



Vicious circle in Zirconia Bonding: A Review

Dr Priyanka Somashekhar¹, Dr Kalavathy N², Dr Mitha Shetty³, Dr
Archana Sanketh⁴, Dr Anuradha V⁵, Dr Netra Patil⁶

BDS, MDS (Prosthodontics)

Name of Institution:

D.A.P.M.R.V Denatal college, bengaluru

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ABSTRACT:

The preferred material for fixed dental restorations is zirconium dioxide ceramics because of their excellent mechanical and optical properties. However, these materials have a drawback in that they do not adhere well to natural tissues or synthetic substrates. Traditional adhesive techniques used with silica-based ceramics do not work effectively with zirconia. Currently, several technologies are being utilized clinically to overcome this problem, and other approaches are under investigation. (1) Most focus on surface modification of the inert surfaces of high strength ceramics. The ability to chemically functionalize the surface of zirconia appears to be critical in achieving adhesive bonding. This article discusses the current options and newer technologies being developed to address this issue.

Key words: Zirconium dioxide ceramics; Adhesion; Bonding; Surface Modification; Surface Functionalization; Zirconia

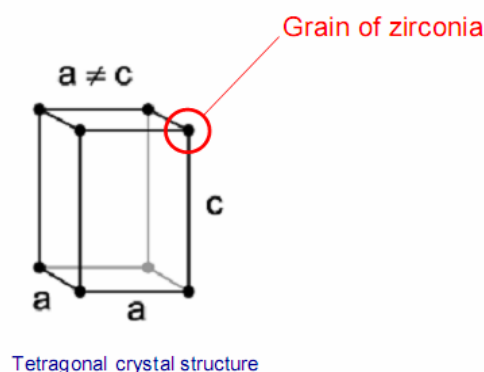
I. INTRODUCTION:

The growing belief that metal-free dentistry will alter the traditional restorative spectrum has been stymied by the brittle nature of the ceramics. Therefore, they have been developed Y-TZP commonly known as "ZIRCONIA" (2). The emergence of zirconia alongside CAD/CAM technology has allowed the field of dental science to realize its aspirations. (3) This zirconia contains 3 mol% of yttria (Y₂O₃) as a stabilizer. Compared to all other ceramic core materials, Zirconia has exceptional flexural strength (900-1000 MPa) and fracture toughness (5.5 - 7.4 MPa·m^{1/2}), resulting in a highly fracture resistant material. [1]. However, several problems arise because of its high surface stability, particularly with regard to the effectiveness and longevity of the chemical or mechanical bond with the various cementing systems. Due to zirconia's high acid

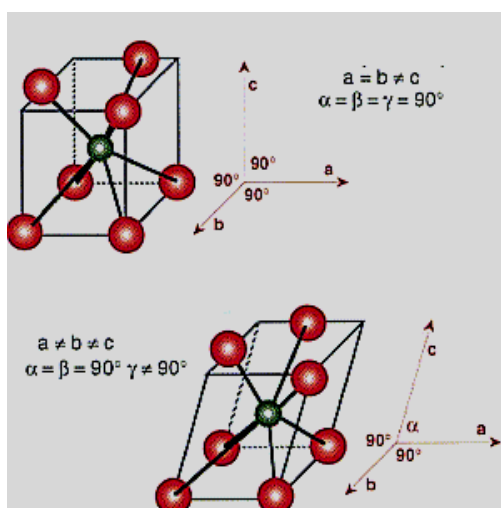
resistance and the lack of a glassy matrix on which these substances act, the common etching methods with hydrofluoric acid and silanization techniques that were previously employed for other ceramic systems have not been worked well against it [2]. Unfortunately, the composition and physical properties of ZrO₂ differ from traditional silica-based materials such as porcelain. Zirconia is not easily etched by HF and requires very aggressive mechanical abrasion methods to increase surface roughness, potentially leading to strength-reducing surface defects [3-5]. In this article we discuss: (1) Zirconia as a bioceramic material (2) Chemico-Mechanical coupling bond (3) zirconia and CAD/CAM Dentistry (4) The bond between zirconia and veneering ceramics, (5) The bonding of zirconia with resin based luting cements, (6) Enamel wear against polished and glazed zirconia restoration and (7) Evaluation of clinical efficacy on zirconia restoration.

