.1. Materials Used.....	41
3.2. Methods.....	46
3.2.1 Preparation of Experimental Specimens.....	46
3.2.2. Cementation Procedure.....	50
3.2.3. The Aging Level Procedure.....	55
3.2.4. Shear Bond Strength Testing.....	56
3.2.5. Failure Analysis.....	57
3.2.6. Statistical Evaluations.....	58
4. Results.....	59
5. Discussion.....	64
6. Conclusion.....	77
7. References.....	78

LIST OF TABLES

	Page Number
Table 1: Classification of dental ceramics according to glass and filter content.....	7
Table 2: Chemical composition, physical, mechanical and thermal properties of Y-TZP	15
Table 3: Materials used in the study.....	42
Table 4: The values mean shear bond strength of the groups.....	59
Table 5: Evaluation of the effect of cement type and storage levels on shear bond strength.....	59
Table 6: Evaluation of bonding strength according to different types of cements in the different storage conditions.....	60
Table 7: Post hoc evaluation.....	60
Table 8: Comparison between the values of bonding strength of the different types of cements in short-term and thermocycle.....	62
Table 9: Mode of failure of groups for each specimen.....	63

LIST OF FIGURES

	Page Number
Figure 1: Classification of all-ceramic systems.....	6
Figure 2: Tetragonal and monoclinic crystallographic phases of zirconia.....	20
Figure 3: Phase transformation from (t) to (m).....	21
Figure 4: Microcracks closing because of the crystals volume.....	21
Figure 5: An illustration showing reaction of a phosphate monomer group to the oxide ceramic hydroxyl group.....	34
Figure 6: Zirconia block (Starcream®Z-Nature A2).....	41
Figure 7: CAD/CAM system (CORI TEC 350i Loader, imes-icore, Germany).....	43
Figure 8: Computer Aided Design (CAD) models of test zirconia disks.....	44
Figure 9: Computer Aided Design (CAD) Definitive Zirconia disks.....	44
Figure 10: CAM milling machine.....	45
Figure 11: Milling of zirconia disks from presintred zirconium block.....	45
Figure 12: Pre-sintering zirconia disks with large size.....	45
Figure 13: Furnace for zirconia sintering ZIRKONZAHN Keramikofen 1500.....	45
Figure 14: Sintering zirconia disks with suitable size (10mm X 3mm).....	45
Figure 15: Silicon carbide paper.....	47
Figure 16: Bolishing of zirconia bonding surface.....	47
Figure 17: Polishing machine (Phoenix Beta Grinder/ Polisher).....	47
Figure 18: Surface roughness is measured by Perthometer MI device.....	48
Figure 19: Airblasting with AL ₂ O ₃ (Renfert, Basic master).....	49
Figure 20: 10 mm distance from the surface.....	49
Figure 21: Z prime plus,Bisco.....	50
Figure 22: Duo-Link, Bisco.....	50
Figure 23: Light cure polymerization of the cement.....	51
Figure 24: Kerr Optilux 501.....	51
Figure 25: Clearfil ceramic primer Plus; kuraray.....	52
Figure 26: Panavia SA; Kurary.....	52
Figure 27: Light cure polymerization of the cement.....	52

Figure 28: Single bond universal adhesive; 3M.....	53
Figure 29: Rely X Ultimate; 3M.....	53
Figure 30: Prime applied by applicator brush	53
Figure 31: Mixing of from base paste and catalyst past	53
Figure 32: Translucent plastic split mold	54
Figure 33: Three subgroups stored in distilled water.....	55
Figure 34: Thermocycling machine.....	55
Figure 35: Samples embedded in a chemical acrylic resin	56
Figure 36: Sample fixed in the Universal testing machine.....	57
Figure 37: Bar-chart for the different types of cements in the 24h water storage and thermocycle.....	61

LIST OF ABBREVIATION AND SYMBOLS

ADA	American Dental Association
Al ₂ O ₃	Aluminum trioxide (Alumina)
ANOVA	Analysis of variance
ATZ	Alumina Toughened Zirconia
Bis-GMA	Bisphenol A glycidyle methacrylate
C	Cubic phase
°C	Degree Celsius
CAD/CAM	Computer Aided Design/ computer Aided Manufacturing
CaO	Calcium oxide (Calcia)
CeO ₂	Cerium oxide
Co.	Company
CTE	Coefficient of thermal expansion
E	Modulus of Elasticity
FDP	Fixed dental Prostheses
FSZ	Fully- Stabilized Zirconia
GPa	Giga Pascal
HEMA	2-hydroxyethyl methacrylate
ISO/TR	International Standards Organization
K ₂ O	Potassium oxide
LTD	Low temperature degradation
M	Monoclinic phase
MDP	10-methacryloxydecyl dihydrogen phosphate
MgO	Magnesium oxide
min	Minute
mm	Millimeter
Mol%	Mole percentage, it is unite of atoms measurement
MPa	Mega Pascal
N	Newton
n	Number of specimen
nm	Nanometer

PFM	Porcelain fused to metal
PSZ	Partially- Stabilized Zirconia
SD	Standard deviation
Si ₃ N	Silicon nitrides
SiO ₂	Silicon dioxide
T	Tetragonal phase
TEGDMA	Triethylene glycol dimethacrylate
UDMA	Urethane dimethacrylate
μm	Micrometer
Vol%	Volume percentage
Wt%	Weight percentage
Y-TZP	Yttria- stabilized tetragonal zirconia polycrystalline
ZrO ₂	Zirconium dioxide
ZTA	Zirconia Toughened Alumina

ABSTRACT

Salem,R. (2018). In- Vitro Evaluation of Shear Bond Strength of Three Primer/Resin Cement Systems to Monolithic Zirconia. Yeditepe University, Institute of Health Science, Department of Prosthodontics, MSc thesis, Istanbul.

PURPOSE: This in-vitro study aimed to evaluate the shear bond strength of several types of primer/ resin cements to monolithic zirconia with different levels of storage.

MATERIALS AND METHODS: The disk-shaped specimens of monolithic zirconia (n=72) were prepared by CAD/CAM system (CORI TEC 350i Loader, Imes-Core, Germany) (10mm x 3mm). All the specimens were polished with silicone carbide paper, then the bonding surface was prepared by surface pretreatment with air-borne particle abrasion (Al₂O₃, 120µm). Monolithic zirconia discs were divided into 3 groups (n=24), according to the 3 primer/ cement systems; 3M (Single bond universal adhesive/ Rely X Ultimate), Kuraray (Clearfil ceramic primer plus/ Panavia SA), and Bisco (Z prime plus/ Due-Link). After bonding procedure according to manufacturers` instructions, each group was further divided into 2 subgroups (n=12) according to the storage levels; 24-hours storage in water at 37C° and thermocycling (5000 cycles). After these procedures, shear bond strength tests were performed for all specimens. Failure types were also evaluated. The data were analyzed using one-way and two-way analysis of variance (ANOVA) and Tukey HSD test. Significance was set at p<0.005.

RESULTS: There were significant differences between the mean shear bond strength values of 3 groups of adhesive systems in both storage levels (p<0.05). The highest shear bond strength value was observed in Kuraray adhesive system (12.52±1.34 MPa) and the lowest shear bond strength value was observed in Bisco adhesive system (5.32±0.54 MPa) in thermocycled groups (p<0.05). Similarly, in short-term storage groups, Kuraray had the highest (16.47±1.5 MPa) and Bisco had the lowest shear bond strength values (7.43±1.06 MPa) (p<0.05). Regardless to the type of adhesive systems, thermocycling significantly decreased the shear bond strength of all cement groups (p<0.05). The predominant failure mode was adhesive failure (49%) whereas mixed failure was 45% and cohesive failure was 6%.

CONCLUSION: Thermocycling decreased the shear bond strength of all adhesive resin cements to monolithic zirconia. Kuraray adhesive system had the highest shear bond strength and Bisco adhesive system had the lowest shear bond strength.

KEY WORDS: Monolithic zirconia, CAD/CAM, composite resin, primer agent, shear bond strength, thermocycling.



ÖZET

Salem,R. (2018). Üç Tip Primer-Rezin Siman Sisteminin Monolitik Zirkonya ile Bağlanma Kuvvetinin In-Vitro Değerlendirilmesi. Yeditepe Üniversitesi Sağlık Bilimleri Enstitüsü, Protez ABD., Master Tezi, İstanbul.

AMAÇ: Bu in-vitro tez çalışmasında, farklı tiplerdeki primer/rezin siman sistemlerinin farklı saklama koşullarında monolitik zirkonyaya olan makaslama dirençlerinin değerlendirilmesi amaçlanmıştır.

GEREÇ VE YÖNTEM: Disk şeklindeki monolitik zirkonya örnekleri (n = 72) CAD/CAM sistemi (CORI TEC 350i Loader, Imes-Icore, Germany) (10mm x 3mm) ile hazırlandı. Tüm örnekler silikon karbid zımpara kağıdı ile cilalandı, daha sonra yapıştırma yüzeyi 120µm'lik Al₂O₃ ile pürüzlendirildi. Daha sonra monolitik zirkonya diskler, kullanılan primer/rezin sistemine göre 3 gruba (n = 24) ayrıldı; 3M (Single bond universal adhesive/ Rely X Ultimate), Kuraray (Clearfil ceramic primer plus/ Panavia SA) ve Bisco (Z prime plus/ Due-Link). Rezin simanların üretici firma talimatlarına göre yapıştırılmasından sonra, her grup saklama koşullarına göre 2 alt gruba (n = 12) ayrıldı; 37C°'de su içinde 24 saat bekletme ve termosiklus (5000 döngü). Bu işlemlerden sonra tüm örneklerde makaslama direnci testleri yapıldı ve kırılma tipleri değerlendirildi. Veriler tek yönlü ve iki yönlü varyans analizi (ANOVA) ve Tukey HSD testi kullanılarak analiz edildi. Anlamlılık p <0,05 olarak belirlendi.

BULGULAR: Her iki saklama koşulunda, 3 farklı tipteki adeziv sistemlerinin makaslama dirençleri arasında anlamlı farklılıklar bulundu (p<0,05). Termosiklus uygulanan gruplarda, en yüksek makaslama direnci değeri Kuraray adeziv sisteminde (12.52±1.34 MPa), en düşük makaslama direnci değeri ise Bisco adeziv sisteminde (5.32±0.54 MPa) gözlemlendi (p<0,05). Benzer şekilde, kısa süreli bekletme uygulanan gruplarda, en yüksek makaslama direnci değeri Kuraray adeziv sisteminde (16.47±1.5 MPa), en düşük makaslama direnci değeri ise Bisco adeziv sisteminde (7.43±1.06 MPa) gözlemlendi (p<0,05). Adeziv sistemlerin türüne bakılmaksızın, termosiklus işleminin, tüm rezin siman gruplarının makaslama dirençleri değerlerini önemli ölçüde azalttığı görüldü (p<0,05). En yaygın görülen kırılma tipi adeziv kırılma iken (%49), kombine kırılma oranı %45 ve koheziv kırılma oranı %6 olarak belirlendi.

SONUÇ: Termosiklus işleminin, tüm adeziv sistemlerinin monolitik zirkonyaya olan makaslama direncini azalttığı görüldü. Kuraray adeziv sistemi en yüksek makaslama direncine sahip iken Bisco adeziv sistemi en düşük makaslama direncine sahipti.

ANAHTAR KELİMELER: Monolitik zirkonya, CAD/CAM, kompozit rezin, makaslama dayanımı, termosiklus.



1. BACKGROUND AND OBJECTIVE

Prosthetics' restorations have been used for decades to restore compromised and heavily damaged teeth and for improvements of aesthetic (1). Due to the more request for highly aesthetic restorations and biocompatibility, in recent years clinicians and patients have become more attracted in all-ceramic restorations. Consequently, throughout the last two decades all-ceramic restorations have become more popular. . On the other hand, the major drawback of dental ceramics are brittleness, low tensile strength, crack propagation, wear resistance, and marginal accuracy (2).

Various different types of ceramic systems have been applied in recent years as inlay, onlay, veneer, multi-unit posterior fixed partial dentures or as a core substrate for a ceramic crown (3). In attempt to improve the mechanical and optical characteristics, CAD/CAM (Computer Aided Design/ Computer Aided Manufacturing) ceramic blocks have been presented (1, 3). New CAD/CAM materials and systems have been developed in the last decade for production of all-ceramic restorations. Dental CAD/CAM technology has benefits in terms of time consuming, materials savings, standardization of the fabrication process and predictability of the restorations (1).

Although dental ceramics are very hard, they are also brittle and should be reinforced by a stronger framework in order to resist occlusal loads, especially in posterior regions. Therefore, Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) has been deemed one of the strongest, toughest materials and has high biocompatibility among the many commercially existing dental ceramic systems. Hence, zirconia ceramic material has a wide clinical usage, including implant, implant abutments, endodontic posts, orthodontic brackets and frameworks for fixed restorations (4). However, cracking or chipping of veneering ceramic is considerable the major complication of the zirconia based restorations. For this reason, monolithic zirconia has been introduced to overcome this problem, as well as to use in patients with limited interocclusal space (5).

The amount of retention of a luting restoration that depends on many factors include height, width, taper of the abutment and the type of luting agent (6). Because the main indication of the monolithic zirconia is posterior crown with limited interocclusal space (5), shorter abutments might be desirable and loss of retention has been exhibited to be a common cause of fixed restoration failure. The use of cements with adhesive properties can overcome this problem. In addition, the use of adhesive cements with ceramic restoration that enable to improve the optical properties of restorations (6).

The clinical success of fixed ceramic prosthesis appears to be strongly dependent on the type of luting cement and its procedure. Due to the zirconia ceramic is chemically inert and glass-free, polycrystalline microstructure for this reason it is difficult to fulfill a durable adhere to the resin cement. There are several of surface treatment have been presented to improve the adhesion of zirconia. The most commonly used methods for bonding to zirconia restoration include the use of sandblasting in combination with adhesive monomers have MDP (10-methacryloyloxydecyl dihydrogenphosphate) (7). Self-adhesive resin cements have monomers existing in the composition that have react with dental zirconia, improving the adhesion of resin cement to zirconia (8). The wide variability of available primers that introduced by manufacturers which makes it difficult for clinicians to select the right system for specific clinical situations. Moreover, slight information is available on the aging procedure of the self-adhesive resin cement (9, 10). Therefore, the aim of the present study that in vitro study is to evaluate the shear bond strength of three types of primer/ resin cement systems to monolithic zirconia with short-term storage and thermal cycling to stimulate aging.

Null hypothesis of this study that:

1- There would not be significant difference in the share bond strength of the composite cements between both in storage condition (short and long term).

2- There would not be significant difference of the shear bond strength between the various types of primer/cement systems.

2. INTRODUCTION

2.1. Dental Ceramics

In the past thirty years, the use of ceramic in the dental field has had tremendous growth and development (11). Both dentists and patients have opted for all-ceramic restoration rather than the traditional due to concerns about biocompatibility and aesthetics when dealing with dental restorations (3). In the field of dentistry, the use of ceramics varies greatly. It can be used as a cover over metal implants or as veneers, as well as crowns and bridges for missing teeth, dentures, ceramic posts, and abutments (12).

First originating from Greek, ceramic, which was then called 'keramos' takes the meaning of 'pottery'. Ceramic is also traced to the Sanskrit language, which means 'burned earth'. Originally the ceramic components were Earth clays, which were heated then formed into pottery (3).

Ceramic, which is defined by the American Ceramic Society as non-metal based, inorganic, composed of a crystalline structure, and possess the compounds of oxygen and metallic and non-metal based parts such as aluminum and oxygen (alumina- Al_2O_3), as well as calcium with oxygen (calcia – CaO), or silicon with nitrogen (nitride – Si_3N_4) (12). Due to the nature of these bonds at an atomic level, being either ionic or covalent, creates a compound that is strong but also brittle. The strength of this material is under compression, but it is weak under tension. This material contrasts with the not brittle and ductile metals. This is due to atomic bonding of the metal (3).

There are four categories of ceramic classifications: (1) silicates, (2) oxides, (3) non-oxides, and (4) glass. The ceramic from the silicate classification holds the characteristics of a porous structure because of the amorphous glass phase. SiO_2 is the main ingredients while small additions of crystalline Al_2O_3 , MgO , ZrO_2 and other oxides. This is the category of dental porcelain. The second category of oxide ceramics is seen in the principal crystalline phase (Al_2O_3 , MgO , and ZrO_2) but the glass phase is either small or non-existent. Next, the non-oxide ceramics are not used in dentistry due

to the processing. Temperatures are high and the method is complicated. This results in the color and opacity not suitable for dental work. Finally, glass ceramics show a partial crystallization, which is the result of nucleation and the growth of crystals within the glass matrix (13).

Ceramics come in different variations of opaqueness, ranging in very translucent to fully opaque. In a general sense, when the ceramic is non-crystalline or composed of a glass microstructure, it is more translucent. Whereas, the more crystalline the ceramic structure is, the more opaque it appears. Although, there are other factors that affect the opacity of ceramics, these include the size of the particles within the ceramic, the density of those particles, the refractive index, and how porous it is (3).

2.1.1. The History of Dental Ceramic

The first ceramic items that were found were made of earthenware and stone, which were found in Southern China. These primitive ceramics were mainly composed of a mixture of clay, kaolin, feldspar, and quartz. Ceramics like this were easily chipped due to the low firing temperature. These first ceramics were opaque and brownish grey in color because of the debris in the clay that was used in the manufacturing process (14). It took decades until Europeans could master the techniques of manufacturing porcelain (15). In the early 1700's, Bottger replaced the feldspar for a new ingredient, lime (calcium oxide), this was due to the increase in firing temperature that the Europeans used. As a ceramic, porcelain is of high quality due to its low porosity, hardness, and clean look. The components of porcelain must be pure in order to create a quality product. Dental ceramics made of feldspar evolved from this porcelain while in development.

In the mid 1770's, Alexis Duchateau, a French pharmacist, along with Nicholas Dubois de Chemant, created the first denture to be made from porcelain at the Guerhard Porcelain factory. This would replace Duchateau's previous denture creation that was made of ivory, which stained and held odors (16). From then, De Chemant shifted his work to improve the opaqueness by changing the ternary (three-part) center phase diagram to the formulation, which was high in feldspar (17).

