Assessment of Different Surface Treatments Effect on Surface Roughness of Zirconia and Its Shear Bond Strength to Human Dentin

Manal R. Abu-Eittah

Lecturer, Fixed Prosthodontics Department, Faculty of Dentistry, Minia University, Minia, Egypt.
manalrafei@yahoo.com

Abstract: Aim of the study: The aim of this study was to assess the different surface treatments effect of yttrium oxide partially stabilized tetragonal zirconia polycrystal (Y-TZP) dental ceramic on its surface roughness and shear bond strength to dentin. Surface topography of zirconia was studied with atomic force microscopy AFM. **Materials and Methods**: A Total of 35 discs of zirconia dental ceramic of 5mm diameter and 2mm thickness were used in this study and divided into 5 groups according to surface treatments as follows: gp1-C: no treatment, gp2-G :grinding with 600 grit diamond disc,gp3- SB : samples were sandblasted with 50 µm Al_2O_3 particles,gp4-SC : samples were treated with modified tribochemical protocol, and gp5-AE : samples were immersed in experimental hot etching solution of Hcl and ferric chloride for 15 minutes. The surface roughness R_a of all samples groups was measured by a prolifimetre. The surface topography was inspected by atomic force microscopy AFM. Freshly extracted molars were collected. Their crowns were sectioned using a diamond disc to obtain occlusal deep dentin flat surfaces. The roots of the teeth were invested within acrylic resin blocks. The zirconia samples were cemented to the dentin surface by RelyX™ Unicem aplicap™, light-cured according to manufacturer instructions. The blocks were stored for 21 days in distilled water at room temperature. All specimens were subjected to 5000 thermo-cycles between 5 and 55C^o, and thereafter, subjected to shear bond strength test (1 mm/min). Data of surface roughness and shear bond strength were statistically analyzed. **Results**: 1- No significant difference in surface roughness R_a of groups 1,and 2, while the highest recorded R_a values were in groups 5,$p<0.05$. 2- Shear bond strength of gp-5 (acid etching) was the significantly highest recorded value (24.3MPa±3.2) while there was no significant difference between groups 1, and2 with the least recorded bond strength $p<0.05$. 3- Modified tribochemical procedure improved shear bond strength (13.4±4.5), $p<0.05$. **Conclusions**:1- Although it needed much time to be performed, yet, proposed modified tribochemical technique is valid method in increasing Y-ZTP /dentin bond strength and recommended to be applied rather than conventional tribochemical method.. 2- The use of hot etching solution of Hcl and ferric chloride $FeCl_3$ is recommended as an effective and simple method which could be performed easily in labs to modify surface of zirconia chemically and mechanically, so that, enhance bonding to dentin surface even after water storage and thermo-cycling.3-Self adhesive cement RelyX Unicem, produced a comparable results to resin cement with the advantages of reduced time and sensitive steps of conventional bonding procedure.

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Keywords: Zirconia, self adhesive cement, surface roughness, shear bond strength

1. Introduction

The increased popularity of all-ceramic materials as an alternative to metal ceramic restorations is attributed to their excellent aesthetics, chemical stability, and biocompatibility.

New high-performance non-etchable ceramics, such as alumina and zirconia, are becoming common in indirect restorations [(1)]**.** The use of zirconia-based ceramics for dental restorations has gained popularity due to their superior fracture strength and toughness compared to other dental ceramic systems [(2)]**.** Zirconia is polymorphic in nature that displays a different stable crystal structure at different temperatures with no change in chemistry. It exists in three crystalline forms: monoclinic at low temperatures, tetragonal above 1170°C and cubic above 2370°C [(3,4)]. Researchers found that zirconia alloying with lower valance oxides such as CaO (calcia), MgO (magnesia), Y_2O_3(ytrria), or CeO (ceria) can retain tetragonal or cubic phases in the room temperature depending on the amount of these oxides.However, the tetragonal form is in fact 'metastable' at the room temperature [(5)]

Zirconia materials differ from other high strength dental ceramics because of their distinct mechanism of stress-induced transformation toughening, which means that the material undergoes micro structural changes, volume increase 3-4%, when submitted to stress [(6)] while most ceramics are very brittle and cannot withstand more than a 0.1% change in volume.