1. Zirconia as a bioceramic material

In 1789, The German chemist Martin Heinrich Klaproth discovered zirconium oxide (ZrO₂), commonly referred to as zirconia, as a reaction produced by heating a gem called zircon [6]. The term Zirconium is coming from the Arabic Zargon 14 (golden) and the Persian terms Zar (gold) and Gun (colour). Zr is a white metal (atomic number 40) with a density of 6.51.



Zirconia is polymorphic, implying that it has a distinctive equipoise (stable) crystal structure at varying temperatures while maintaining the same chemical form. There are three crystalline forms of it: monoclinic at lower temperatures, tetragonal at 1170 °C, and cubic at 2370 °C [7,8]. After cooling, the crystal structure of the material changes from a tetragonal crystal to a monoclinic crystal. This causes a 3-4% increase in the volume of the material, which can lead to significant stresses. These stresses can lead to the formation of cracks, which in turn can lead to sagging, crumpling and failure. Ruff et al. discovered that by incorporating a small quantity of calcium, the cubic phase of ZrO_2 could be stabilized, enabling its utilization as an engineering material.



Over the years, other metal oxides like cerium oxide (CeO_2), magnesia (MgO), and yttria (Y_2O_3) have been used to create a range of partially stabilized zirconia (PSZ) compositions, which are primarily cubic phase at room

temperature, with monoclinic and tetragonal precipitates as a minor phase [7]. PSZ is of particular interest because of its transformation toughening properties [9]. When a crack begins and spreads in a partially stabilized zirconia material under external force, the tetragonal phase near the crack tip can convert into a monoclinic phase repeatedly. The subsequent volume expansion from the transformation produces a compressive stresses near the crack tip. ZrO_2 was recently introduced into dentistry for its superior aesthetic potential in comparison to metal-ceramic structures. Zirconia is being investigated as a dental material for various clinical applications, such as brackets for orthodontic treatments [10], endodontic posts and dowels [11,12], abutments [13,14], single crowns [15] and fixed partial dentures [16]. Bonding to ZrO_2 has become an increasingly common problem in recent years. As already mentioned, typical adhesive bonds on ZrO_2 surfaces are ineffective due to their non-polar and inert properties. Additionally, hydrofluoric acid etchants do not provide sufficient surface roughness for easy micromechanical adhesion. The process involves using Al_2O_3 particles to abrade the surface, then applying a tribosilica coating that allows for the formation of chemical bonds with a silane coupling agent and resin cement. This is a complicated method that does not provide bond strengths comparable with those observed for silane-bonded porcelain. [4,17,18]. There is concern that using air particle abrasion on ZrO_2 ceramics could cause microfractures, weakening them and potentially causing them to fail unexpectedly. The current methods for bonding ZrO_2 ceramics are not suitable for all medical uses, and it is unclear how long they will last.

2 Chemico-Mechanical coupling bond

A resilient bond is necessary to securely attach ZrO_2 to teeth or other surfaces. Mechanical bonding via micromechanical interlocking from surface roughening and, if feasible, chemical bonding between ceramic and cement are essential for resin bonding success. For surface roughening silica-based ceramics, phosphoric acid (H_3PO_4) or hydrofluoric acid (HF) etching are frequently suggested techniques [75]. This produces a clean, rough surface that increases surface area available for mechanical interlocking and enhances wettability. It is challenging to roughen the surface for mechanical retention on nonsilica-based ceramics, such as ZrO_2 , due to the ineffectiveness