Post 1750, porcelain was attempted to be used in dentistry but it was largely unsuccessful by the hand of Pierre Fauchard among others. At the turn of the next century, an Italian dentist by the name of Giuseoangelo Fonzi introduced a new porcelain tooth that contained platinum pins embedded within the ceramic, which held it in place. He called it “terrometallic in-corruptibles” (18).

In the late 19th century, the first successful porcelain inlay and crowns were fused and used in dentistry by Dr. Charles Land. To fabricate the crowns, a technique of used platinum foil for the substructure coupled with a high heat gas furnace, as Dr. Land described. These new crowns were aesthetically pleasing, although the flexural strength was so low that many crowns failed usage (15).

Well into the 20th century, production for dental ceramic increased because Weinstein M. and Weinstein AB. introduced the metal and ceramic crown. It was patented by using the porcelain formulation containing feldspar in which control is used on the sintering temperature and heat expansion. Also, the feldspathic porcelains bonded chemically to produce alloys, which were compatible together (19). Some patients have problems with restorative materials made from metal. These problems could be allergies, staining of the gums, or metallic ions being released into the gum tissue. Because of this, there has been a concentration of improving metal restorations systems and developing better looking and performing materials (20).

The first introduction of high-strength dental porcelain was done by McLean and Hughes in 1965. They developed a feldspathic core that was reinforced by alumina within the glass matrix, which had increased resistance because it contained crystals. Although, this method increased the opacity, it was undesirable (21). This process used specialty glass made from slip casting, which was fused to porous alumina. This tripled the strength of the material when compared to earlier material. It was named INCERAM (1988) (15, 16).

Procera All Ceram was created in Sweden in 1993. This was a big development in dental ceramics. The material contained sintered alumina (99.9%) within the core, which was covered in a veneer made of feldspathic porcelain. The outside veneer layer met aesthetic demand (22).

2.1.2 Properties of Dental Ceramic

Ceramics are known for their insolubility and high biocompatibility, which is chemically inert when it is compared against other dental materials. The biocompatibility increase when the material is glazed or polished. In addition, Dental ceramics are a hardness, resistance to abrasion and have ability to mimic natural teeth with translucency, color matching, brightness, reflection, as well as texture. Due to the chemical stability of the ceramic that durable and stable when fused into the oral cavity. Depending on the ionic or covalent bond, ceramic is a brittle. Additionally, in the radiograph it is a radiopacity material that permit for clear diagnosis of recurrent caries and marginal accuracy (23).

2.1.3. The Classification of Dental Ceramic

The American Dental Association (ADA) has classified dental ceramics into groups according to their composition. There are three groups based on the formulation characteristics, which are as followed: Glass-matrix ceramics, Polycrystalline ceramics and Resin-matrix ceramics (24) (Figure 1) (Table 1).

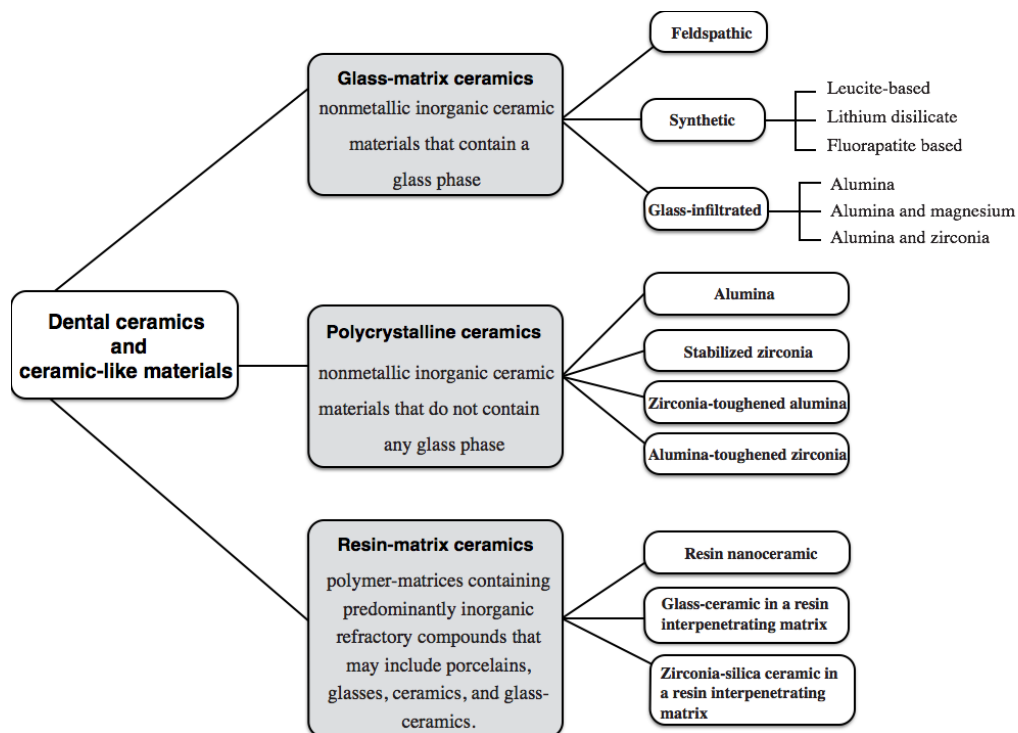


Figure 1. Classification of all-ceramic systems (24).

Table 1: Classification of dental ceramics according to glass and filler content.

Type of ceramic	Material	Purpose	Example systems	Manufacturing Technique	Flexural strength (MPa)	Fracture toughness (MPa·m ^{1/2})
Predominantly Glass	Feldspathic Porcelain	Veneering Porcelains	VM9 Vintage	Hand layered	102 85	0.7 -1.3
Particle-filled glass (High glass content) (Low glass content)	Leucite reinforced (SiO ₂ -Al ₂ O ₃ -K ₂ O)	Monolithic Restorations or Core ceramic	IPS Press	Heat pressed	182	1.77
	Lithium disilicate(SiO ₂ -Li ₂ O)	Monolithic restorations or Core ceramic	IPS e.max Press	Heat pressed, Milled	300-400	2.8 - 3.5
	Glass-infiltrated alumina oxide	Core ceramic	In-Ceram Alumina	Slip cast, milled	236-600	3 - 4.5
	Glass-infiltrated alumina oxide with 35% partially stabilised zirconia	Core ceramic	In-Ceram Zirconia	Slip cast, milled	421-800	6 – 8
Polycrystalline (No glass content)	Alumina Oxide (Al ₂ O ₃)	Core ceramic	Procera Alumina	Densely sintered	400	4.5 – 6
	Zirconia (Y-TZP)	Core ceramic Or Monolithic Restorations	Cercon HT	Milled	900 – 1200	9 – 10
	Zirconia (Ce-TZP)	Monolithic restorations	NanoZr	Milled	1290	8.62
Hybrid Ceramic	Ceramic network 86% (feldspathic+ Alumina oxide) +Polymer network 14%	Monolithic Restorations	Enamic	Milled	150 - 160	1.5

2.1.3.1 Glass-Matrix Ceramics

Dental ceramic that mostly contains a glass phase, it is divided into:

2.1.3.1.1 Feldspathic Glass Ceramics

This group of ceramics is traditionally based on the three part (ternary) material system. It consists of natural clay, quartz (silica), kaolin (hydrated aluminosilicate), and natural feldspar (potassium and sodium aluminosilicate mixture). When leucite crystals (K_2O , Al_2O_3 , $4SiO_2$) are formed from potash feldspar during the crystalline phase, at a volume of 5-25%, which is done when the feldspar is fired at $1150^\circ C$. Thus, the result is a polycrystalline ceramic containing feldspar, which is created by controlling the crystallization of the glass (3, 25). The crystallization process begins when the crystals begin to grow and nucleate from the heat. By controlling the heat in this process, it ensures that the nucleation occurs and that the proper number of crystals grow to the correct size. The leucite particles within the glass create a translucent effect and also inhibit cracking from coefficient of thermal expansion by improving the strength of the ceramic. The properties of this type of ceramic match natural teeth properties due to the high glass content (26). In contrast, the older versions of the feldspathic ceramics were unusable because of the large size and distribution of the leucite particles, which created low flexural strength and fractural toughness (60 and 70 MPa) (27). Ceramic must be strengthened by the core or adhesively bonded to the tooth to reduce the risk of fractures from occlusal load pressure. Thus, it is common for veneers to be layered on a core (ceramic or metallic) or existing tooth to provide it with support and strength within the dual layered system (3).

2.1.3.1.2 Synthetic Glass-Matrix Ceramics

The glass in this category contains filler particles. The particles are added to the glass' base composition, which improves the mechanical properties. For instance, the mechanical properties that are improved include thermal expansion, contraction load, and strength. Usually being crystalline, these fillers can dissolve during the etching process; this creates multiple micromechanical retentive properties. Thus, enabling bonding.

The glass which contains particles can have a large range of glass-to-crystalline ratios as well as crystal types. These glasses can be divided into four different groups. The composition is similar to pure glass, although there are differences in the varying

amounts of crystal that have been grown or added to the base composition. The types of crystals used are leucite, lithium disilicate and fluoroapatite (28).

2.1.3.1.2.1 Leucite-Based

By using silica or quartz (silicon dioxide) mixed with varying quantities of alumina, glass-based systems are made. In leucite-based ceramics, the glass matrix has the properties of an alumino-silicate glass. This means that the proportion of leucite crystals can range from 35% to 45% by volume. The proportion improves the biomechanical properties of the glass as well as reinforces it (25). In addition, by using a leucite filler, the glass' flexural strength can increase to 105-120 MPa. This type of glass ceramic was first called VITA VMK 68 ceramic (VITA Zahnfabrik, Bad Sackingen, Germany) in the late 1960's. It was first shown as powder/liquid form to be used as a metal-ceramic veneer (29). It had an advantage of being very translucent (30). The next ceramic was introduced in 1990, which was called the IPS Empress ceramic (Ivoclar, Vivadent, Schaan, Liechtenstein). This overcame the problem of shrinking from the porous powder and liquid form of its predecessor. It is the most widely used pressable ceramic that is reinforced by leucite (3). This new version showed a flexural strength of 160-180 MPa due to the addition of leucite crystals and heating techniques (31). The IPS Empress ceramic crowns were tested and withstood 11 years and an 84% survival rate when implemented as onlays, inlays, crown restorations, or veneers in the anterior region of the mouth (32).

2.1.3.1.2.2 Lithium-Disilicate Glass Ceramic

Consisting of many small, dense, interlocking, random plate-like crystals, lithium-disilicate glass ceramic is the next category. Making up 70% of the glass' volume, lithium disilicate ($\text{Li}_2\text{Si}_2\text{O}_5$) is formed during the crystalline phase (33). The crystals are uniformly distributed within the glass with a 4 μm length and 0.5 μm diameter. This uniformity makes the ceramic stronger because the needle-like crystals absorb the impact and deflecting and stopping cracks, thus increasing the flexural strength. The lithium disilicate ceramic can withstand 350-450 MPa (34). This strength is double that of the leucite glass ceramic (35), while the fracture toughness is triple (28).

When first introduced in 1998 by Ivoclar Vivadent, the lithium disilicate ceramic was in ingot form (IPS Empress II, Ivoclar, Vivadent, Schaan, Liechtenstein). This

ceramic was to be used with the technique of pressing at 920°C. It was called IPS Empress II, which had a survival rate of 95.24% to 100% during single crown restoration during multiple clinical studies of 5 to 10 years after implementation. After this, a new ceramic was introduced which had better physical properties and better translucency in lithium disilicate glass, it was called IPS e.max Press (37). Ingots that are pressable vary in opacity; they can range from high to medium opacity and low to high transparency. When fabricating monolithic inlays, posterior crowns, onlays, or for anterior three-unit FDPs and crowns, this ceramic is recommended for usage (35). It was reported that the survival rates of the IPS e.max Press Single crowns had a rate of 97.4% at 5 years and 94.8% at 8 years post procedure (38). Lithium disilicate was revolutionized when CAD/CAM restorations were introduced in 2005 for milling techniques. The new material was IPS e.max CAD (Ivoclar, Schaan, Liechtenstein). Saving time and costs, as well as reproducibility of the restoration are some of the advantages of the CAD/CAM system. The new material consists of 40% lithium meta-silicate crystals that are partially crystallized, this allows easy milling of the ceramic.

From the ingot, a procedure of recrystallization takes place after processing. This procedure is done for 10 minutes at 850°C. This allows the lithium meta-silicate to evolve into lithium disilicate crystals. The evolution of the crystals gives the ceramic its mechanical and esthetic properties. When the ceramic is fully crystallized in the IPS e.max CAD ceramic, the flexural strength is 360 MPa. There are a few different implementations for this material, which include, short span posterior FDPs either with conventional or adhesive cementations (39), single crowns, onlays, monolithic inlays, , and anterior FDPs. When studies, IPS e.max CAD showed results of a 100% survival rate after 2 years on single crowns, and a survival rate of 96.3% at 4 years on posterior crowns (41).

When compared to leucite ceramics, this glass has increased mechanical properties. It is seen as very translucent with a low refractive index due to the lithium disilicate crystals (3).

2.1.3.1.2.3 Fluorapatite-Based

The ceramics in this category contain fluoride calcium phosphate ($\text{Ca}_5(\text{PO}_4)_3\text{F}$). They include IPS e.max Ceram, Vivadent, Fluoroapatite, Ivoclar, and ZirPress. They all have the ability to be a final restoration or be layered because they are an aluminosilicate glass. The crystals within this ceramic are fluorapatite, which gives it the ability to match the lithium disilicate pressable or machine material because of its properties and CTE (3).

2.1.3.1.3 Glass-Infiltrated

2.1.3.1.3.1 In-Ceram Alumina (Glass-Infiltrated Alumina)

In 1988, In-Ceram was introduced. This ceramic uses the 'slip-casting' process during fabrication. Slip-casting involved condensing porcelain slip, which is aqueous. This material is put on a refractory die with pores, which is then heated, which sinters the glass produced by capillary actions when heated at high temperatures. The result of this process reduces pores and defects while increasing strength and toughness when compared to the traditional feldspathic porcelain (42). As an alternative system, the core of In-Ceram (Vita) possesses a core of 85% alumina. In this process, slip-casting is also used on a refractory die to form the ceramic core. It is also sintered after drying at 1120°C for 10 hours. Since alumina has a high melting point, the interpenetrating phase of the process materials are produced separately. First, the porous matrix is made within the alumina and crystalline phase, this results in a porous core strength of 6-10 MPa. The pores of the core are filled with lanthanum aluminosilicate glass. This filler glass is fired for 4-6 hours at 1100°C, thus creating a low viscosity material. To do this, capillary action must be used to pour the molten glass to cover and fill the pores. This creates a dense core and interpenetrating ceramic with an increased strength (e.g. In-Ceram Alumina) (42).

2.1.3.1.3.2 In-Ceram Spinell (Glass-Infiltrated Magnesium Alumina)

In 1994, In-Ceram Spinell was introduced. Its manufacturing process is similar to that of the In-Ceram Alumina. Although, the porous core that it fills is synthetically produced made of magnesium aluminate ($\text{Mg Al}_2\text{O}_3$). This improves optical properties, increases translucency of 25%, but decreased flexural strength. (E.g In-Ceram Spinell, Vita) (24).

2.1.3.1.3.3 Alumina and Zirconia (In-Ceram Zirconia)

By using zirconium oxide combined with aluminum oxide, the zirconia system is created. This is a framework which results in an increase in flexural strength within the core. The glass proportions are 20-25% of the total material. There is relative increase of alumina particles, however, protect the material against cracking that related to zirconium oxide. This ceramic's strength is about 700 MPa, and it also hold good marginal accuracy. Although the biocompatibility is good, it has poor translucency (e.g. In-Ceram Zirconia) (15, 25).

2.1.3.2. Polycrystalline Ceramics

This type of ceramic is strong with high fracture toughness due to the fine-grain crystalline composition. It also is possess no glass phase in its composition, therefore it is difficult when etched with hydrofluoric acid. These ceramics are opaque when compared to other types of glass ceramics. But, since they have unfavorable translucency, they are unusable as monolithic materials (24).

These monophase ceramics are solid sintered with a structure when the sintered crystals are organized without any matrix. This result forms a glass-free polycrystalline material that is dense, and free from glass and air. To obtain this material, there are multiple processing techniques (28).

2.1.3.2.1 Alumina Procera (Pure Densely Sintered Alumina)

When first introduced in the mid-1990 by Nobel Biocare, the material consisted of a high purity (99.5%) of Al_2O_3 . It had a core made of CAD/CAM. It possesses a high strength and hardness of 17 to 20 GPa. It has the highest elastic modulus ($E=300$ GPa) of all ceramics used in the dental field, but is susceptible to bulk fractures (43). Since the core of this ceramic can fracture, new materials with better properties have been introduced to strengthen the properties. The strength can be found in stabilized zirconia while reducing the usage of alumina (e.g. Procera AllCeram, Nobel Biocare, In-Ceram AL) (24).

2.1.3.2.2. Stabilized Zirconia

Zirconia that is pure can be found in three different allotropic forms. These are monoclinic, which in room temperature is a stable material. Although, as the temperature increases it will turn to tetragonal and then into cubic. This process transformation is due to the shear strain and crystal volume increase (4%). This is useful because the expansion closes any cracks in the material that know as transformation toughness and thusly improves the mechanical properties. This transformation toughness can only be achieved if the tetragonal and cubic phases are stabilized when at room temperature. When metal oxide stabilizers are added to the pure zirconia, it transforms the material into the tetragonal phase when a temperature of over 1000°C is reached as well as the cubic and tetragonal phases are mixed at a low temperature. Depending the microstructure, zirconia can be classified into three groups. Fully stabilized (FSZ), partially-stabilized zirconia (PSZ), and tetragonal zirconia polycrystals (TZP). In a cubic form, FSZ holds 8% of yttrium oxide (Y_2O_3). PSZ is formed from nanosized particles that are either tetragonal or monoclinic in a cubic matrix. If the material is stabilized with yttria or ceria that are monolithic in the tetragonal phase, then the material is TZP (22, 44).