The addition of 8 mol % MgO to ZrO_2 results in the creation of a stable matrix of cubic phase grains, with a metastable phase of tetragonal crystals that precipitate during cooling. In the Y_2O_3 - ZrO_2 system, the addition of 2–3 mol % Y_2O_3 to ZrO_2 produces a meta-stable matrix of tetragonal crystals referred to as yttria stabilized tetragonal zirconia polycrystals (Y-TZP) [7,8].Y-TZP ceramics can actively resist crack propagation through transformation from a tetragonal to a monoclinic phase at the tip of a crack, which is accompanied by a volume increase[6].The mechanical properties of Y-TZP materials, such as flexural and fracture resistance, are considerably higher than those of other dental ceramics. The flexural strength of Y-TZP ceramics can reach values from 700 to 1200 MPa[9,10] .These values exceed the maximal occlusal loads during normal chewing[9].It has a fracture toughness of 9–10 MPa/mm2, which is almost twice the value obtained for alumina-based materials and almost three times the value demonstrated by lithium disilicate-based ceramics [11]**.** Zirconia or "Ceramic steel" has been used extensively in fabrication of extra-coronal restorations especially, crowns, abutments and retainers for implant supported fixed partial denture in esthetic zone, and long span fixed partial dentures [12]. Y-TZP materials might also exhibit fracture resistance higher than 2,000 N, which is almost twice the value obtained for alumina-based materials and at least three times the value demonstrated by lithium disilicate-based ceramics[13]**.**

One of the inherent weakness points of Zirconia is the lack of durable and adequate bond with tooth structure, as the material is chemically inert.

Different luting strategies (i.e. conventional cements, glassionomer cements, self-adhesive cements) have been proposed for luting zirconia frameworks in the attempt to ensure retentive ,and well adapted restorations [13,14]

Previous investigations have been focused on different chemo-mechanical surface treatments in order to optimize the cement/zirconia bonding mechanism. The rationale of these conditioning processes relies on increasing the surface area available for bonding and establishing stronger and durable restorations [15, 16].

It is important for high retention, prevention of microleakage, and increased fracture/fatigue resistance, that bonding techniques be optimized. Strong resin bonding relies on micromechanical interlocking and adhesive chemical bonding to the ceramic surface, which requires surface roughening for mechanical bonding and surface activation for chemical adhesion. Bonding to traditional silica-based ceramics, generally employing both mechanical and adhesive retention, has been well researched, and cement bond strengths are predictable. Unfortunately, the composition and physical properties of ZrO_2 differ from conventional silica-based materials like porcelain. Zirconia is not readily etched by HF, and requires very aggressive mechanical abrasion methods to be used to increase surface roughness [17-19]**.**Therefore, in order to achieve acceptable cementation in a wide range of clinical applications, alternate surface modification methods, ideally utilizing chemical adhesion in addition to mechanical retention, are required for zirconia ceramics.

Several studies were performed to investigate the mechanical properties of zirconia-reinforced ceramics as well as the techniques to enhance the bond strength of luting cement to the ceramic surface [20, 25]. It was reported that conventional acid etching had no positive effect on the resin bond to zirconia-reinforced ceramics**. Derand and Derand(2000)**[26] proved that an autopolymerizing resin cement exhibited the highest bond strength regardless of the surface treatment (silica coating, airborne particle abrasion, HF etching or grinding with diamond rotary instruments), The same results were previously reported by **Kern and Wegner(1998)**[27] who achieved a durable bond to zirconia-reinforced ceramic only by using resin composites containing phosphate monomers (MDP). The use of phosphoric acid primers or phosphate-modified resin cements has been shown to produce silane-like adhesion, through a similar type of hydroxylation-driven chemistry. However, a controversial results also have been reported, as recorded bond strength values in the literature through the use of these agents are generally lower than the values reported for tribochemical silica coating, coupled with silane and resin cement[23]

It was also reported that the infilteration of fused glass micro-pearls to the surface of ZrO2 has been shown to increase the bond strength of resin cements to ZrO2 In these studies, a slurry of micro-pearls was painted on a ZrO2 surface and fired in a furnace. The fused glass film increased surface roughness of ZrO2, allowing increased micro-retention. The silica-rich film also allows for silanization of ZrO2 before bonding, making it possible to form siloxane bonds to resin cement. The results showed that use of this fused micro-pearl film significantly increased the bond strength of ZrO2 (11.3–18.4 MPa) [24,25] . Clinicians are still confused regarding the most effective way to treat the fitting surface of indirect ceramic restoration before placement with various adhesives and luting cements. The best method to promote a durable bond between the ceramic and tooth structure is still unknown.