of H_3PO_4 and HF. Because of the difficulty in creating mechanical and chemical bonding in ZrO_2 , alternative methods have been explored to bond ZrO_2 using resins. Surface grinding is a commonly used alternative for roughening the surface of ZrO_2 to improve mechanical bonding. Surface grinding can be done in a number of ways, including with a diamond bur [20], particle air-abrasion with Al_2O_3 or other abrasive particles that range in size from 50 to 250 μm [19–20], and abrasive paper or wheels (SiCor Al_2O_3). Selective infiltration etching (SIE) is a new surface roughening method that has been investigated for ZrO_2 . This uses a heat-induced maturation process to pre-stress surface grain boundaries in ZrO_2 to allow infiltration of boundaries with molten glass. The glass is then etched out using HF, creating a 3D network of inter-granular porosity that allows nano-mechanical interlocking of resin cement. The impact of treatments on the mechanical properties of ZrO_2 materials is debated, with both positive and negative results being reported [21–22]. Additionally, particle abrasion can lead to a sharp cracks and structural defects, making zirconia more prone to radial cracking during use [23].

Organo-silanes, generally referred to simply as “silanes” in dentistry, are compounds that contain a silicon (Si) atom or atoms, are similar to orthoesters in structure, and display dual reactivity. One end of a silane molecule is organically functional (e.g., vinyl-CH₂, amino-NH₂), and can polymerize with an organic matrix (e.g., a methacrylate). The other end is generally comprised of alkoxy groups (e.g., methoxy-OCH₃, ethoxy-OCH₂CH₃), which can react with a hydroxylated surface, like porcelain. Due to the lack of silica in ZrO_2 , silica-coating techniques have been explored to utilize the chemical bonding provided by silanization. Experimentation with different silane coupling agents has resulted in enhancement of luting of ZrO_2 . Matinlinna et al. [24] researched use of three trialkoxysilanes, 3-methacryloyloxypropyltrimethoxysilane (MPS), 3-acryloyloxypropyltrimethoxysilane (ACPS), and 3-isocyanatopropyltriethoxysilane (ICS), in enhancing the bonding of two resin cements, an experimental Bis-GMA and commercial Bis-GMA (RelyX ARC, 3M ESPE, Seefeld, Germany), to ZrO_2 . They determined that application of a tribochemical coating, followed by silanization with MPS and ACPS, were successful in bonding the two cements to ZrO_2 . Recent advancements in silicoating technology, spe-

cifically the Pyrosil Pen Technology (Pyrosil Pen, Sura,

Instruments, Jena, Germany), have made it easier to use in dental procedures. However, research has shown that there is no significant difference in bond strength between different types of ceramics. ZrO_2 -based ceramics have been found to have a lower bond strength compared to silicoated silica and alumina-based ceramics. This could be attributed to the fact that the ceramic surface was only ground using 800 grit grinding paper, resulting in a lack of micromechanical bonding [24].