Two compound materials can be prepared in the ZrO_2 - Al_2O_3 system. If ZrO_2 is reinforced with alumina particles, then it is ATZ. If Al_2O_3 is reinforced with zirconia particles then it is ZTA. Both of these zirconia possess a higher fracture value when compared to ceramics that are monophase (45).

2.1.3.2.2.1 Yttrium-Oxide Partially Stabilized Zirconia (Y-PSZ)

Y-PSZ is a tetragonal ceramic material with fine grained zirconia. It consists completely metastable tetragonal grains that are small (Y-TZP). Also, the addition of a stabilizing agent of yttrium oxide of 2-3 mol% Al_2O_3 (Y_2O) created a stable material (46). This material is used in the dental industry because of its high flexural strength (900 – 1200 MPa), as well as the biocompatibility, superior mechanical properties, and aesthetic aspects (46, 47). The uses of this zirconia can be seen in root canal posts, implant abutments, dental implants, fixed partial dentures (FDPs), and the framework for all ceramic posterior crowns (48, 49).

Although, depending on the grain size within the zirconia, the mechanical properties change. If the size of the grains are larger than $1\mu\text{m}$, then it can transform the tetragonal phase to monoclinic phase. But, if the grains are less than $0.2\mu\text{m}$ in size, then it is impossible to perform transformation toughening process. In addition, the longer and higher temperatures during sintering cause the growth of larger grain sizes. These grain sizes can play a critical role in the final properties of stability in the zirconia (50).

When related to yttrium-oxide concentration that takes place, the spontaneous transformation happens from the T to M of the grains, which is the critical grain size. But, if a fine grain structure is used during this process, then it will be inhibited. Making the grain size smaller or increasing the stabilizing oxide concentration will lessen the transformation rate. When this reduction of size occurs, the metastability lessens, but if the stabilizing oxide concentration is increased more than 3.5%, the nucleation of significant amounts of the stable cubic phase may occur. The grain size must be smaller than $0.8\mu\text{m}$ while the stabilizing oxide amount is no more than 3 mol% to achieve a tetragonal metastable phase at room temperature (51).

Ceramics of the Y-TZP category can be produced by covering the ZrO_2 grains with Y_2O_3 or with the co-precipitation of Y_2O_3 and ZrO_2 salts. The compressive layers on the ceramic's surface is a remarkable characteristic of Y-TZP. Grains that are tetragonal and on the surface can spontaneously transform to monoclinic grains because they are not restrained by the matrix. This transformation improves the wear and mechanical properties of the material. Also, the essential properties of Y-TZP are deemed a great interest to biomedical engineering. These properties include coefficient of thermal expansion similar to iron, corrosion resistance in acids and alkalis, modulus of elasticity similar to steel, electrical insulation, low thermal conductivity, non-magnetic behavior, wear resistance, fracture toughness, hardness, and high strength (52) (Table 2).

In-Ceram Zirconia (Vita, Bad Sackingen, Germany) is a glass-infiltrated alumina ceramic that is zirconia-toughened and commonly used. When fabricated, the process is either slip-casting or soft machining using CAD/CAM (33). This material is more translucent than Y-TZP because of the glass phase, but since it has a minimal zirconia content as well as containing glass and pores, its mechanical properties are low and its use is short term FPDs in the premolar and anterior areas of the oral cavity (2).

Table 2: Chemical composition, physical, mechanical and thermal properties of Y-TZP

Property	Y-TZP
Chemical composition (wt %)	
Al ₂ O ₃	<0.5
Other oxides	<0.5
Physical properties	
Bulk Density (g/cm ³)	6.05
Grain size (μm)	0.2
Monoclinic phase (%)	<1
Porosity (%)	<0.1
Mechanical Properties	
Flexural strength(4 points) (MPa)	1666
Elastic modulus (GPa)	201
Vickers Hardness (HV)	1270
Fracture toughness (Kgf / mm ^{2/3})	16.8
Fracture toughness (MPa m ⁻¹)	7-10
Compressive strength (MPa)	4900
Impact strength (MPa)	137
Thermal properties	
Thermal expansion coefficient (x 10 ⁻⁶ /C)	11x 10 ⁻⁶ K ⁻¹
Thermal Conductivity (W/ mK)	2
Specific Heat (J/kg°K)	500

2.1.3.2.2 Ceria-Partially Stabilized Zirconia

This material consist of 10 mol% of CeO₂ stabilized TZP (white grains) as a matrix. The Al₂O₃ (black grains) as the second phase are of 30 vol%. The grain's size is approximately 0.49 μm. An important part of the structure is the intergranular nanostructure, this consists of several 10-100 nm-sized Al₂O₃ particles. These particles are inside the ZrO₂ grains and numerous of ZrO₂ particles about 10nm-sized restricted within Al₂O₃. Thus, resulting in better mechanical properties than the typical Y-TZP because of the structural element (53).

Currently, NanoZr is available in the commercial market. This material is a nanocomposite structure with zirconia and alumina that is nano and submicron-size. It was accepted in 2006 by the Ministry of Health, Labour, and Welfare.

When compared to Y-TZP in studies, NanoZr showed that it possesses improved mechanical properties due to its strength, high fracture toughness, and better aging resistance. When compared to 3Y-TZP, its cyclic fatigue strength is double (54) and with a resistance to low-temperature age degradation (LTD) if in a water-based environment (53, 55).

2.1.3.2.3. Zirconia Toughened Alumina (ZTA)

ZTA ceramics are in an alumina matrix consisting of zirconia, which has less than 50% of alumina by weight as a second phase. The material shows a high fracture toughness and stress intensity factor threshold compared to alumina, which makes it a good candidate to use for dental prosthesis framework (56).

Because of the combination of composites and nanocomposites of alumina-zirconia, improved mechanical properties are shown in both materials. These properties include fracture toughness and a slow crack growth propagation threshold. Also, it is possible that the ageing phenomenon could be reduced or avoided (45), depending on the zirconia content. With an increase in zirconia grains, the transformation becomes easier, if the zirconia is lessened, then the aging rate is slower. Slower aging rates of ZTA have been observed when compared to 3Y-TZP (57).

2.1.3.2.4 Alumina Toughened Zirconia (ATZ)

Early in the 2000s, for orthopedic implants that had low thermal degradation in Y-TZP were recommended alumina-zirconia composites (58).

ATZ has 50% less weight from zirconia, which was recently developed. The ceramic combines the elements of hardness and wear resistance of the alumina with the zirconia fracture toughness and biaxial bending strength (59). The ATZ toughness can be higher than yttria-stabilized zirconia. Also, the alumina restrains the zirconia particles, which holds the tetragonal zirconia in a state that is metastable which toughens the material. In addition, since alumina is harder than zirconia, material with hardness of composites with more alumina by volume is better. This leads to a mechanical stability that is higher and a lower aging perception of ATZ (45).

ATZ ceramic that has premium mechanical qualities is from the increased amount of alumina used in the ceramic. This increased raises the hydrothermal stability within the tetragonal phase. Therefore, it is possible that this material could be a barrier for the spread of the transformation phase into the bulk (45).

2.1.3.3 Resin-Matrix Ceramics

Ceramic particles containing an organic matrix of a composite is a new material and is being introduced in the dental field for CAD/CAM usage. This ceramic is porous so it is injected with a monomer mixture and is then cured. This is similar in composition to the fine structure of feldspar ceramic, which is reinforced with aluminum oxide. This technique improves the brittleness in most ceramics because of (1) the natural human dentin that the modulus of elasticity resembles, (2) the material is easier to mill and change, and 3) easy to repair or modify with composite resin (60).

The composition of resin-matrix ceramics can vary, but are generally created for CAD/CAM. This ceramic is categorized into subgroups depending on their inorganic composition (24). Groups are as follows:

2.1.3.3.1 Resin Nanoceramic

This material is a resin matrix that is highly cured and includes 80% nano-ceramic particles by weight. The separated silica nanoparticles, which are 20nm in diameter, and the zirconia nanoparticle, which are 4 to 11 nm in diameter, are combined. These zirconia-silica nanoclusters decrease any interstitial spacing between the filler particles which allow the high nanoceramic content (e.g. Lava Ultimate, 3M ESPE).

2.1.3.3.2. Glass Ceramic in a Resin Interpenetrating Matrix

This material is usually a combination of a network of feldspathic ceramic (86% by weight and 75% by volume) and a network of polymer (14% by weight and 25% by volume). The part that is ceramic consists of 58%-63% SiO₂, 20%- 23% Al₂O₃, 9% -11% Na₂O, 4%- 6% K₂O, 0.5%- 2% B₂O₃, less than 1% of Zr₂O and CaO. Urethane dimethacrylate (UDMA) and triethylene glycol dimethacrylate (TEGDMA) make up the composition of the polymer network. This is considered a hybrid ceramic by the manufacturer (eg. Enamic, Vita).

2.1.3.3.3 Zirconia-Silica Ceramic in a Resin Interpenetrating Matrix

This material's inorganic content includes more than 60% by weight. It also has different organic matrixes and different ratios of ceramic by weight. These include micro-fumed silica, pigments (eg, Shofu Block HC, Shofu), UDMA, TEGDMA, silica powder, and zirconium silicate. It can also be a composite of 85% ultrafine zirconia-silica particles, which are spherical 0.6 μm. They are imbedded into a polymer matrix which includes a patented ternary initiator system, TEGDMA, and bisphenol A glycidyl methacrylate (Bis-GMA) (MZ100 Block, Paradigm MZ-100 Blocks, 3M ESPE).

2.2 Polycrystalline Zirconia

2.2.1 History

The name "Zirconium" derived from the Arabic word 'Zargon' and originated from Persian for Zar (gold) and Gun (color), zirconium means gold in color. ZrO₂, known as zirconium dioxide, was discovered by German chemist Martin Heinrich Klaproth. Klaproth in 1789 was working on processes to heat gems (52, 61) when he discovered it. When it was biomedically applied in 1969 (52), it spanned literature to be written about it by Christel in 1988 its production and use for artificial femoral heads (2). This materials application continued into the 1990s, these applications included frameworks, fixed

partial dental prosthesis (FPDP), implants and implant abutments, crown cores, orthodontic brackets, and endodontic posts (2, 62, 63).

If in powder form, Zircon may look blue-black, while in solid form it shows as a gray-white material. It is an oxidized form of the zirconium metal (ZrO_2) (64). The metal's atomic number is 40, possessing a density of 6.49g/cm^3 , with a boiling point of 3580°C and a melting point of 1852°C . The material's structure consists of a hexagonal structure (61, 65). The material is also resistant to corrosion (66). Although, in nature it is not a pure oxide. The two main sources of zirconium are baddelyite (ZrO_2) and zirconate ($ZrO_2\text{-SiO}_2$, $ZrSiO_4$). From these two sources, the material is chemically extracted for use (65, 66). Zirconia, which is zirconia dioxide (ZrO_2), which comes from baddelyite, presents itself at room temperature as a monoclinic crystal structure, which is a coarse oxide. When in powder form, it can be purified and synthetically processed at high temperatures, resulting in a cubic structure, hence the name, cubic zirconia (66, 67).

Of all dental ceramic, zirconia has the highest reported mechanical properties. Its properties are similar to stainless steel while the color matches natural teeth (68, 69). The resistance to traction is $900\text{-}1200\text{ MPa}$ whereas the compression resistance is at 2000 MPa (69).

2.2.2 Phases of Zirconia

The polymorphic crystalline structures in zirconia are organized in crystalline cells that are classified into three different crystallographic phases (Figure 2):

- Monoclinic (M) form remains stable from room temperature to 1170°C . It shows a deformed prism with parallel-piped sides. When in this stage, the material has low mechanical properties which reduce cohesion of the ceramic leaving it less dense.
- The tetragonal (T) form, which is stable in 1170°C - 2370°C temperatures, forms a straight prism which is rectangular and thus improving the mechanical properties.
- Cubic (C) zirconia has a temperature range of 2370°C to melting point. Its structure is a straight prism and has square sides while possessing moderate mechanical properties (47, 70). When the material has cooled, the material increases 3-5% in volume, which creates the transformation from tetragonal (t) to monoclinic (m) phase, which can be a failure. At 950°C , the transformation begins and is reversible (47, 61, 71).

“Ceramic Steel” which is described by Garvie et al., is zirconia that uses phase transformation to improve mechanical strength and toughness in this type of ceramic (72).

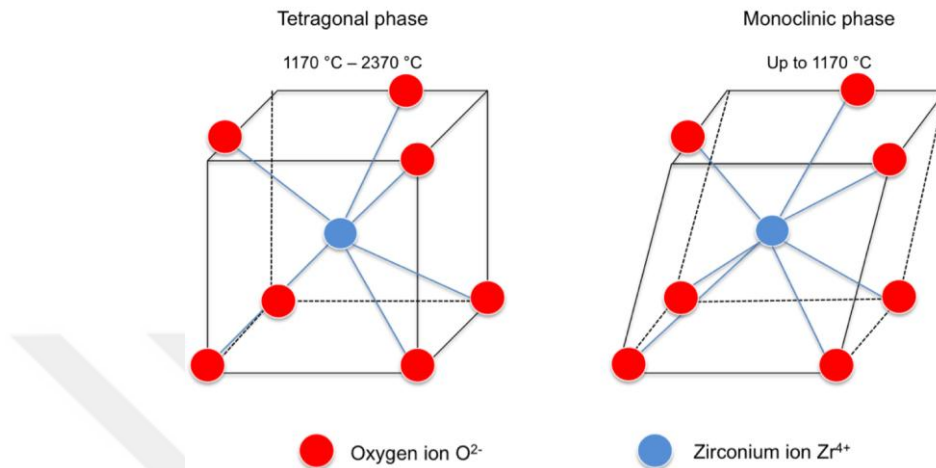


Figure 2: Tetragonal and monoclinic crystallographic phases of zirconia (70).

2.2.3. Stabilized Zirconia

When zirconia is mixed with different oxides, it can be stabilized in the tetragonal or cubic phases when at room temperature. It can also be used to control the volume expansion with yttrium oxide (Y_2O_3), calcium oxide (CaO) and magnesium oxide (MgO) (45, 46, 73). If the amount of oxide is sufficient, then a fully stabilized cubic phase can be produced. If 3wt%- 5wt% is added, then a partially stabilized zirconia (PSZ) exists (64). When in a multiphase form, partially stabilized zirconia is cubic zirconia in the major phase, whereas the minor phase is tetragonal and monoclinic zirconia (65).

Possessing a high initial flexural strength and fracture toughness, partially stabilized zirconia, like yttrium-oxide (Y-TZP) exhibits mechanical properties well enough for dentistry (73, 74).

2.2.4 Transformation Toughening of Zirconia

Because it is not under stress, the tetragonal zirconia phase is stable. When in the metastable phase $t\text{-ZrO}_2$, it is under stress that transforms to the monoclinic phase with the crystal sizes increase by 3% by volume (Figure 3). When in transformation, the energy is diverted away from potential cracks, this process is called ‘transformation toughening’. Also, with the change in volume, the compressive stress increases which also stops cracking (Figure 4) (13, 75). The transformation of toughening gives the zirconia excellent mechanical properties (64).

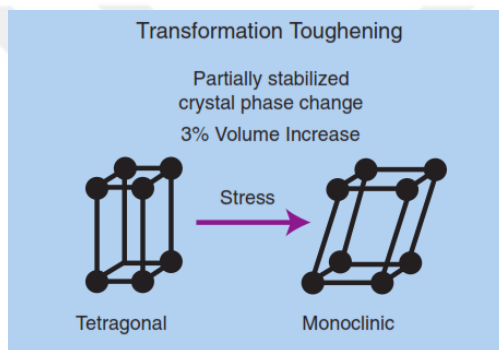


Figure 3: Phase transformation from (t) to (m) (64)

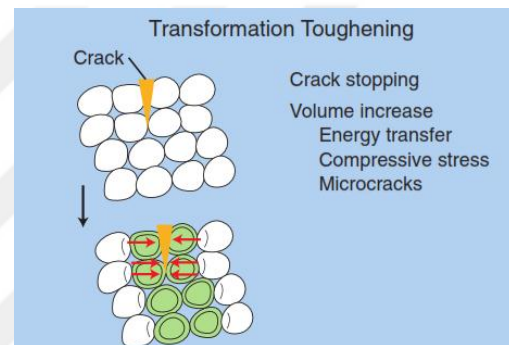


Figure 4: Microcracks closing because of the crystals volume expansion (64)

2.2.5 Biological Characteristics of Zirconia

2.2.5.1 Biocompatibility and Degree of Toxicity

Studies of *in vitro* and *in vivo* have shown that the biocompatibility of zirconia is high, especially as a purified powder from radioactive contents (76). These materials are chemically inert, which permit excellent cell adhesion, also no negative responses have been reported (77). In terms of periodontal health, no studies have stated a change in the biological health of the patient’s soft or hard tissue surrounding the zirconia restorations (65). Although, an inflammatory reaction can occur in the mouth due to particles from being released from the manufacturing process or from the low temperature degradation (LTD) of the zirconia (66, 78). These results have suggested that the proper material for implant abutments is zirconium oxide due to its low bacterial colonization potential (65).

In vitro tests have shown results similar to alumina in lower toxicity than titanium oxide in zirconia. Studies have not detected chromosomal alterations or mutagenic in blood cells or fibroblasts, cytotoxicity, or carcinogenicity (70).

2.2.5.2 Radioactivity

When in powder, zirconia contains minimal amounts of thorium (^{228}Th) actinide series and uranium-radium (^{226}Ra), which are radioactive elements (70). To separate the materials would be costly and difficult (66). Zirconia with low radioactive levels ($< 100 \text{ Gyh}^{-1}$) can be achieved after the purging process. These levels can be externally exposed to organs and tissues, which is approved by the European radiation limits (75, 79).