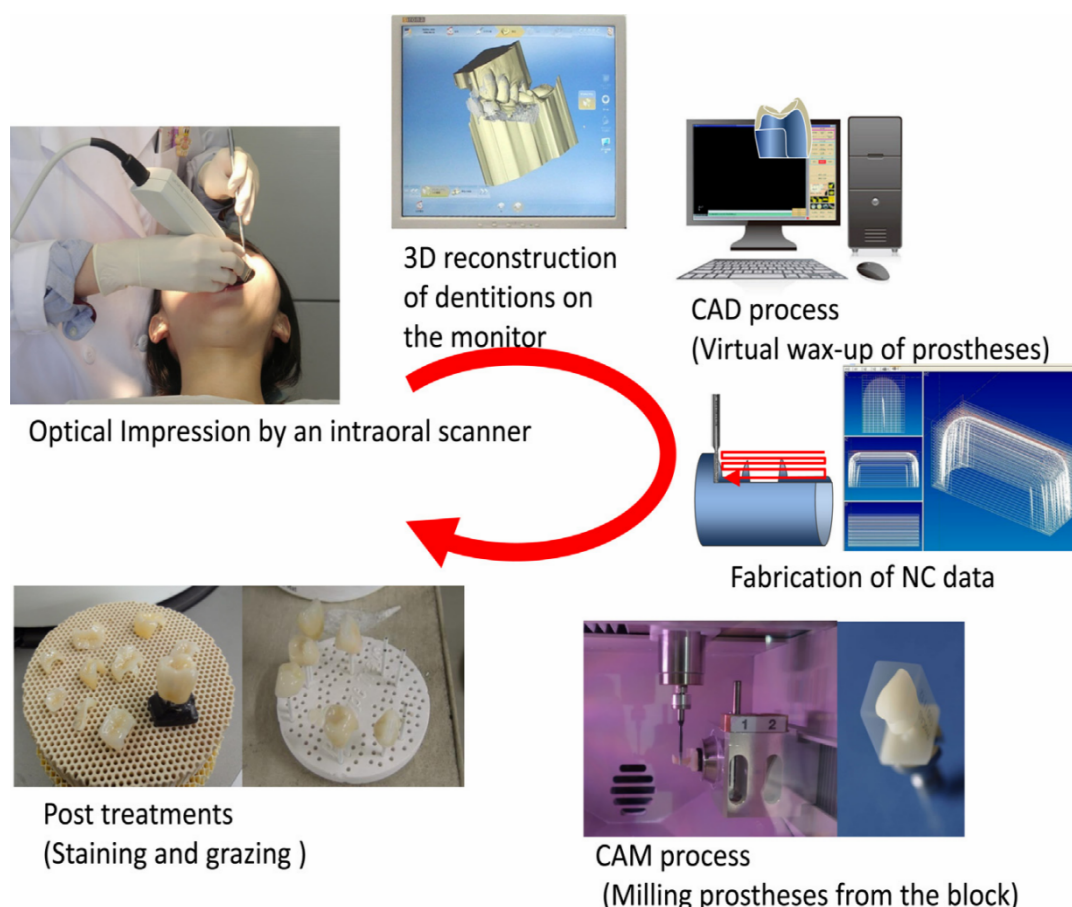
3. Zirconia and CAD/CAM Dentistry.

Zirconia-based ceramics, specifically Y-TZP, are a viable alternative to metal frameworks for dental prostheses [25,26]. Y-TZP frameworks can be made by milling a solid block using CAD/CAM

procedures through two different systems.

The first system allows for milling directly from fully sintered ceramic blocks, resulting in a better fit but with the drawback of tool wear. The second system involves milling from partially-sintered or green blocks, followed by post-sintering at high temperature to strengthen the framework. This system is currently popular for fabricating zirconia frameworks using the main CAD/CAM systems available in the world market. Although this technique has the advantage of easy machinability without tool wear and chipping of the material, the dimensions of the frameworks need to be adjusted to allow for compensating sintering shrinkage during the post-sintering process to ensure the finished frameworks fit well. The clinical evaluation found that the fit of zirconia-ceramic fixed

dental prostheses (FDPs) made with CAD/CAM systems was similar to conventional metal ceramic restorations [25]. However, for FDPs with 3-unit and 4-unit frameworks, the shrinkage of the pontic part caused a bigger difference in the fit of the crown next to the pontic. Therefore, when using partially-sintered or green blocks, we need to be careful about the distortion of zirconia-based FDPs with longer spans [26]. The procedures used to fabricate CAD-CAM FDPs are shown in Fig. 1. An intraoral digitizer scanned the intraoral abutment in order to generate an optical impression. The monitor displayed reconstructed digital data as three-dimensional visuals, and it was used to virtually build the ideal FDP morphology. A numerically controlled machine was used to grind a block in order to fabricate real FDPs.



4.The bond atzirconia / veneering ceramics

One of the specialized ways of using zirconia in dentistry is to fabricate zirconia frames upon which tooth-colored veneering ceramic is bonded. At present, there are two widely used methods of securing ceramic onto zirconia frames: the layering technique and the press technique. In the layering technique, porcelain powder is applied onto the zirconia frame before firing. In the press technique, the lost wax technique is used to create the restoration. Homogeneous ceramic ingot is heated and then forced under pressure into a wax formed void. For both the layering technique and the press technique, the coefficient of thermal expansion of the veneering ceramic is set to be the same as or slightly lower than that of zirconia. This is because a large difference in the coefficient of thermal expansion between a zirconia frame and veneering ceramic will cause residual stress on the crown, thus resulting in reduced reliability of the restoration. There are some studies comparing the layering technique with the press technique, however, many reports argue that the dislodgement or fracture of veneered ceramics is more affected

by frame design than differences in molding techniques [26-28]. The integration of metal and porcelain in PFM crowns involves both mechanical and chemical bonding. However, there is not enough evidence to prove the presence of chemical bonding between zirconia and veneering ceramics, although there is one study[29] suggesting it. Therefore, it is believed that mechanical bonding is the main factor in the integration of zirconia-based restorations. A standard (ISO9693) exists for evaluating the bond strength between metal and porcelain through a bending test, and PFM restorations used in clinical practice should have a bond strength of 25 MPa or higher.[30]. Although there have not been many reports [31–33] concerning the evaluation of zirconia-to-porcelain integration using a bending test (ISO9693), all of those reported that the bond strength was 25 MPa or more. The bonding process between zirconia and veneering ceramics in dentistry still has many unanswered questions about how it works. Further research



and the development of a dependable clinical procedure will be needed in the future.

5. Bond of zirconia with resin-based luting cements:

In order to obtain the strong bond to zirconia ceramics in clinical conditions, it is important for the bonding surface to be roughened, activated for chemical bonding and free of any contaminants. The most commonly used material to attach a ceramic prosthesis to teeth is resin-based composite cement. However, it is difficult to bond ZrO_2 (a type of ceramic) to teeth using traditional resin composite cements because it does not contain silica. Previous studies [34] have shown that a resin-based composite cement containing phosphate monomer (7) can create a strong bond with alumina, but Bis-GMA (another type of resin) cannot bond with particle air-abraded alumina. The long-term bond strength of resin-based composite cements with phosphate monomer and ZrO_2 was first reported by Kern and Wegner [35]. Methods for chemically altering the surface of zirconia using silicon compounds and then applying silane monomers have been presented. Janda et al. [36] compared bonding performance of silica, alumina, and two zirconia ceramic materials treated with a flame treatment and silane priming. Although the flame treatment was successful for all ceramic materials, the results showed that the silica and alumina ceramics had stronger bond strengths than the zirconia ceramic materials. According to reports, the use of silica coating, silane, and MDP together is currently considered one of the most dependable bonding systems for zirconia [37-40]. Tanaka et al. [40] found that a strong bond was formed on Rocatec-coated Katana zirconia when a phosphate monomer and silane were used together. This was confirmed through X-ray photoelectron spectroscopy analysis. This bonding mechanism is substantially the same mechanism as bonding to feldspathic porcelain with silane/MDP bonding agent. In a study by Nakayama et al. [41], the bonding between a zirconia material and tri-n-butylborane (TBB) initiated luting agent was evaluated using different primers. The researchers found that using either the Alloy Primer or the Estenia Opaque Primer, both of which contain MDP, resulted in strong and long-

lasting bonding between the zirconia and the TBB-initiated luting agent.