2.2.6 Optical Characteristics

Although it possesses superior mechanical properties, zirconia is opaque and its translucency is insufficient (5). Because of this, the material is used on dark substrates to mask blackened teeth, pins, and metal cores as infrastructures (75). The optical behavior of zirconia is due to the grains being greater than the length of light. This creates a high refractive index with a high opacity coupled with a low absorption coefficient in the visible and infrared spectrum (30, 66). Because of this, zirconia must be covered with ceramics that are translucent to mimic the tooth's appearance (80). When compared with metal alloys, zirconia's high radiopacity improves the ceramic's radiographic evaluation of marginal integrity, as well as the removal of cement and recurring decay (75).

In contrast, when zirconia is compared to alumina and glass, which are high in translucency, possess inferior mechanical properties than those of zirconia (30).

When light transmits through Y-TZP it changes depending on: (1) the zirconia's framework composition and thickness; and (2) the veneer porcelain's physical characteristics and degree of glazing it underwent (65, 81). If the particle size is reduced within the zirconia powder (ZrO_2) and is then mixed with a binder for compaction and an increase of the density of the green state occurs as well as the removal of the pores, then it will possess a more natural appearance, and thus the light transmission of full contour zirconia is increased (65).

2.2.7 Aging of Zirconium

The aging of zirconium, also known as low temperature degradation (LTD), is a slow but spontaneous phenomenon which occurs at low temperatures (150-400°C) within a moist environment over time, this was reported first by Kobayashi (82). This takes place happens on the surface level of the ceramic and progresses to the bulk of material (5), which slowly transforms a metastable tetragonal phase into a stable monoclinic phase (82). This transformation depends on certain variables that are imbalanced, these can include the presence of a low yttria content, cubic phase, large particle size the presence of residual stress or specific guidance from the surface (66).

As aging occurs, the roughening of the material leads to wear and micro cracks, which result in premature failure due to the creation of particle debris and slow crack growth (75). Thus, to prevent LTD, a smooth surface is needed (5). Therefore, to decrease LTD, the material must contain small-sized particles, an increased amount of stabilizing oxide, or composite formations with aluminum oxide (Al_2O_3) (66). When under stress during the aging process, the alumina particles prevent the tetragonal zirconia to relax (83).

2.2.8 Manufacturing Procedures by Using CAD/CAM

CAD/CAM techniques are used during the prefabrication for zirconia frame works. They are either ‘soft-machining’ of blocks that are pre-sintered’ or ‘hard machining’ of completely sintered blocks (84).

2.2.8.1 Soft Machining

This process for 3Y-TZP is a diffused manufacturing system, it mills pre-sintered blocks, and after processing they are fully sintered. These blocks are considered in a ‘green state’. They are compacted zirconia powders and binders produced through a cold, isostatic-pressing process.

The supporting abutments or the crown/FDP wax patterns are scanned, either by contact or non-contact scanners. Once scanned, CAD software builds an enlarged, virtual framework. When put into the CAM milling system, the blank is carved out by using accurate dimensions from the framework, and 25% in volume shrinkage occurs to the

framework during sinterization to revert to its proper dimensions (75). Therefore, the zirconia's restoration fit will be warranted (85).

2.2.8.2 Hard Machining

The material used are 3y-TZP blocks that have been fully sintered. To prepare the material, it is pre-sintered to reach a density of 95% theoretical density when below 1500°C. Next, through hot isostatic pressing, the blocks are processed at high temperatures between 1400-1500 °C. This temperature coupled with high pressure from the inert atmospheric gas results in a homogenous, 99% theoretical dense, fully sintered zirconia block.

These blocks can then be used with a software milling system to create and shape the framework to the needed dimensions (47). Since there is no shrinkage, this system creates a superior fit, but the matching is inferior due to the hardness and low machinability of the fully sintered material (86).

Framework from zirconia is more accepted than metal framework because of its esthetics, although it is opaque and too white. To stimulate the natural tooth color, framework of colored zirconia was introduced (87). To create colored framework, metal oxides such as iron, bismuth, cerium or a combination to the zirconia powder. The other method is to dip the framework into a solution of metal salts after the machining process (5, 88). The shade of color depends on the solution concentration. Colored framework have no effect on the mechanical properties or crystalline phases (89).

2.2.9 Veneering of Zirconia Substructures

With the use of computer aided design and computer aided manufacturing technology (CAD/CAM), zirconia is widely used in dental applications. Zirconia is white and opaque, while it can be produced to be colored; it is only translucent in thin layers. So, feldspathic porcelains must be veneered to the zirconia core for a natural tooth look to occur, just like in metal-ceramic restorations.

At the current time, veneering zirconia restorations have two commercial methods. These methods are typical hand layering with the power and liquid technique, and securing the porcelain with heat pressing. From the success of two glass ceramics

there were particle-filled (reinforced with leucite and lithium disilicates containing ceramics), heat pressing gained popularity (90).

Tooth-supported or implant supported restorations are what zirconia ceramic applications encompass (91). Within studies, framework material of zirconia has a high reliability (2). Although, the chipping and fractures of porcelain are a drawback for zirconia restorations. For tooth-supported restorations, the chipping rate is 14% after 5 years for a single crown, while implant-supported restorations showed 31% chipping rate for the same time frame (91). Also, studies showed that the chipping rate of three-unit FDPs after 5 years was at 15.2% (49). When the failure was examined, the interface between the veneering material and core of zirconia showed to be the epicenter of the failure (93).

In terms of causes in a reduction of the core to veneer bond strength, five factors have been identified: (1) inherent flaw creation within processing, (2) pre-stresses from the different coefficient of thermal expansion (CTE) between the core and veneering material, (3) phase transformation of the core-veneer interface crystals from thermal issues or loading stress, (4) the core becoming poor wet by the veneering material, and (5) shrinkage from firing of the veneer (94).

Implementations to reduce chipping is framework design, as it must provide uniform support for the veneering with a slow cooling rate (95, 96).

2.2.9.1 Slow Cooling Rate

Since studies have shown that zirconia ceramic is a poor thermal conductor, therefore, manufacturers advised a slow cooling process during zirconia restorations. This will prevent the development of residual tensile stresses on the veneer (96). This recommendation is not backed by studies, and only a few in vitro studies researched the cooling rate stability of zirconia restorations (96, 97, 98).

Fast cooling was found by Komine to reduce the shear bond strength within one brand of veneer but not in other veneer/zirconia disks (98).

2.2.9.2 Anatomical Framework Design

Zirconia restorations use a framework of high strength ceramic to withstand cyclic loading forces, which are resemble to the metal-ceramic restorations design. The fracture resistance and preparation design contribute to the strength of the structure (99). Single based crowns of Y-TZP, it is recommended to be prepared through the shoulder finish line as both a mechanical and periodontal perspective. Although, as a less invasion options, a slight chamfer can be used, not a pronounced or deep chamfer, as this is not recommended. Disproven by Fenske et al, an in vitro study showed that increased material thickness did not automatically increase strength when researching fracture resistance within shoulder width. For more delicate preparations, an increase in Weibull modulus was displayed in crowns formed from pressable leucite-reinforced ceramic (IPS Empress, Ivoclar Vivadent, FLSchaan). Friedlander and Doyle investigated glass ceramic crowns, they exhibited a total convergence angle of 10° with a 1.2mm shoulder finish and a sharp axiokingival line angle which possessed the highest fracture resistance in preparation design. A suitable single-tooth restoration of an all-ceramic should have a thickness of 1.6mm with a load bearing capacity of 2000N. If there is any decrease in minimal thickness, it would be capable of withstanding higher loads (100).

2.2.9.3 Thickness of Veneer

A thin porcelain layer is stronger than layers that are more than 1.5 to 2 mm (101). When cooling the veneer, temperature vary throughout the porcelain. This results is temperatures above and below the glass transition temperature for the ceramic. When the porcelain is thicker, the thermal variances increase creating residual stresses (102). Multiple studies have studied the relationship between the veneering porcelain's thickness and residual stress development from various geometries. Sphero-cylindrical hollow forms are typical of crowns and FPDs. The thickness varies throughout the framework, which makes it geometry dependent due to its anatomical form and residual stresses (103). This results in various location stresses within the restoration because of the variation in thermal properties from different cooling rates since the porcelain/core thickness ratios are irregular (104).

In addition, to avoid chipping of the porcelain, there are two alternatives solution. One option is FDPs that are of hybrid-structure with CAD/CAM produced porcelain veneer parts, which adhere to zirconia framework fabricated by CAD/CAM. The second

option is to use zirconia FDPs that are fully contoured. Both of these options delicate manual work can be done by digital procedures. But, more clinical studies are needed to prove the options' usefulness (86).

2.2.10 Full Anatomic Zirconia Restorations (Monolithic Zirconia)

Another option to prevent chipping is by using monolithic zirconia for restorations. This method does not use veneering, but rather a single piece of zirconia. When coloring oxides are added to zirconia that is full-contour, it is possible to obtain a natural tooth color, therefore a tooth colored veneer is not needed (105). With the advanced of CAD/CAM technology, monolithic zirconia for restorations have increased in popularity (5, 86). To eliminate veneer cracking, this zirconia is used for single crowns in the posterior region (5). There is a smaller requirement in tooth reduction for this zirconia, when compared to other ceramic methods. Therefore, the crown has 0.5mm occlusal thickness with the same strength as PFM. It can be especially useful for patients who have an inter-occlusal space that is small (106). To make the production process faster and less expensive, the zirconia is milled and shaded before sintering. Yttria stabilized tetragonal zirconia polycrystalline (Y-TZP) is able to keep its strength properties but become translucent dependent on sintering conditions, this found by Kim. It has been concluded that optimal temperatures with less sintering time can produce grain sizes that are smaller with enhanced translucency (107, 108). Different methods can be applied to full-contour zirconia to increase its translucency and aesthetics, these methods include; fabrication processes, sintering temperature, and the addition of applied coloring liquids (109).

Monolithic zirconia consist of 2 types of materials, these being opaque and translucent zirconia. The one with the better flexural strength in the posterior region is the opaque zirconia. Although, the translucent zirconia possess properties that are more natural appearance (5). BruxZir by Glidewell and LAVA Plus by 3M ESPE are different types of monolithic zirconia with high translucent. Bruxzir ceramic is created by eliminating any pores, using a high sintering process 1530°C with a 6 hour dwell time, and the elimination of light-scattering alumina sintering aids. The high translucency of Lava plus (3M ESPE) has an increased green compact with decrease a sintering temperature of 1450°C at a 2 hour dwell time, and a reduction in use of alumina sintering aids, , which all result in a fine grain size (110). The shading system for LAVA is unique

as it gives production labs many options to shade and customize the ceramic. Once the green-state block has been milled, 18 different dyeing liquids can be chosen in the laboratory which then cover the 16 Vita Classical A1- D4 to obtain a custom color. During the sintering phase, the colored dye is applied which makes the colored ions combine into the zirconia. The material can be put in the posterior or anterior of the mouth due to its strength, high translucency, and improved esthetics (5).

There are some concerns about the long-term stability of full anatomic zirconia restorations because of the coloring method and possible surface staining (105). Another concern is the concept of accelerated aging in the zirconia. When humidity is exposed to the material, the grains of zirconia change from tetragonal (t) to monoclinic (m), which is irreversible. This change affects the stability of the surface and bulk of the material (78). It is unknown if low thermal degradation (LTD) has a long term impact on the zirconia in a clinical setting (70).

When in a pre-sintered state, the monolithic zirconia can be colored to match the natural teeth. In addition, glazing or polishing can be achieved a natural looking material with a smooth surface. Different polishing techniques either manual or machine include rubber wheels, diamond points, or abrasive pastes. The glazing process either firing by heating the restoration for 1-2 minutes at glazing temperature to create glossy surface or by glass coating that created by firing a transparent glass only on the surface (111).

2.2.10.1 Monolithic Zirconia Properties

2.2.10.1.1 Wear Properties

Hence used as a full contour, the material creates a concern for wearing of antagonist enamel because it is very hard (86). In several studies, the wear ability of the material had been evaluated. The published results of the study show that the lowest wear on the antagonists was the polish zirconia compared to the glazed zirconia. This result is due to the glazing on the zirconia eventually wears down in a clinical function which shows a rough and abrasive surface texture on the zirconia. The study also published that with chair-side occlusal adjustments; the layer of glaze can be removed easily (5). The glaze's wear depends on the particle size in the microstructure and their homogeneity (86). From in vitro studies, a safe use of polished zirconia is when it is an antagonist to enamel or feldspathic porcelain (109).

2.2.10.1.2 Surface Roughness

The opposing teeth can increase the wear rate from improper surface treatment creating surface roughness. Ghazal et al. states that the roughness of the zirconia should be at a maximum of 0.75 μm . (2, 102). When polished, the monolithic zirconia's surface roughness greatly by aging procedures, founded by Alghazzawi, due to the phase transformation (tetragonal to monoclinic) with volume expansion. This was from the grain push-out during the LTD, which contributed to the surfacing becoming rough (113).

2.2.10.1.3 Fracture Strength

A study by Sun et al. reported that metal-ceramic crown was equal to monolithic zirconia crowns with thickness of 1mm. Thus, the material could be used in load bearing areas without the issue of chipping, which is commonly seen in veneers. Also, when comparing it to veneers, lithium disilicate and metal-ceramics, the monolithic zirconia had a higher strength (114). Zesewitz et al reported in a study that when bonded with glass-ionomer or adhesive resin, the zirconia showed its highest strength, when compared to lithium disilicate and feldspathic ceramics. (5, 115).

2.2.10.1.4 Optical Properties

Monolithic zirconia is a restoration made of mono layers of restorations. Because of this, when colored liquids are applied, glazing, polishing, or surface characterization is processed, the zirconia is able to look like natural teeth (5). Kim reported in a study showed that when the applications of coloring liquid increased, the lightened and opalescence decreased (116). In a different study by the same researcher Kim, it was reported the processes of polishing and glazing lessened the lightness of the material, while yellowness increased with glazing, and applying coloring liquid made the material yellow and darker (117).

2.2.10.1.5 Marginal Fit

When compared to veneered zirconia in a study, monolithic zirconia proved to have greater passivity of fit. It showed that strain development increased when ceramic veneering of zirconia framework happened. While, less strain appeared in monolithic restorations (118).

Zirconia application in clinical setting vary, they include full and partial coverage crowns or FPDs, fabrication of veneers, posts and cores, implants and abutments. Zirconia is also used in auxiliary components as dental products, like extracoronal attachments, cutting burs, surgical drills, and orthodontic brackets. Although, the cementation procedure is highly effective of the success of fixed ceramic prostheses (9, 66).

2.3 Adhesion in Dentistry

With the aid of an adhesive, holding together two surfaces by force and process is the concept of adhesion (ISO/TR 11405: 1993). Though physical and chemical processes, adhesion creates a bond between the adherent and adhesive sides of the material. The adhesion process contains multiple mechanisms, which are simultaneously observed:

1. Mechanical adhesion that adhesive preparation is dependent on the micro or macroscopic irregularities of the adherent.
2. With chemical adhesion, a chemical bond is produced between the layers of the adherent and adhesive. The bonds that are strong are primary bonds being ionic and covalent, which weak secondary bonds are Hydrogen bond or Van der Waal's forces.

A strong adhesive bond is necessary in Prosthodontics. This bond improves marginal adaptation, creates high retention, prevents micro infiltration, and increases the strength against fractures for the natural tooth and restoration. Micro-mechanical connections are based in this bonding. The creation of roughness on the material's surface and a clean state is needed in chemical adhesion to ensure the chemical activation on the surface. Surface roughness treatments through mechanical means includes rotating tools abrasion, alumina particle sandblasting, acid etching as a chemical treatment are all accepted processes (119).

2.3.1. Classical Dental Ceramics Adhesion

If the following protocol is used, then adhering glass ceramics that contain silica can be predicable with lasting results. A favorable ceramic bonding surface can be achieved with hydrofluoric acid (HF) etching (119, 120). When the HF is added to ceramics made with silica, the internal glass matrix dissolves and can be removed by rinsing. This creates microscopic pores and a surface with high energy, which is micro-

retentive. The HF treatment creates a hydroxyl group (-OH) which is dense on the surface, this creates an increase between the silica and silanes connection on the surface layer (121).

Silanes bond to silica dioxide (SiO_2) on the surface of the ceramic through the -OH group which act as bi-functional molecules. In addition, these silanes possess a co-polymerizing functional group within the organic matrix resins. Through the process of silanization, the wettability of the ceramic's surface increases. Therefore it can be seen through the process of condensation reaction when bonding the ceramic happens between the silanol groups (Si-OH) on the surface with the hydrolyzed silane molecule of the silanol group. This creates joints of siloxanes (Si-O-Si), where the subproduct is water. When there is an additional reaction, which happens during the reaction of curing of resin when being cemented between the organic portion of silane and methacrylate groups (122).

2.3.2. Crystalline Dental Ceramics Adhesion

When compared to classic ceramic, the zirconia crystalline and alumina mechanical properties and composition differ substantially. Etching with HF is useless with a silica-free material and does not enable chemical bonding between the silane and silica materials, which is needed for silanization. Therefore, new techniques to produce strong and durable adhesion are needed (123). Also, by using aggressive techniques for the modification of the surface can lead to potential susceptibility to LTD and reduced strength (124). Zirconia bonding has recently been a subject of interest. Zirconia does not react to traditional adhesive chemistry because it is inert and non-polar. The current adhesive bonding techniques for zirconia bio-ceramics durability long-term is unknown and is not suitable for all clinical applications (125).

In regards to recent research, zirconia ceramic bonding has focus on different approaches. The mechanical retention of the ceramic can be accomplished by either modifying the surface structure with particle abrasion, or by adding glass of the surface of the material. Also, satisfactory results were shown when chemical bonding occurred when a phosphate ester monomer 10-methacryloyloxydecyl dihydrogenphosphate (MDP) was used in conjunction with particle abrasion that was airborne (126).

2.3.2.1 Luting Cements Mostly Used with Zirconia Ceramics

The two bonding options for zirconia restorations to natural teeth are resin cements and conventional cements. The more preferred option is by resin cements due to the advantages of good retention, marginal seal, and improved fracture resistance (9), as well as high optical properties with low solubility (127).