6. Enamel wear against polished and glazed zirconia restoration:

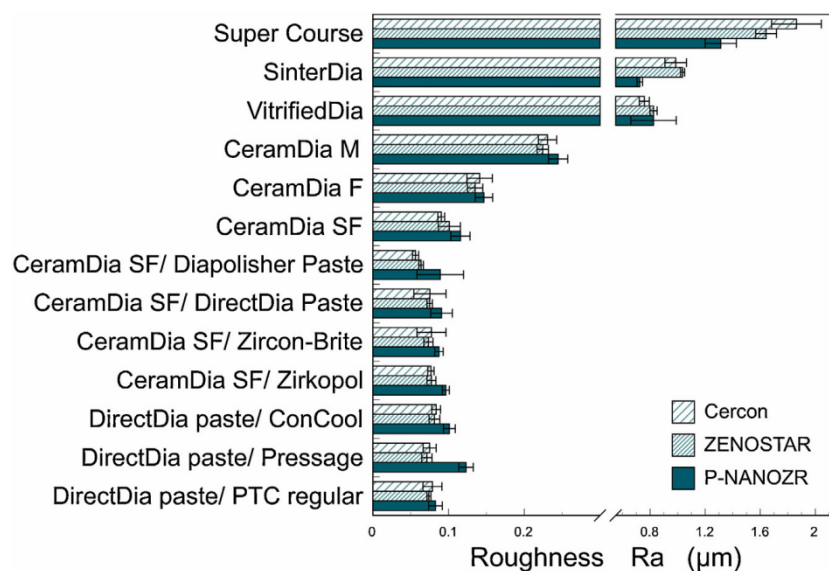
Different types of ceramics have been used in dentistry for restorative purposes. Zirconia is considered the best material in terms of strength and physical properties. However, when used for aesthetically pleasing dental restorations like crowns and bridges, zirconia is typically covered with feldspathic porcelain because it lacks sufficient translucency. Unfortunately, the porcelain veneer alone is not strong enough to serve as a dental restoration, particularly for posterior teeth. This has led to instances of clinical failure, with most cases attributed to porcelain chipping [42,43]. A new type of zirconia called high translucent zirconia has been introduced in dentistry [44,45]. It can be used for full contour restorations without the need for a covering porcelain, meaning that the zirconia surface is exposed to the mouth. The wear of opposing teeth is a significant concern. Dentists use mirror polishing to prevent wear on the enamel that opposes zirconia restorations (8). However, there is a misconception that antagonist enamel is easily worn due to its hardness (9). Additionally, it is unclear if glazing zirconia effectively prevents wear on opposing teeth. Recent studies have raised concerns about the wear of veneering porcelains on the opposing teeth. However, research has indicated that zirconia restoration with a proper surface polish causes the least amount of wear on the opposing enamel when compared to other dental materials.

These findings suggest that the wear of dental enamel caused by opposing surfaces is significantly influenced by the level of surface smoothness. **Figure 2** displays the roughness of three different types of dental zirconia after undergoing various grinding and polishing techniques [45]. Super Course, Sinter Dia, Vitrified Dia, and Ceram Dia M, F, and SF are rotary instruments used for grinding. Super Course, Sinter Dia, and Vitrified Dia exhibited high levels of roughness, exceeding 1 mm. However, Ceram Dia M, F, and SF had relatively low roughness, possibly due to the use of diamond grains fixed with artificial rubber. After grinding with Ceram Dia M, F, and SF, polishing was conducted using diamond pastes such as Diapolisher paste, Direct Dia paste, Zircon-Brite, and Zirkopol. The surface of the zirconia was made smoother by polishing, and the



type of zirconia and diamond polishing paste used did not make a difference. Different cleaning pastes like ConCool, Pressage, and PTC regular used in professional mechanical teeth cleaning (PMTC) did not affect the surface roughness when used after a specific polishing paste like Direct Dia . **Fig 3** shows the glossiness of the same specimens increased at 60 degrees as the size of the diamond grains used in grinding instruments decreased, and further increased with additional polishing. However, the cleaning pastes used in professional mechanical teeth cleaning (PMTC)(50) did not cause any significant changes. This suggests that the cleaning process does not interfere with maintaining proper oral hygiene when zirconia restoratives are used.

Fig. 4 shows the correlation between the glossiness and the surface roughness. The glossiness increased steeply with decreasing roughness to less than 0.3 mm. It suggests whether or not the final polishing is sufficient determines the final gloss of zirconia restoratives.



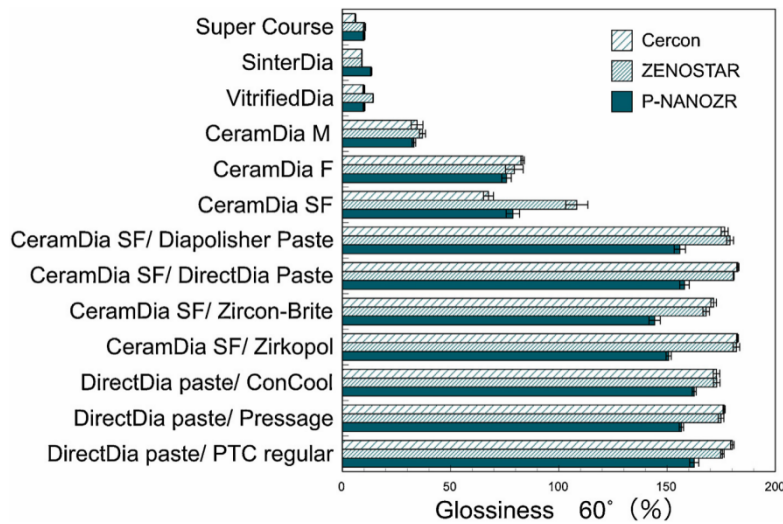


Fig 3: Glossiness of three types of dental zirconia finished with 13 types of grinding and polishing condition.

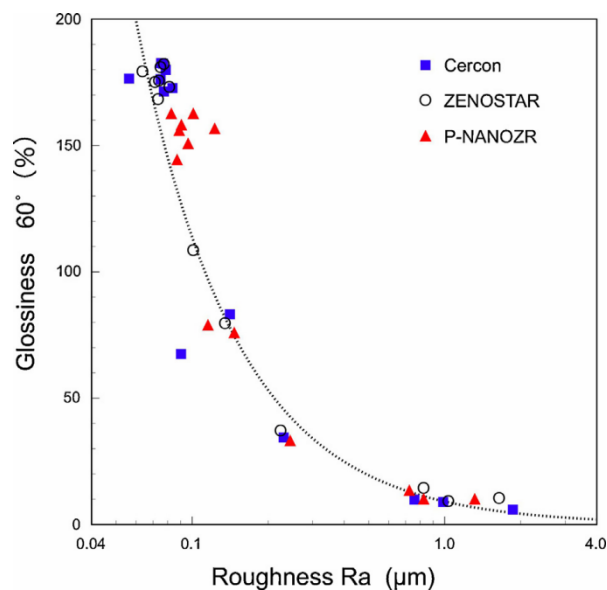


Fig. 4. Relation between surface roughness and glossiness of three types of dental zirconia finished with 13 types of grinding and polishing condition.

The amount of wear on restorative materials depends on their structure and particle size. Zirconia, which has a consistent structure, can be polished to a mirror finish with the right tools and materials. There is no need to worry about enamel wear when zirconia restorations are used. However, if the surface of the zirconia is rough, it can cause significant wear on opposing enamel. Therefore, it is important to polish the surface of zirconia restorations when making occlusal adjustments, and glazing is not recommended for finishing the surface.

7. Evaluation of clinical efficacy on zirconia restoration.

CAD/CAM-produced Y-TZP-based systems are in considerable demand in esthetic and stress-bearing regions. The highly esthetic nature of zirconia with its superior physical properties and biocompatibility makes it an effective restorative system to meet the demands of modern patients [46-48]. Currently, endowing a removable knob to the dental prosthesis apparatus has made it possible to treat temporary cementation which means temporary crowns are usually made of acrylic or composite and cemented with zinc oxide eugenol/non eugenol cements. Partially stabilized Zirconia is considered the top choice for all-



ceramic restorations due to its excellent strength and fracture resistance, as supported by numerous research studies since the late 1990s[49]. In order to benefit from the strength of the core material, the bond between the core and veneer must be strong enough to handle the functional stresses that the esthetic veneer puts on it. CAD/CAM-produced zirconia was introduced in Japan in 2005. Several clinical studies have found that porcelain veneers on posterior zirconia-based ceramic restorations often chip or fracture at a higher rate.

II. CONCLUSION:

Y-TZP, a type of dental material, has strong mechanical properties and is resistant to fractures, but it lacks translucency. To address this, porcelain is often layered onto the Y-TZP framework. Recent advancements in scanning, CAD software, networked machining centers, and other dental CAD/CAM technologies have made it easier to fabricate Y-TZP frameworks with a good fit. This has made zirconia-based fixed partial dentures (FPDs) more promising. However, dentists and dental technicians still need to collaborate and follow proper clinical procedures, even with the help of CAD/CAM technology. Longer clinical evaluations are necessary to further prove the effectiveness of zirconia-based FPDs, especially with new options available.

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