The resin ceramic's composition, fluidity, cohesive resistance, and wetting capacity have shown a greater potential for bonding to zirconia than with other materials. The opacity of the zirconia stops halogen light transmission and produces postoperative sensitivity. The most used prosthesis cementation is either by chemical activation or dual cements. The dual resin cements have a greater reaction to adhering to ceramic because they contain methacrylates of multifunctional acidity (128). The success of restorations is highly affected by the choice of adhesion method used between the restoration and tooth (129).

2.3.2.1.1 Composition of Resin Cements

The composition of resin cements are fluid composites possessing a low viscosity. Within the composition of the material, there is a monomeric system that is divided into conventional resins or acid groups of resin composite cement. The conventional resins based, bisphenol A-glycidyl methacrylate (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA) or on urethane dimethacrylate (UEDMA). Inorganic particles (aluminum, lithium, and particles of glass, silica or colloidal silica) are also added and treated with silane, a bonding agent. The fluidity of the material depends on the amount of these polymers used and the polymerization process. This process can use a photoactivation method, a chemical process, or both combined as a dual technique (119, 128).

The resin that contains acid groups can be divided into subgroups by an adhesive monomer. The divided subgroups possess 10-methacryloyloxydecyl dihydrogen phosphate (MDP) and self-adhesive resin cements have multifunctional acidic methacrylate monomers (such as, carboxylic acid, phosphoric acid ester or amino acid derivatives). The resin cement that is self-adhesive are less time consuming and easier to use when compared with conventional resin cement, which needs a pre-treatment of the natural tooth before the application of adhesives (130).

Capable of bonding with natural enamel and dentin, resin cement is active luting material, which can also bond with indirect restoration surfaces. Although, the application technique can greatly affect the level of difficulty associated with using resin cements. Resin cement usage needs a bonding procedure. This procedure is necessary as multiple applications of a complicated method is used when bonding the dental substrate to the surface of the restoration (ceramic, composite, etc.). Restorative treatment failure and postoperative sensitivity can occur, therefore the application method of the cement, the material, and operator are all factors. The application of cement that is self-adhesive in a clinical setting is only one step, the base is mixed with catalyst pastes and is then applied to the bonding surfaces (131).

The noted problem in chemically bonding Y-TZP with resin is that it has a complex surface with Zr atoms, it is inert, and non-reactive. Modern dental research literature has proven that several studies suggest to use a luting resin containing phosphate monomer. This material give a stronger bond value rather than conventional luting cement when applied to zirconia (132, 133).

2.3.2.1.2 Phosphate Monomer

When zirconia and alumina are of non-silica composition, they are difficult to bond using a traditional silanisation approach to the tooth structure, this is due to fact that silica-based ceramics are less chemically stable than those based in oxide because they are not readily hydrolyzed (119, 134). Functional phosphate monomer in cement bonds well when the material is densely sintered, a ceramic that is oxide based and alumina ceramics that are glass-infiltrated (135). As a mediator between organic and inorganic substrates, which is similar to organosilance, phosphate monomer possesses an organofunctional group. This group reacts with the resin cement's organic matrix and on the other end the phosphate ester group (136). When the hydroxyl group and functional phosphate ester group react on the ceramic oxide's surface, a bond is achieved (Figure 5) (123).

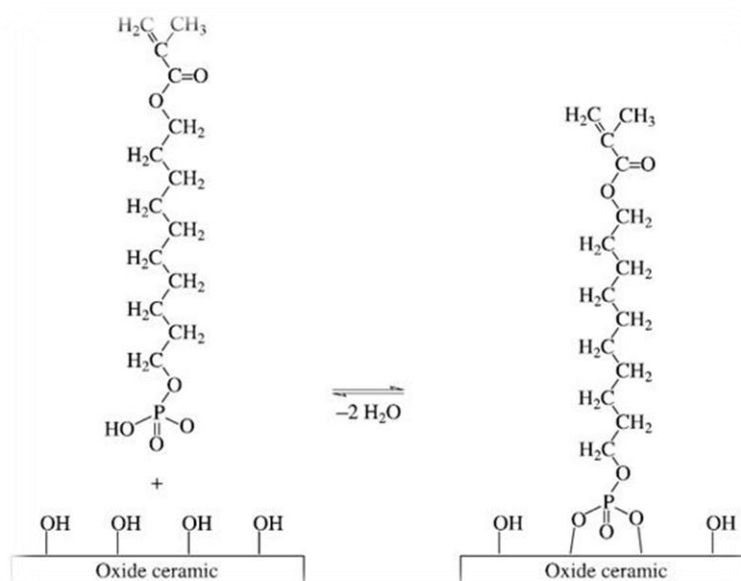


Figure 5: An illustration showing reaction of a phosphate monomer group to the oxide ceramic hydroxyl group (136)

Some of the modern, phosphate monomer-containing bonding systems are Panavia 21 (Kuraray Co. Ltd), Multilink Automix (Ivoclar-Vivadent), and RelyX Unicem (3M ESPE, Seefeld, Germany) (137). Panavia 21 has shown in studies that the material can provide a durable, long-lasting bond when adhered to zirconia and alumina that is oxide based (123, 137). Through chemical bonds, ceramic or metal materials bond with all phosphate monomer-containing systems. These monomers are not all the same as they are used by different manufacturers. Panavia products (Panavia F2.0 and Panavia 21 resin cements; Kuraray Co. Ltd, Osaka, Japan) uses 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) that produced by Kuraray. RelyX Unicem was developed by 3M ESPE using phosphorylated methacrylate, which has two groups of phosphoric acid groups while possessing carbon groups that are double bonded used for cross-linking. A Metal and/or zirconia primer is used in the Multilink-Automix (Ivoclar Vivadent) system as a treatment for a separate surface, because it contains an acid acrylate with phosphoric possessing a phosphate terminal where there are two bonding sites for the oxygen bond between the resin matrix (137, 138).

Resin cement that contains MDP is still a popular choice in chemical applications for luting zirconia restorations because it possesses low incident of a loss of retention and

failure (134). To significantly improve the bond strength, a ceramic primer with 10-MDP is needed as an addition, to bond zirconia to the cement with resin composite (130). Since the resins can contain different monomers, there is a variety of compositions which effect the bond strength values. For example, the different primers include zirconate coupler, MDP, thiophosphate methacryloyloxyalkyl derivates, 4-methacryloxy-ethyl trimellitate ashy-dride, and thiophosphate methacryloyloxyalkyl derivates (139).

2.4 Surface Conditioning to Improve Resin to Zirconia Adhesion

A key requirement to achieve a strong adhesive bond is that the substrate surface is dry, clean, and free of contaminates. To condition the surface, a method of procedures must be followed to improve the affinity to the adhesive agent and increase the surface's energy. This substrate's surface energy needs to greater than adhesive agent's molecules cohesive forces, this allows for the wettability to be as high as possible (129, 140).

Due to the creation of mechanical and chemical bonding difficulty in zirconia, bonding zirconia with resin cement alterative processes have be researched. In the below sections, important techniques will be described regarding the dental usage of zirconia surface conditioning (140).

2.4.1 Surface Treatment Methods Causing Micromechanical Interlocking

2.4.1.1 Sandblasting

The technique of sandblasting can create a surface with high wettability, while increasing irregularities and roughness on the ceramic's surface. It can also be a process for cleaning the surface of substrates, which will allow the resin cement to flow to the surface (52, 61). A key factor that has been identified for achieving a zirconia-based ceramic double bond is the use of airborne particle abrasion with alumina. With particle abrasion use, particles that vary in size have been used, but there is no evidence of size superiority (141). Although, is has been reported in an in vitro study that the effect of the sandblasting is controversial some of them showed fatigue was caused in the material structure and mechanical weakening related to phase transformation. In opposing reports, is it said that the mechanical characteristics of zirconia are strengthened from sandblasting (52, 61). While there are several different treatments for Y-TZP surfaces, the selection of the most appropriate method has still yet to be determined as there are opposing studies. Also, there is no published literature to be found to describe monolithic

zirconia during phase transition during the variety of airborne particle abrasion methods (141).

2.4.1.2 Hot Chemical Etching

The process of controlling corrosion and selective etching on zirconia ceramic surfaces is the method of hot etching by solution. This results in the enhancement of the possibility of resin cements mechanically interlocking while creating a rough surface. The modification of the grain boundaries by the etching solution removes the high-energy grain boundaries that are less arranged (142).

2.4.1.3 Laser Treatment

Erbium-doped yttrium aluminum garnet, also known as ER: YAG is a laser which can remove particles via the process of ablation of vaporization and micro-explosions. Heating and cooling temperature changes can be obtained through laser effects; these effects begin the damaging of the material from phase transformation. A suggestion has been made to reduce the power of the laser and to use constant water-cooling to enable surface irradiation. Although, it is questionable as results due to the fact that in in-vitro experiments the laser irradiation is not as effective as using the air particle abrasion to increase bond strength (140).

2.4.1.4 Nano-Structured Alumina Coating

This surface treatment method is dependent on an alumina coating which is nano-structured that has a good wettability and a high surface area, this will creating an interlocking at a micro-mechanical level. This will create a layer that is nanostructure which can be achieved when the formation of lalamellar (AlOOH) from hydrolysis of alumina nitride when put onto the surface of the zirconia after a series of heat treatment processes have been performed. This creates an end result of an alumina coating that is discontinuous and nanostructured (240 μm thickness). This has been found that bond strength was greatly improved with bonded with resin cements (61).

2.4.2 Surface Treatment Methods Causing Chemical Bonding and Micro-Mechanical Interlocking

2.4.2.1 Pyrochemical Silica Coating

Silica coating usages can be used for many methods. Introduced in the early 1980s was a system involving thermal coating with silica (Silicoater MD system, Heraeus Kulzer, Wehrheim, Germany). This process involves the ceramic zirconia's surface being sandblasted and then silica coated. After these steps, the ceramic's surface is then coated with silane. This silane has been formed when the silica coating was increased in temperature for the Silicoater MD apparatus substrate (61).

2.4.2.2 Tribochemical Silica Coating

Tribochemistry possesses the basic principles which create chemical and physicochemical changes during the mechanical energy application of the material. There are two systems The *Rocatec*TM and *CoJet*TM (3M ESPE, Seefeld, Germany) that used this process with alumina particles that are silica-coated for compressed air expulsion for substrate surface blasting. This impact on the surface particles on the substrate causes a transfer of kinetic energy. This kinetic energy is then absorbed causing a microscopic fusion when met with the substrate surface. It creates an increase in temperature (1200°C) to the surface for a short moment. These alumina particles that are silica-coated are able to penetrate the substrate's surface and embed themselves into the surface material, therefore it is left with a silica coating. The coated surface can then be primed by silanization for usage for then the adhesive cement can be laid for bonding (143).

2.4.2.3 Selective Infiltration Etching (SIE)

The SIE method of surface condition consists of a zirconia surface that has been coated by a layer of glass that is thin, which acts as a conditioning agent when it has been heated to a temperature that is above the standard of glass transition heating temperature. When the glass becomes molten, it is able to infiltrate micro-granular limits structure of the zirconia, which exerts surface tension and capillary forces. In the last stage, an acid bath is used to remove the material once it has been cooled to room temperature. This eventually makes a three dimensional 3D inter-granular network of pores, which then allows the resin cement to interlock in a nano-mechanical fashion (138).

2.5 *In Vitro* Testing Methodology

2.5.1 Interfacial Degradation by Artificial Aging

Fastened aging, also known as *in vitro* interfacial fatigue, are the most commonly used techniques. These techniques include thermo cycling and water storage. These methods of aging are based on the ISO International Standards Organization widely used standards for dental materials (ISO TR11450 standard, 1994), which can be combined in usage or used as separate processes.

Initially, several bonding procedures are available for Y-TZP to obtain a strong bond. However, the bonding procedure used with the material must be able to withstand the aggressive oral environment situations. The bond must withstand pH fluctuations, mastication forces, temperature shocks, and humidity. Many studies have shown that the use of water storage and/or thermo cycling can help reduce the fatigue to the bond between zirconia and resin. This bond can cause micro leakage, time lapsed deterioration, and loss of retention (144).

2.5.1.1 Chemical Degradation

The artificial aging technique that is most widely used is the process of long period water storage. It has been reported that the cause of the decrease in bonding effectiveness was the direct result of hydrolysis interference of the bonding interface. When there is a diffusion of liquids on the bonding interface, hydrolytic degradation occurs. The diffusion occurs over time as it takes time for the penetration of water in between the interface of the bond to cause a chemical breakdown (145). The polymer matrix's mechanical properties will decrease when water can infiltrate the interface. This causes a reduction in friction forces and swelling between the chains of polymer, which is known by the technical term of 'plasticization'. In clinical trials and studies, saliva solutions that are artificial can be used as a variable, but it has been shown that degradation from pure water has shown very similar results to the saliva (146).

2.5.1.2 Thermal Degradation

Thermo cycling is the other commonly used technique for artificial aging. The regimen of thermo cycling which has been determined by the ISO TR 11450 standard (1994) as an appropriate method, consists of a cycle of water, 500 times, with

temperatures between 5 to 55°C (145). Gale (1999), concluded in a literature study that one year of functioning in vivo are approximately equal to 10,000 cycles. Whereas the concept of 500 cycles is the minimum for the stimulation of long term bonding effectiveness (147).

Resin and ceramic that have different coefficient linear values of thermal expansion (LCTE) can affect the failure rate mechanism on the interface being bonded. These LCTE ceramic materials are generally lower than the counterpart of resin luting cements LCTEs. The differences between the two materials create unequal changes within the dimensions and cause thermal stressing on the bonding interface, thus affecting the bond. Percolation, the process of fluids flowing in and out, is caused from the bonding stresses, which can propagate cracking along the interfaces that bond. This cracking leads to gap formation, which skews the dimensions of the gap causing the percolation. Percolation is a form of hydrolytic duration due to the fluids (147). The process of thermo cycling can result in chemical degradation at an accelerated rate as well as the stress from combined contraction and expansion stresses. On the specific test setup, each effect of the variables are highly dependent on the study. After reviewing the first aging method of hydrolysis, it can be concluded that thermo cycling on very small specimens should be applied, and any post aging preparation should not be used (145).

2.5.1.3 Mechanical Degradation

An issue that can affect adhesion is mechanical loading. By using a simulation of chewing to mimic the stress of in vivo, the interface can be aged and then the bond strength can be measured.

It is unknown and not fully understood about the long term effects of dynamic loading and it is needed to be investigated further to completely understand the interaction, which are complex, and the zirconia-resin bond performance strength and their effects (148).

2.5.2 Tests for Adhesion Measurement of Bond Strength

2.5.2.1 Shear Bond Strength Test

The test of shear bond strength is a test with two materials. These materials use an adhesive agent to form a connection between them and are then loaded in shear,

eventually separation will occur. To calculate the strength of the bond, the sum of the bond strength is divided by the force applied at a maximum at the time of bond failure in the failed area of the cross section of the bond. The testing method of shear bond strength is widely used due to the ease of use, fast production of results from testing, and the clear testing protocol. Also to note, shear stresses are stimulated by the test, which is considered by many as a resulting failure in the oral cavity from the bond failure of restorative material (149). A large disadvantage of testing the shear bond strength is that the test specimen is required to be large. By having a large specimen, a premature failure can occur because of the ceramic's structural flaws; therefore it is possible for failure to happen before the maximum bond strength level is ever reached (150). Multiple researchers have used the shear bond strength test on veneer and ceramic to test the bond strength (149).

2.5.2.2 Tensile Bond Strength

The strength test testing the tensile bond uses a metal rod, on one end is bonded porcelain, or bonded between the middle ends of two metal rods. Force is then applied as longitudinal tensile force of the rod trying to separate the metal from the porcelain along the rod's long axis. The calculation for this bond strength is to divide the bond failure axial load by the bonded area at the cross section (150). It has been reported that the specimen geometry greatly influences the results of the tensile strength results as well as the distributions of stress, as non-uniform, when the load force is applied. If tested alone, the data and information provided by the results of the tensile bond strength may not conclude about the bond strength of the materials used in the test (151).

2.5.2.3 Flexural Bond Strength Test

There have been reported problems that have been associated with testing brittle materials when testing with direct tension. Due to this, the most widely promoted test for flexibility and bending in the ceramic industry is the flexural bond strength test, as it is regarded as the best in determining strength. For this test, the measure of flexural strength is done in a three point test or four point test. For both tests, failure occurs when the load applied increased to its maximum (152).

3. MATERIALS AND METHODS

This study was accomplished in Yeditepe University Faculty of Dentistry, Department of Prosthodontics, to evaluate the shear bond strength of CAD/CAM fabricated monolithic zirconia ceramic materials with 3 different types of primer/cement systems at different storage conditions. To determine the sample size for the present study, the power analysis was performed using the G* power program, and it was determined that the minimum number for each group should be 12 (power: 0.80 and α : 0.05, effect size d: 0.542, SD: 3.7). The total number of samples was 72.

3.1. Materials Used

Monolithic zirconia material (Starcream®Z-Nature A2, H.C.Starck Germany) (Figure 6) was provided by the manufacture in large disk-shaped blocks. The monolithic zirconia samples were prepared in pre-sintered blocks using CAD/CAM system (CORI TEC 350i Loader, Imes-Icore, Germany) (Figure 7-12) and then sintered to the final required dimension (10 mm in diameter and 3 mm in height) in special high temperature furnace (Figure 13). The specimen dimensions were produced according to ISO standards for dental ceramics (ISO 6872, 2008) (Figure 14). Composition of the materials used in this study in the table 3.

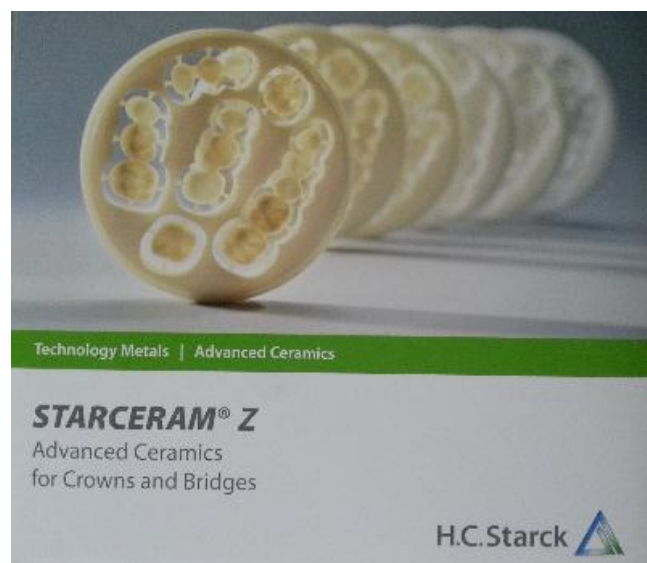


Figure 6: Zirconia block (Starcream®Z-Nature A2)

Table 3: Materials used in this study

Brand of materials	Composition	LOT Number/ Manufacturer
Zirconium Starcream®Z-Nature A2	ZrO ₂ (87-95%) Y ₂ O ₃ (4.9-5.3%) HfO ₂ (<5%) Diiron trioxide (0.1-2%)	50585968 H.C.Starck Germany
Rely X Ultimate Clicker Adhesive resin cement	Base: Methacrylate monomers/radiopaque, silanated fillers/initiators/stabilizers /rheological additives Catalyst: Methacrylate monomers /radiopaque, alkaline fillers/initiators/ rheological additives /stabilizers/pigments fluorescence dye /dark cure activator for Scotchbond Universal adhesive	644702 3M ESEP Germany
Single bond universal adhesive	MDP/ Dimethacrylate resins/ HEMA/ Vitrebond™ Copolymer/filler/ Ethanol/ water/ initiators/ silane.	609973 3M ESEP Germany
Panavia SA cement plus	Past A: MDP/ Bis-GMA/ TEGDMA / Hydrophobic aromatic dimethacrylate/ HEMA/ Silanated barium glass filler/silanated colloidal silica/ dl- camphorquinone /peroxide/ catalysts /pigments. Paste B: Hydrophobic aromatic dimethacrylate/ hydrophobic aliphatic dimethacrylate// Silanated barium glass filler/ surface treated sodium fluoride/ Accelerators/ Pigments.	850023 Kuraray-Noritake Dental Inc Okayama, Japan
Clearfil Ceramic Prime plus	3-Methacryloxypropyl trimethoxysilane/ MDP/ Ethanol.	1V0001 Kuraray Noritake Dental Inc. Okayama, Japan
Duo-Link Composite luting cement	Base: Bis-GMA /TEGDMA/UDMA/glass filler Catalyst: Bis-GMA/TEGDMA/glass fillers	1700000706 Bisco, Inc USA
Z-Prime Plus	MDP/carboxylic acid monomer/biphenyl dimethacrylate/ethanol	1600007579 Bisco, Inc USA



Figure 7: CAD/CAM system (CORI TEC 350i Loader, imes-icore, Germany)

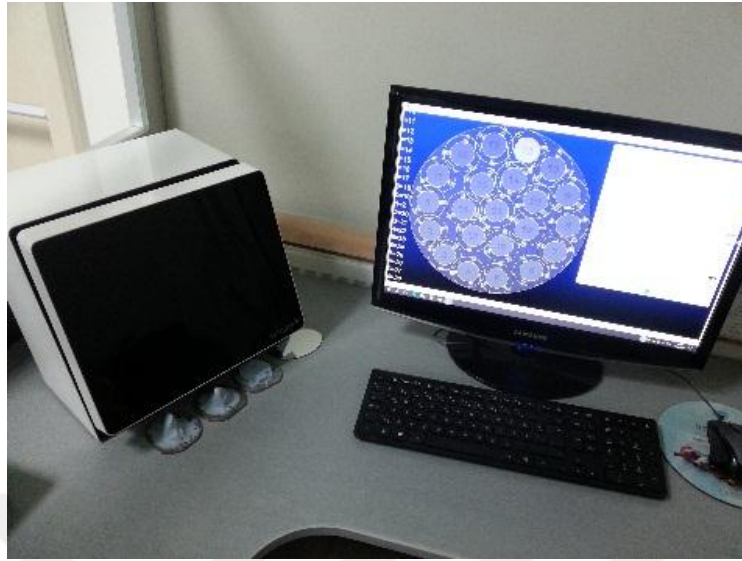


Figure 8: Computer Aided Design (CAD) models of zirconia disks

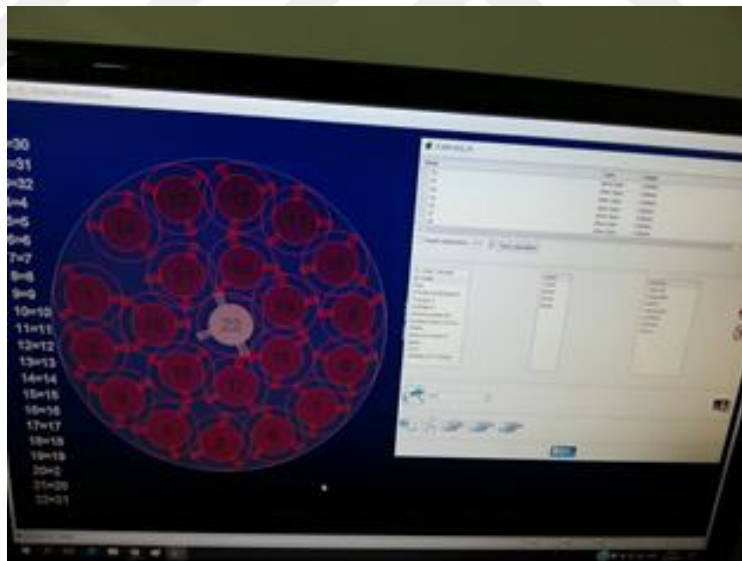


Figure 9: Computer Aided Design (CAD) definitive zirconia disks

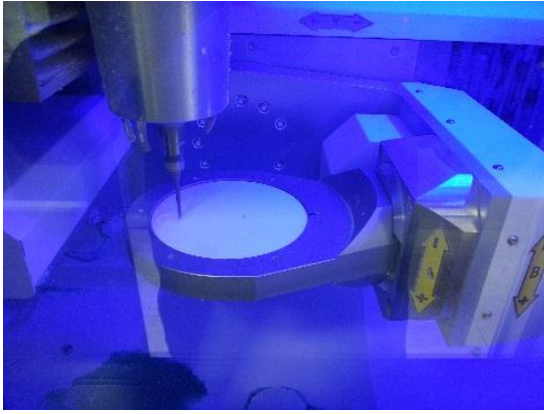


Figure 10: CAM milling machine



Figure 11: Milling of zirconia disks from presintered zirconium block



Figure 12: Pre-sintering zirconia disks with larger size



Figure 13: Furnace for zirconia sintering ZIRKONZAHN Keramikofen 1500

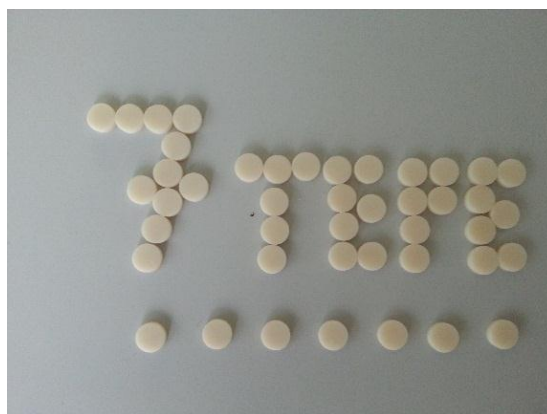


Figure 14: Sintering zirconia disks with desired size (10mm X 3mm)

3.2. Methods

3.2.1. Preparation of Experimental Specimens

In this study, 72 monolithic zirconia discs with 10 mm of diameter and 3 mm of length (10mm x 3mm) were used. The bonding surface of monolithic zirconia specimens were polished consecutively with 320, 600, 800 and 1200 grit silicon carbide papers (English Abrasive, London, England) (Figure 15) under water-cooling on a polishing machine (Phoenix Beta Grinder/ Polisher, Buehler, Germany) (Figure 16-17) to achieve standardized surface roughness. The surface roughness of each sample was measured by a surface profilometer (Pethometer M1, Mahr, Germany) (Figure 18). Three measurements for each specimen were recorded at different locations and in different directions. The roughness value (Ra) of each specimen was calculated as the average of the three measurements. The average roughness value was between 0.106 and 0.146 and any sample deviated from that average was polished again by silicon carbide papers. Then, airborne particle abrasion (sandblasting) was applied on the bonding surface with 120 μm aluminum oxide (Al_2O_3) particles size for 15 seconds at 3.5 bar pressure and at 10 mm distance from the surface (Renfert, Basic master, Germany) (Figure 19-20). Finally, the disk specimens were ultrasonically cleaned in distilled water for 3 minutes.



Figure 15: Silicon carbide paper



Figure 16: Polishing of zirconia bonding surface



Figure 17: Polishing machine (Phoenix Beta Grinder/ Polisher)



Figure 18: Perthometer MI device for surface roughness measurement



Figure 19: Airblasting with Al_2O_3 (Renfert, Basic master)

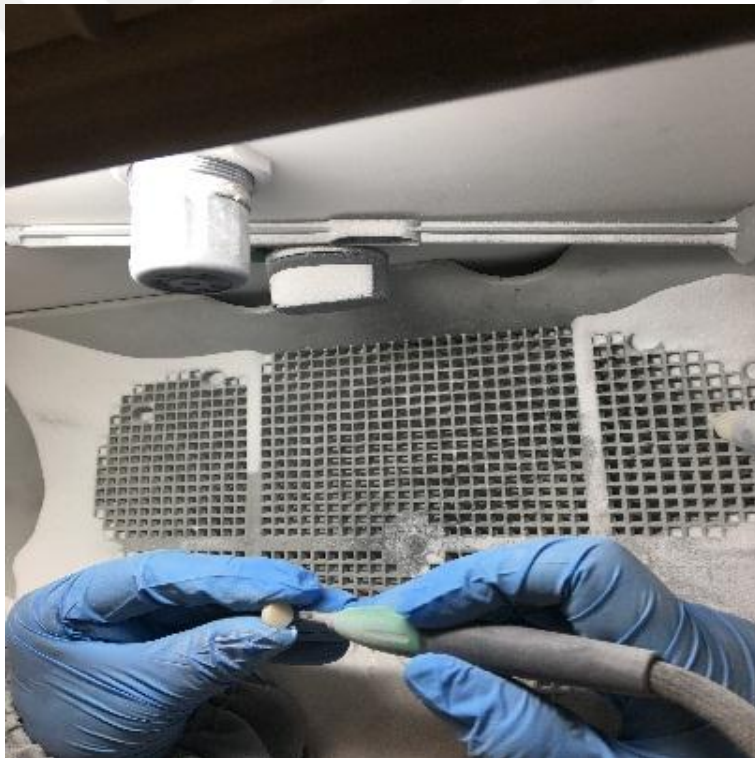


Figure 20: 10 mm distance from the surface

3.2.2. Cementation Procedure

Monolithic zirconia disks (Starcream®Z-Nature A2, H.C.Starck Germany) were divided into 3 main groups according to the type of primer/ resin cement system (n=24); in group 1 : Z prime plus/ Due-Link; (Bisco Inc. USA) was used, in group 2 : Clearfil ceramic primer plus/ Panavia SA; (Kurary, Noritak Dental Inc, Okayama, Japan) was used and in group 3: Single bond universal adhesive/ Rely X Ultimate; (3M ESEP Germany) was used. After that, the monolithic zirconia disks were placed in a translucent mold; primer and cement were prepared according to the manufacturers' instructions:

In group 1; (Z prime plus/ Duo-Link, Bisco Inc. USA) (Figure 21, 22), 2 coats of Z prime plus were applied with applicator brush, uniformly wetting the prepared surface of monolithic zirconia and dried with an air syringe for 3 seconds. Then an auto mix Duo-Link cement was injected on the bonding surface and light cured for polymerization for 30 seconds (Figure 23). The samples were removed from the mold and light cured once again for 10 seconds with a halogen photo polymerization device (Kerr Optilux 501) (Figure 24).



Figure 21: Z prime plus, Bisco



Figure 22: Duo-Link, Bisco

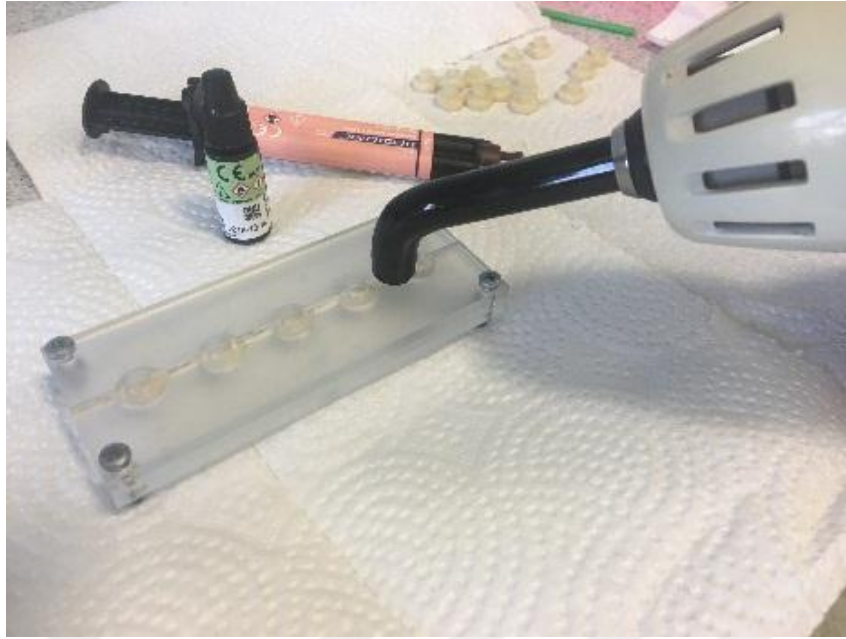


Figure 23: Light cure polymerization of the cement



Figure 24: Kerr Optilux 501

In group 2; (Clearfil ceramic primer plus/ Panavia SA; Kurary Noritak Dental Inc, Okayama, Japan) (Figure 25) 2 coats of the Clearfil ceramic primer plus were applied to the bonding surface of monolithic zirconia with small applicator brush and dried the entire adherend surface using air syringe for 3 seconds. Then, an auto mix paste of cement was injected on the entire adherend surface of monolithic zirconia disks and light cured for 10 seconds (Figure 26, 27). The samples were removed from the mold and light cured once again out the mold for 10 seconds with a halogen photo polymerization device (Kerr Optilux 501) (Figure 24).



Figure 25: Clearfil ceramic primer Plus; kuraray



Figure 26: Panavia SA; Kurary



Figure 27: Light cure polymerization of the cement

In group 3; (Single bond universal adhesive/ Rely X Ultimate; 3M ESEP Germany) (Figure 28, 29), 2 coats of Single bond universal adhesive were applied with disposable applicator brush to the entire surface of monolithic zirconia to be luted and allowed it to react for 20 seconds (Figure 30). Dried the surface by using air syringe (for evaporated water free solvent) for 3 seconds. Then the Rely X Ultimate in equal amount from base paste and catalyst past were mixed into homogenous paste within 20 seconds (Figure 31) was used spatula. The cement paste was applied on the primer then light cured with a halogen photo polymerization for 30 seconds and for 10 seconds when the samples removed from the mold (Kerr Optilux 501) (Figure 24).



Figure 28: Single bond universal adhesive; 3M



Figure 29: Rely X Ultimate; 3M



Figure 30: Primer applied by applicator brush



Figure 31: Mixing the base and catalyst pasts

The bonding procedure was done by one operator and the same mold during the experimental (Figure 32).



Figure 32: Translucent plastic split mold

3.2.3. The Aging Level Procedure

Each group was divided further into 2 subgroups (A1 /B1, A2 /B2, A3/B3) (n=12) according to the different storage condition: long term and short term storage. In the subgroups A1, A2 and A3, the samples were stored in distilled water for 24 hours at 37c° (Figure 33). In the subgroups B1, B2 and B3, the samples were subjected to thermalcycling (Salibrus Technica, turkey); 5000 cycles, between 5 c° and 55 c°, with a dwell time of 15 seconds at each temperature, and a transfer time from one bath to the others of 10 seconds. 5000 cycles equal to six months of clinical function. (Figure 34).



Figure 33: Three subgroups stored in distilled water

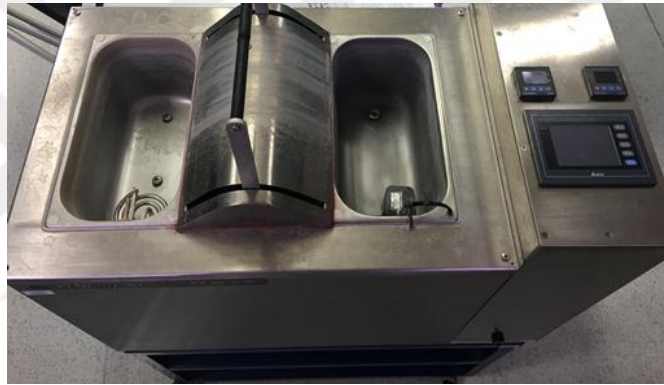


Figure 34: Thermocycling machine

3.2.4. Shear Bond Strength Testing

All samples were embedded in chemical cured acrylic resin with metal blocks (Figure 35). The shear bond strength test was performed using a Universal testing machine (Model 3345, Instron Corp., Norwood, MA, USA) (Figure 36). Shear bond testing of all samples were achieved at cross head speed of 1mm/min. A knife-edge blade equipment was employed parallel to shearing force as near as possible to the interface between the monolithic zirconia and the resin cement.

The forces during failure were registered in Newton (N), then the forces were changed into MPa, using the following formula:

$$\text{Shear stress (MPa)} = \text{Load (N)} / \text{Area (mm}^2\text{)}$$

$$\text{Where Area} = (\pi \times d^2) / 4$$

Where d = exact diameter of the bonding surface

As for the mean failure load and standard deviation for each group, they were calculated from these data.



Figure 35: Samples embedded in a chemical acrylic resin



Figure 36: Samples fixed in the universal testing machine

3.2.5. Failure Analysis

Stereomicroscope (Model 73446, Carl Zeiss Surgical GmbH, Oberkochen, Germany) at 12x magnification was used to assess mode of failure, which was classified as (1) adhesive failure when fracture between monolithic zirconia and composite resin cement; resin-free monolithic zirconia surface, (2) cohesive failure when the fracture within the composite resin cement or (3) mixed when the surface exhibiting monolithic zirconia and remnants of composite cement (adhesive and cohesive phases).

3.2.6. Statistical Evaluations

During the assessment of the data obtained in the study, IBM SPSS 22 (IBM SPSS, Turkey) program was used for statistical analysis. During the assessment of the study data, conformity of the parameters to the normal distribution was assessed by the Kolmogorov–Smirnov test and it was determined that the parameters were conformed to the normal distribution. Two-way ANOVA and One-way ANOVA test was used for the intergroup comparisons of parameters with normal distribution and Tukey`s HDS test was used for the determination of the group causing difference. Student t test was used for the intergroup comparisons of parameters with normal distribution. Significance was evaluated at a level of $p<0.05$.

4. RESULTS

The mean shear bond strength values of each group are presented in Table 4.

Table 4: The mean shear bond strength values (MPa) of the groups

Cement type	Short term	Thermocycle
	Mean±SD	Mean±SD
Bisco	7.43±1.06	5.32±0.54
3M	11.91±0.84	8.89±1.05
Kuraray	16.47±1.5	12.52±1.34

The Two-way ANOVA test indicated that there was a statistically significant difference between the mean shear bond strength values of the 3 groups of resin cements (p: 0.000; p<0.05). There was also a statistically significant difference between the mean shear bond strength values of the 2 different aging groups (p: 0.000; p<0.05). The cement types occurred to interact with the storage types with regard to the bond strength in the experiment (p: 0.020; p<0.05) (Table 5).

Table 5: Evaluation of the effect of cement type and storage levels on shear bond strength

Source	Type III Sum of Squares	Df	Mean Square	F	P
Corrected Model	965.8199	5	193.164	159.411	0.000*
Intercept	7824.906	1	7824.906	6457.587	0.000*
Cement	790.9206	2	395.4603	326.358	0.000*
Storage level	164.7994	1	164.7994	136.003	0.000*
Cement * storage level	10.09981	2	5.049905	4.167	0.020*

Two way ANOVA Test * p<0.05

According to One-way ANOVA test, at both storage levels, there was a statistically significant difference between the shear bond strength values of the cements ($p: 0.000$; $p<0.05$) (Table 6). As a result of post hoc evaluation to determine which cement type caused the difference; the shear bond strength of Kuraray cement (Clearfil ceramic primer plus/ Panavia SA) was found to be significantly higher than Bisco cement (Z prime plus/ Duo-Link) and 3M cement (Single bond universal adhesive/ Rely X Ultimate) ($p<0.05$). The mean shear bond strength of 3M cement group (Single bond universal adhesive/ Rely X Ultimate) was found to be significantly higher than Bisco cement (Z prime plus/ Duo-Link) (Table 7) (Figure 37).

Table 6: Evaluation of bond strength (MPa) according to various types of cements in different storage conditions

	Short term	Thermocycle
	Mean±SD	Mean±SD
Bisco	7.43±1.06	5.32±0.54
3M	11.91±0.84	8.89±1.05
Kuraray	16.47±1.5	12.52±1.34
P	0.000*	0.000*

One way ANOVA Test * $p<0.05$

Table 7: Post hoc evaluation

	Short term	Thermocycle
	P	P
Bisco-3M	0.000*	0.000*
Bisco-Kuraray	0.000*	0.000*
3M-Kuraray	0.000*	0.000*

Tukey`s HSD Test * $p<0.05$

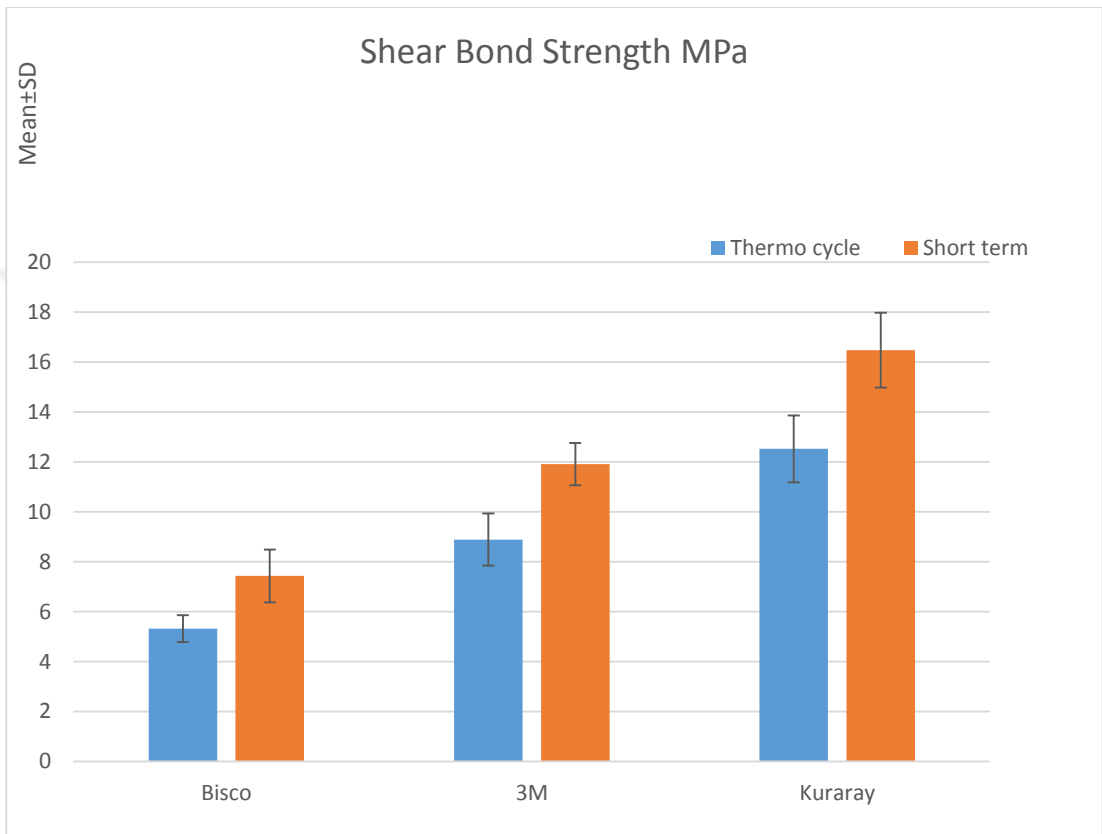


Figure 37: Bar-chart for the different types of cements in both storage levels

According to Student t-Test in Table 8, the comparison between the values of shear bond strength of the different types of cements in short-term and thermocycle indicated that the mean shear bond strength value of Bisco cement (Z prime plus/ Duo-Link) in short-term storage was statistically higher than thermocycle (p: 0.000; p<0.05). The mean shear bond strength value of 3M cement (Single bond universal adhesive/ Rely X Ultimate) in short-term storage was statistically higher than thermocycle (p: 0.000; p<0.05). The mean shear bond strength of Kuraray cement (Clearfil ceramic primer plus/ Panavia SA) in short-term storage was statistically higher than thermocycle (p: 0.000; p<0.05).

Table 8: Comparison between the values of bond strength (MPa) of the different types of cements in short-term and thermocycle

	Short term	Thermo cycle	P
	Mean±SD	Mean±SD	
Bisco	7.43±1.06	5.32±054	0.000*
3M	11.91±0.84	8.89±1.05	0.000*
Kuraray	16.47±1.5	12.52±1.34	0.000*
Student t Test	* p<0.05		

According to the Table 9; percentage of the mode of failure were 49% adhesive, 6% cohesive and 45% mixed. Bisco cement at short term demonstrated 83% adhesive and 17% mixed failure with monolithic zirconia. Whereas, 58% adhesive and 42% mixed failure were found for both 3M and Kuraray cements at short term. After thermocycling, Bisco cement demonstrated 67% adhesive and 33% mixed failure. An average of 17% adhesive, 8% cohesive and 75% mixed failure were found for 3M cement. Kuraray cement demonstrated 8% adhesive, 25% cohesive and 67% mixed failure.

Table 9: Mode of failure of groups for each specimen

Groups	Adhesive failure	Cohesive failure	Mixed failure
Bisco (24hr)	10 (83%)	0	2 (17%)
3M (24hr)	7 (58%)	0	5 (42%)
Kuraray (24hr)	7 (58%)	0	5 (42%)
Bisco (5000 TC)	8 (67%)	0	4 (33%)
3M (5000 TC)	2 (17%)	1 (8%)	9 (75%)
Kuraray (5000TC)	1 (8%)	3 (25%)	8 (67%)
Total	35 (49%)	4 (6%)	33 (45%)

5. DISCUSSION

Recently, high demand for metal-free, highly esthetic and biocompatible dental restorations with high flexural strength has increased. Many types of all-ceramic restorations have been developed in the recent years (141). Yttria-stabilized tetragonal zirconia was introduced for dental use as a core material for all-ceramic restorations (9). Zirconia was compared to other all-ceramics systems and the results showed that zirconia has the highest resistance to fracture (141).

Clinical failure of the zirconia restorations, regardless of which type of zirconia veneering system was applied, is mostly related to chipping or fracture of the ceramic veneer (109). The causes of failure are the differences in the coefficient thermal expansion (CTE) between the zirconia core and the veneering ceramic, rapid cooling rates, improper framework design, low flexural strength and low fracture toughness of veneering ceramic compared to the zirconia infrastructure (109, 152). There are other factors which may play role in this failure such as the thickness of the porcelain, the amount of occlusal force and the location and size of occlusal contacts (153).

Various techniques have been introduced to overcome the chipping problem. Some of these are press on technique via pressing ceramic veneer over to zirconia copings or double veneering technique by layering apply of ceramic veneer on zirconia copings (109), CAD/CAM produced veneer, modification of the framework design and modification of the firing procedures (5).

Recently, full-contour zirconia restoration called a monolithic zirconia restoration system to overcome veneering failure was introduced (141). Monolithic zirconia has polycrystalline structure and lack of silica in its composition. This is why acid etching and silanization are not efficient. Therefore, to achieve acceptable bonding between resin cement and monolithic zirconia, alternative methods are required which is a considerable challenge for the researchers (134). Chemical adhesion created by resin cements is the most accountable factor for bonding to zirconia, which making it necessary to choose the appropriate cement type (128).

Many manufactures produce different types of adhesive systems which have different compositions and the monomer types. For this reason, it is difficult for clinicians to select the best type of adhesive systems according to the clinical situations (9). Furthermore, there are multiple articles that evaluated the bond strength values to the zirconia substructures, on the other hand, there are very limited investigations which has been published to evaluate the effect of surface treatment on bond strength of the resin cements to the monolithic zirconia restorations (141). According to author's knowledge, there is no any study focused on the effect of various resin cements and adhesive system types on the shear bond strength of monolithic zirconia restoration, especially in the long term aging condition. Therefore, the aim of this study was to evaluate the shear bond strength of monolithic zirconia with three different types of primers and cements from different companies (3M, Kuraray and Bisco) in different storage conditions such as long term and short term storage.

Resin cement has been demonstrated to be the best choice for zirconia ceramic restorations (69). According to Palacio et al. (154), it was found that the shear bond strengths of the composite resin cements were different, depending on the cement types (between 5.1 MPa and 6 MPa). Derand and Derand (155) demonstrated that shear bond strength for zirconia ceramic restoration and resin composite cement was 8.9 MPa. Self-adhesive composite cements may not have sufficient mechanical strength when used both on the surface of zirconia ceramic and tooth without any surface pretreatment (156). For this reason, it was advised that primers should be applied before the cements, because it plays a useful role to improve adhesion between the zirconia and self-adhesive cements (157).

Conventional resin cements could not improve the bonding to zirconia ceramics, because they do not have functional monomers like 10-methacryloyloxydecyl dihydrogen phosphate monomer (10-MDP) or other types of acidic monomers in their composition which achieve a chemical bond to metal oxides ceramics (158).

The mechanism of bonding of 10-MDP to the zirconia has not been completely clarified yet. Two bonding models have been suggested as the mechanisms models of interaction of zirconia with 10-MDP monomer. First model is that 10-MDP monomer may be absorbed on the surface of zirconia by hydrogen bonding that occurs between

P=O (oxo group) and Zr-OH group. The second model is that 10-MDP monomer may interact with zirconia surface through ionic bonding. There are studies indicated that primers and cements containing 10-MDP and bonded with zirconia produced comparatively high and durable bond strength (158, 159). Yoshida et al. (158), found higher shear bond strength values before and after subjected to thermocycling for zirconia ceramics treated with 10-MDP. In a similar study, Kim et al. (160) reported that bonding to the zirconia was improved when 10-MDP containing primer was applied. They estimated that this primer eliminated hydrophilic components like water and subsequently improved bond strength of resin-modified glass ionomer and composite resin cements to zirconia.

MDP is comparatively hydrophobic monomer because it has 10-Carbon chain and contains two terminal ends; one is a hydrophilic phosphate which chemically adheres to the surface of zirconia and the other is polymerizable methacrylate which adheres to the resin cement (161). There are many commercial ceramic primer systems which are prepared to be used with zirconia ceramic restorations. They differ in the type and concentration of phosphate ester monomers, time of application, clinical mechanism for use and proprietary formulas (157). The self-adhesive resin cements that contain phosphate monomer are assured to be more effective in adhering to non-glass based polycrystalline ceramics (161).

According to previous studies, they were demonstrated that surface treatment with MDP-containing primer reinforced both the initial bond strength and thermal fatigue resistance of the bond. (134, 162, 163). Oyagüe et al. (164) demonstrated that MDP-containing adhesive system was recommended to the zirconia bonding and pretreatments of the zirconia surface were not necessary.

Many in vitro studies showed that airborne-particle abrasion (APA) with alumina particles (Al_2O_3) is the most preferred type of surface treatment for zirconia to achieve durable bond, because it is a simple, practical and effective method (123,160, 165,166,167) Yang et al. (168) found that APA is the most efficient method of surface cleaning after contamination with saliva when compared to phosphoric acid treatment, washing by water or isopropanol. Subasi and Inan (169) studied the influence of different methods of surface treatment on the surface roughness of zirconia and they found that all

types of surface conditioning methods increased the surface roughness values when compared with untreated zirconia surfaces. Also, they demonstrated that the airborne abrasion was the most effective treatment. Sandblasting is used to form irregularities and roughening the surface of zirconia for established micromechanical interlock with the resin cement and to increase the surface area and wettability to flaw the resin cement to the surface (9). Airborne-particle abrasion with alumina have various parameters that required to be taken into the consideration for more effective particles. The first parameter is the size of particle. There are different size of alumina grain, ranging between 25 to 250 μm . The second is pressure starts from 0.05 to 0.45 MPa (2 to 4 bar). The third is the distance between the nozzle and the sample that ranged from 5 to 20 mm. The fourth parameter is the application time of alumina particles ranged from 5 to 30 seconds. The fifth parameter is the angle of particles on the sample surface mostly 45° or 90° (141, 170).

Treatment of zirconia surface by sandblasting to make the micromechanical interlock can be done by larger or smaller size of particles and was not significantly different between the both sizes. According to Moon et al. (141), it was reported that airborne-particle abrasion provided a powerful process to increase the bond strength of the composite cement and flexural strength of the zirconia. It was also explained by Kosmac et al. (171) that, there are two competing factors effecting the strength of surface-treated zirconia ceramics. The first is residual surface compressive stresses that provide strengthening of the zirconia and the other factor is the possible to create faults and microcracks that cause strength degradation. For this reason, the effect of the sandblasting is controversial. Compressive stresses are formed due to the phase transformation from tetragonal to monoclinic phase that increase the flexural strength of the zirconia by resisting spread of crack. The main feature of the zirconia is the fracture toughness and that determines by the amount of tetragonal which is able to transform to monoclinic under compressive stress and mostly that transformation was depended on the size of alumina abrasive size (172).

The amount of created monoclinic phase varied according to the four parameters of APA, which increased with larger particle size, longer time, higher pressure and larger incidence angel (141, 173, 174). Furthermore, until now, no literature review could be found describing exactly the protocols of air borne particles abrasive for phase

transformation of monolithic zirconia (141). Kirmali et al. (4) demonstrated that Er, Cr: YSGG laser irradiation and airborne-particles abrasion with size 120 μm appeared effective process for surface treatment of zirconia. Petrauskas et al. (175) found that when zirconia ceramic surface was abraded, cement accomplished the best result. They used alumina particles with larger size (120 μm) and under low pressure to achieve a higher mechanical roughness and bonding. For these reasons, in the current study, 120 μm alumina particles size under 3.5 bar pressure for 15 sec at about 90° was used.

Sandblasting procedure mostly leaves residues on the surface of ceramic, therefore in a lot of studies, ultrasonic cleaning of sandblasted surfaces has been achieved to clean the surface before to bonding (7, 144, 167, 170). In the current study, ultrasonic cleaning in distilled water for 3 minutes was used.

Many studies reported that a strong durable bond between resin cement and zirconium oxide ceramic is achieved by the formation of chemical bonds and micromechanical interlocking (7, 9, 126, 141, 165). Commonly used process for bonding is the combination of airborne particle abrasion with alumina and application of ceramic primer containing adhesive monomer (7). Kitayma et al. (176) demonstrated that bond strength of zirconia increased when primer agent was applied with sandblasting, and they explained the rewetting effect of primer on sandblasted zirconia. Sandblasting with resin cement increased the bond strength to zirconia ceramic compared to untreated and polished zirconia surfaces (165). Meta-analyses of bonding to zirconia concluded that the use of chemical and mechanical surface treatment increased the bond strength of the resin cements to zirconia ceramic (162, 166). Additionally the researchers recognized the following five factors that affect the quality of the bond between the composite cements and zirconia: (1) mechanical pretreatment of the zirconia surface, (2) chemical pretreatment of the zirconia surface, (3) the cement type, (4) artificial aging condition, and (5) type of test methodology (177).

Chemical pretreatment of zirconia surface by apply primer is a good option because of its easy to use and give positive results after air-borne particle abrasion (APA). The present of adhesive monomer in the primers which improving the bond strength between the zirconia and resin cements (180). Now a day, primers are available for different substrate (ceramics, metals, hard tissue). Primer with coupling agent and MDP for zirconia were mixed in difference proportions and found improving the bond of resin

cement not containing phosphate monomer. MDP is an acidic monomer that react with zirconia surfaces which cover with a passive oxide layer. This react makes zirconia ceramic similar to metal. That is why, primer contain MDP used for increasing the bond strength between resin cement and zirconia (9). Furthermore, use of zirconia primers helps wetting of the surface by reducing the contact angle (158). Blatz et al. (125) demonstrated that the shear bond strength (SBS) of the zirconia surfaces that were pretreat with ceramic primer and used self-adhesive cement after subjected to 180 days of water storage and 12000 thermocycling had higher SBS was 16.85 MPa than that without treated surface was 9.45 MPa.

Resin cements with dual cure activation are the most suggested for cementation of zirconia than the other types of cements which are photoactivated or chemically activated due to the opacity of the zirconia, which disturbs the transmission of halogen light (128). As for the evaluating self- adhesive cement that contains acidic monomers based on the phosphate groups, which result showed higher bond strength and durable adhesion to zirconia ceramic than other resin cements (133). Among MDP resin cements, inorganic compounds have important role in producing resistance to hydrolysis. The potential of adhesive to zirconia may be determined by other factors like the viscosity and fillers size of the resin cement (181).

Several researchers have tried to perform aging condition for the composite cement to resemble the situation of bonding new cement to old cement in the oral environment. Some solutions were studies as storage media for bond strength tests like distilled water, 0.05% saturated solution of thymol, saline, 10% formalin solutions and 2% gluteraldehyde (180). The most common method of storage for testing specimens is water for intervals at different time reach to three months. The storage may be at room temperature or at temperature close to oral cavity. Other common media used for aging of the specimens are artificial saliva and sodium hypochlorite. Aging have not any impact on the tensile bond strength of composite cement to dentin, whereas aging for six months in water that lead to decreased shear bond strength (181). In this study the distilled water was selected as storage media before shear bond test.

Thermal cycling has been applied as a storage method to simulate clinical conditions (182). Mair et al. (183) reported that temperature of the oral cavity when eating

ice cream changes between -4°C - 0°C and when eating a hot cheese sandwich ranged between 60°C - 65°C . Dental materials are subjected to different types of stress in the oral cavity like thermal, chemical and mechanical stresses. Both water storage and thermocycling are employed as a common technique for testing of materials in in vitro studies to show their suitability for in vivo situation. Testing the specimens by thermocycling accelerate the diffusion of water through changing the temperature that make stress at the interface of two materials that related to the different of thermal expansion of the two materials (184). Additionally, increase the time of water storage and the cycles number that permit for more precise evaluation of how these factors influence bond strength. Many aging conditions such as storage in saliva, PH cycling, bacterial environments and food-like solutions would produce it possible to better induce mouth conditions (182).

Thermocycling significantly decreased the shear bond strengths of dentin. Miyazaki et al. (185) reported reduce in the mean bond strength of enamel after thermocycling, whereas bond strengths of dentin significantly reduced after 30,000 thermal cycles.

A short thermal cycling regimen of 500 cycles is commended by the ISO TR 11450 standard 2003 (186). In this study, 5000 thermal cycling was used and according to Yap et al. (187), it was reported that 5000 cycles were equal to six months of clinical function. Harper et al. (188) showed that a dwell time of 15 seconds or more than that was unsuitable because patients cannot resist the direct contact for long time of vital teeth with hot or cold substance (189). For this reason, in the current study the duration of water bath was set at 15 seconds.

The mechanical cycling is other type of aging. The amount of force exerted while chewing and swallowing ranged between 70-150 N and the more common stress occurs in the mouth is cyclic compression. The majority of in vitro studies used monotonic experiments like shear, compression, tensile or flexural strength to test the properties of the materials (181). These tests cannot induce cumulative damage (fatigue) that exists in the oral cavity. For this reason, the studies that require fatigue tests are recommended for preferable clinical relevance (183). Celik et al. (190) compared the different types of aging methods as thermocycling, water storage and mechanical fatigue. They found that

thermocycling as aging procedure appeared to be the best method of aging for testing the bond quality. Among all aging techniques which were applied in their study, the remarkable decrease in bond strength was found after thermocycling. For this reason, thermocycling as aging process was selected for this study to observe the influence of the aging on the bonding.

Longevity and durability of the indirect restoration is mostly depended on the ability of adhesive systems and that can be measured by different types of bond strength testes. Bond strength tests can be static or dynamic tests. Shear bond strength (SBS) test is fulfilled in static state that essentially based on the size of the bond area which classified into macro-tests which the bond area is exceed 3mm^2 or micro- tests in which the bond area is lesser than 3 mm^2 (181). The test used in this study was macro shear bond test because the size of bonded area was 5 mm^2 . The value of the bond strength is calculated by dividing the maximum of the force of applied by the cross- sectional area of bonded. In SBS test, shear load was applied between two materials which connected together by adhesive agent, until fracture occurs. Della Bona and Van Noort (191) stated that the most commonly used testing method is the macro-shear bond strength test, because no additional specimen treatment is required for fully sintered zirconia after the bonding process is completed. Beside that due its simplicity, a quick and easy application procedure and minimal equipment requirements, that makes it popular (192). Authors demonstrate that the SBS test is mentioned for ceramic materials (193). Therefore, this test method is used in this study.

Few studies demonstrated the effect of the area on "macro-bond" strengths. Sano et al. (194) found that the bonding areas for rectangular specimens are changed between $0.25\text{-}11.65\text{ mm}^2$. When the bonding area increased, tensile bond strength to dentin decreased, following a logarithmic function. A similar way was observed in shear bond strength where least surface areas had significantly higher values when contrasted with those of larger areas (195).

All of the studies which performed bonding tests with composite materials clearly indicated that the thickness of the composite cement ranged from 2 to 5 mm (182, 196-198). The crosshead speed of shear bond strength testing machine is 0.5 or 1.0 mm/min

being the most common values (46% and 41% respectively) (197). In the present study, the crosshead speed was 1.0 mm and cement height was 3 mm.

As revealed by Two way ANOVA test, the null hypothesis that there should be no difference in the shear bond strength of the composite cements to monolithic zirconia between different storage conditions and no difference between the various types of primer/cement systems could be rejected. The data from the present study revealed significant differences between the SBS values of three adhesive systems that related to the difference in the composition and percentage of functional monomer of the primer/cement systems used. In this study, the highest bond strength in the both storage levels were recorded for Panavia SA / Clearfil prime plus, and the lowest bond strength in the both storage levels were recorded for Duo-link/Z-prime plus. This result may be attributed to the present of MDP monomer in both Panavia SA cement and Clearfil prime plus. It was claimed that MDP monomer had ability to develop strong bond with metallic oxide in the zirconia ceramic surface (159). Rely X Ultimate cement has methacrylate monomers that establishes primary bond with methacrylate resin in the primer and by the way improve the bond (199). This may be explanation why the Rely X Ultimate cement has the best result than Duo-link cement which conventional Bis-GMA resin cement. Three primers that used in the current study have MDP monomer. The exact percentage of the active monomers were not available from manufacturers` data sheets. Although, the Z-prime has two monomers; orghanophosphate and carboxylic monomers, which make it compatible with numerous resin cements and had a good effect on bonding with resin cements after sandblasting (179). However, in this study, Z-prime had the lowest bond strength values. Also, single bond universal adhesive has another monomer (Vitrebond copolymer) which provided more consistent bond under different moisture levels (163). That may be why it had better results than Z-prime in the current study.

According to a systematic review and meta-analysis by Özcan and Bernasconi (166), it was demonstrated from the data evaluation for the veneered zirconia that, 10 MPa was estimated the common denominator for the SBSs values. They found the data extracted of MDP-based cements were exceeded this value while self-adhesive cements were not above this values. This result is in agreement with the current study. According to results of this study in which the monolithic zirconia and Panavia SA cement /Clearfil prime plus were used, the shear bond strength values were exceeded that value (10 MPa)

in the both aging conditions (16.47 ± 1.5 MPa and 12.52 ± 1.34 MPa). On the other hand, Rely X Ultimate/Single bond universal adhesive exceeded this value (10 MPa) in the 24h storage (11.91 ± 0.84 MPa) but could not after thermocycling (8.89 ± 1.05 MPa). The shear bond strength values of Duo-link/Z-prime plus were lower than this value in both storage levels (7.43 ± 1.06 MPa and 5.32 ± 0.54 MPa). The different of the shear bond strength of the available data may be due to the different of the type of cements, chemical compositions and the percentage of MDP monomers of adhesive systems were used.

Wenger et al. (144) tested the shear bond strength of 5 types of cements, before and after long term storage (2 years) and subjected to thermocycling at 37500 cycles. Furthermore, they evaluated the effect of different surface treatment as air-borne abrasion (APA) with alumina particles at size $50 \mu\text{m}$ then applied silanization. They concluded that Bis-GMA based cements had short term stability, pretreatment of the surface improved only the initial bond strength and after that their effect were decreased with the time. They found that only Panavia F2.1 cement with phosphatic monomer had high bond strength values and durability after thermocycling in combination with sandblasting (127). This finding show similarity with the current study, in which the Panavia SA cement had the best result. Because its contain MDP monomer that has ability to bond chemically with the zirconia. Additionally, MDP-containing primer has crosslinking branches (polymerization groups), that react with the Bis-GMA and HEMA of composite resin matrix and achieves strong bonds when the composite resin polymerizes (165). Some authors have explained that resin composite cements which contain bis-GMA work mainly through micromechanical interlocking (130, 200). Furthermore, the self-adhesive phosphate monomer Panavia SA has a terminal end hydroxyl group which provides hydrolytic stability of the resin under acidic conditions and water (201). This could be an explanation for the highest shear bond strength for Panavia SA in the current study.

According to several studies demonstrated that the bond strength increased when the primer and resin cement are used together (130, 162, 163, 165). Clearfil prime plus has 3-Methacryloxypropyl trimethoxysilane, MDP and ethanol. Blatz et al. (125) reported that usage of silane coupling agent/ MDP-containing bonding is played the key factor for durability and reliability of the composite resin bond to sandblasted Procera AllZirkon and not affected by the composite resin cement type. This may be an explanation of the best result for the Clearfil prime plus in the current study.

There was some controversy studies in regarding to the effect of ability of MDP-containing adhesive systems to keep a stable bond pre and post aging in water and thermocycling of sandblasted zirconia surface (201, 202). Li Zhao et al. (163) evaluated the shear bond strength of veneered zirconia blocks with three different types of adhesive systems (1- Scotchbond Universal/ Rely X Ultimate, 2- Clearfil ceramic primer/ Panavia F, and 3- Z-Prime Plus/ Duo-Link). They divided the groups into two; in the first group, the cements were applied without primers and in the second group, they used primers before cements. Thereafter, they subjected the samples to different artificial aging (24h, 30 Day, 30 Day /3000TC). They concluded that all the groups with the primers had higher SBSs compared without primers. Between primer/cement groups, the highest bond strength was obtained with Scotchbond Universal/ Rely X Ultimate (24h was 11.72 MPa; 30Day /300TC was 2.66 MPa). The bond strength values of Clearfil ceramic primer/ Panavia F was (24h was 5.73 MPa; 30Day/300TC was 2.29 MPa). Z-Prime Plus/ Duo-Link had lowest shear bond strength (24h was 5.63 MPa; 30D/300TC was 1.62 MPa). They explained the results due to the present of unique Vitrebond copolymer, furthermore, MDP monomer that found also in the other primer were used (Clearfil ceramic primer and Z-Prime Plus). This copolymer is a methacrylate-modified polyalkenoic acid that has a moisture-stabilizing effectiveness. They also demonstrated that the present of MDP-containing cement did not show positive effect on long- period bond strength to zirconia. When compared with the results of this study, the current study showed that the clearfil ceramic prime plus/ Panavia SA cement plus had higher SBSs in both storage levels (24h was 16.47 MPa; 5000TC was 12.52 MPa). But results of both studies are in agreement with Z-Prime Plus/ Duo-Link had lowest shear bond strength. As a general, all the SBSs values of the three adhesive systems that used in this study were extremely higher than Li Zhao et al. result's, especially after subjected to the thermocycling. The difference may be due to the difference of composition between veneered zirconia and monolithic zirconia. Veneered zirconia has more hardness and less translucency than monolithic zirconia. Also, the difference of results may be due to other causes such as difference of size of specimens, processing technique and storage conditions of specimen (179).

Talal Alnassar et al. (165) studied and compared the influence of different types of ceramic primers on the shear bond strength of RMGIC to the veneered zirconia with and without air-borne alumina particles (APA) and then thermocycling for 10,000 cycles.

They concluded that regardless of the primer used, APA had significant effect on the shear bond strength of RMGIC to zirconia. The highest shear bond strength with APA after subjected to thermocycling was Clearfil ceramic primer (11.9 ± 0.6 MPa) and Z-prime was (11.1 ± 0.6 MPa). When compared with the current study showed that Z-prime had lower value of the SBS although the adhesive system subjected to less cycles (5000 cycles). The SBS of Clearfil primer plus with Panavia SA was (12.52 ± 1.34 MPa) and the SBS of Z-prime plus with Duo-Link cement was (5.32 ± 0.54 MPa) after subjected to thermocycle (5000 cycles). The difference in the results may be due to the difference of the composition of the cement types and its viscosity. Low viscosity resin cements can exhibit easily of flow into the micro-porosity of abraded zirconia surface that achieving a larger adhesive surface (201). Also may be related to the difference of zirconia materials, size of specimens, processing technique and storage conditions of specimen (179).

In this study, regardless to the types of the primer/cement systems used, the shear bond strength values were significantly decreased after subjected to 5000 thermocycles. That was related to the plasticity of the resin cements with moisture absorption effect, which lead to the increased coefficient of thermal expansion and decreased glass transition temperature. These consequences mostly develop during use of slow thermal gradients that shear in the hydrolytic effect of water within the resin-zirconia interface, in addition to degradation of the composite resin cement itself. In the thermocycling, when using the slowly change of temperature, compared to a sharp change of temperature may promote more effective of the aging process (163).

Analysis of mode of failure is important to explain bond strength results. In the present experiment, low bond strength values were mostly associated with the adhesive failures. This finding was recorded by other researchers (201, 203). That may be explained by the adhesive failure predominated in Duo-link/Z-prime plus. Cohesive failure observed within self-adhesive resin cements; Clearfil primer/ Panavia SA and Rely X Ultimate/Single bond universal adhesive; after thermocycling test. This type of failure concur with high bond strength values achieved, which related to chemical affinity between zirconia and acidic monomer of self-adhesive cements (201). Three adhesive system resulted in the mixed failure pattern (adhesive/ cohesive) and predominated in

Clearfil ceramic primer/ Panavia SA. Mixed failure were translated as intermediate bond strength values (201).

There are some limitations of this study. This study was performed in laboratory environment without contaminated specimens and oral moisture condition that can affect the clinical application. The bond strength of the resin cement is sensitive to mechanical and chemical influences in intraoral cavity. Another limitation is that only one brand of monolithic zirconia and only airborne partial abrasion surface treatment were used, and only the thermocycling effect was studied. In this study, the shear bond strength test which has disadvantage of inhomogeneous stress distribution was used (9). The medium used to perform the storage was distilled water, no saliva was used. In future studies, other types of monolithic zirconia brands and /or other pretreatment methods may be compared. The results of this study require clinical verifications.

6. CONCLUSIONS

In this study, the following conclusions can be drawn;

1. There was a significant difference between the shear bond strength (SBS) of 3 groups of adhesive systems in short term 24h water storage ($p<0.05$). Bisco cement (Z prime plus/ Duo-Link) had the lowest SBS value (7.43 ± 1.06 MPa), and Kuraray cement (Clearfil ceramic primer plus/ Panavia SA) had the highest SBS value (16.47 ± 1.5 MPa). 3M cement (Single bond universal adhesive/ Rely X Ultimate) had the SBS value of 11.91 ± 0.84 MPa.
2. There was a significant difference between the SBS of 3 groups of adhesive systems in thermocycling storage ($p<0.05$). Bisco cement (Z prime plus/ Duo-Link) had the lowest SBS value (5.32 ± 0.54 MPa), and Kuraray cement (Clearfil ceramic primer plus/ Panavia SA) had the highest SBS value (12.52 ± 1.34 MPa). 3M cement (Single bond universal adhesive/ Rely X Ultimate) had the SBS value of 8.89 ± 1.05 MPa.
3. Thermocycling decreased the SBS to monolithic zirconia for all adhesive systems tested ($p<0.05$).
4. Predominant type of failure within 3 adhesive systems was adhesive failure (49%), whereas mixed failure was 45% and cohesive failure was 6%.

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8. CURRICULUM VITAE

Personal Information

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Place of Birth	Benghazi	Date of Birth	22.12.1981
Nationality	Libyan	TR ID Number	99112370798
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Education

Degree	Department	Univesity	Graduation year
Master	Prosthodontics	Yeditepe University	2018
Bachelor's Degree	Dentistry	Benghazi	2004
High school	-	Al-Sayida Ruqaya	1999

Languages
I attended many English courses and IELTS
I also attended Turkish language courses at Tömer Center- Ankara University

Work Experience

Work	Place	Duration (Year - Year)
Compulsory internship rotation work in all clinical departments	Benghazi University	2004- 2005
General Dentist	Central Dental Clinic Benghazi	2005 - 2009
Teaching assistant at department of conservative	Benghazi University	2009- 2012

Computer Skills

Program	Year
ICDL license (International Computer Driving License)	2006

Certificates

Certificates	Year
3 rd Libyan Dental Congress	2007
Use of Rotary Instruments in Endodontic	2007
Cariogram Concept Course	2009
2nd Dental Scientific Day	2012
Greatest Congress	2017