Scanning electron microscope, SEM, was used routinely to study the topography of any surface treatments on polymers, alloys, ceramics or any related materials. Because ceramics are insulating substrates, a conductive material, mostly by gold sputtering, must be coated on ceramic surface in order to examine the surface structure by SEM which may to some extent modify the surface topography and misleading the observer. In the last few years the atomic force microscope AFM was used to study the surfaces of insulating materials with no conductive coating materials. This mathematical tool can provide a new way to account for the complexity of the topographical pattern of the treated material surface, which can in turn depend on the surface treatment conditions. In fact, it is generally accepted that the measures of roughness from the distribution of heights (z) alone without any information on their spatial localization on the (x, y) plane is insufficient to completely describe the surface roughness [(21)]. The technique of AFM enables featuring and highlights the edges, steepness, sharpness, depressions, elevations or pores and all of the surface properties in microns and on the nano scale.

The success to chemically activate and functionalize the surface of zirconia appears to be mandatory in enhancing adhesive bonding to the substrate or the tooth structure. It is of great importance to study the effect of some proposed surface treatments on the surface topography of zirconia re-inforced ceramics and correlate with the bonding strength to tooth structure.

Therefore, the aim of this study was to evaluate the effect of some surface treatments on the surface roughness of zirconia reinforced ceramic in addition, the shear bond strength of zirconia Y-TZP discs to the dentin of freshly extracted teeth was studied. The surface topography of zirconia after surface modification was studied with AFM.

2-Materials and Methods:

Composition of Zirconia:

To standardize the shape and size of the samples, a split stainless steel mould with five shaped disc spaces was fabricated. The parts of the mould were fixed together with the help of two stainless steel pines at each terminal of the mould. Each disc has a diameter of 5mm and thickness of 2mm.

Zirkon- Zahn, the material studied, is a core veneered all ceramic system Hot isostatic pressed (HIP) blanks in which ZrO_2 is the main component 90%, 5-5.5% Y_2O_3 and tracesof Al_2O_3, SiO_2 Fe_2O_3, and Na_2O(less than 2%) were used. The core substructure is manually milled from partially sintered Zirconia blanks following the shape and dimension of a resin mock-up frame

This study was conducted on the core material only. Core samples were constructed as follows:

2-1Construction of resin mock-up frame*:*

A thin layer of Vaseline (Unilever Dept ER, UK) was applied to the inner surface of the stainless steel mould. The special resin (Zirkonzahn World Wide - An der Ahr 7 - 39030 Gais/South Tirol (Italy**)** supplied by the manufacturer was packed in the mould forming disc with the specified dimensions.

The formed resin disc was placed on the frame template disc and its outline was marked. Two connection points were also marked joining the mock-up disc to the external frame template. A tungsten bur was used to cut out and separate the outlined drawn disc. The mock-up resin disc frame was placed instead and fixed in position using Attak Flex Gel (Zirkonzahn World Wide - An der Ahr 7 - 39030 Gais/South Tirol (Italy).

Milling process*:* The template was then inserted in the milling table and locked. In the other compartment a Zirconia blank of suitable size was selected and placed. The manual milling process was started and the discs were milled following the dimensions and shape of the resin mock-up disc. Part of the connection base was left intact to hold the disc during later sintering.

2-2 Sintering Process:

Samples were dried under the infrared drying lamp; Zirkonlampe 250(Zirkonzahn World Wide - An der Ahr 7 - 39030 Gais/South Tirol (Italy). The discs were carried to the Zirkonzahn furnace for 8 hours to complete the sintering process following the manufacturer's instructions.

35 samples used in this study were milled following the same procedures and instructions, which were given as mentioned previously from the manufacturer.

2-3 Samples grouping n=7, and surface treatments:

Group1-C(control) : samples were left as sintered without any modification of its surface texture.

Group2-G: samples were ground with 600 grit diamond disc (Fuji star, Japan) under water coolant then, ultra- sonically cleaned in distilled water, left to dry in air.

Group3-SB: samples were Sandblast with 50 µm aluminum trioxide (Remfert, Germany).Particles were blasted with pressure of 2.8 bar for 10 sec. from a distance of 10 mm in a circular movement. Samples were then ultrasonically cleaned with distilled water, left to dry. Then samples were coated by97.7 % 3-methacryloxy-propyltrimethoxysilane (Alfa Aesar, Johnson Matthey Company, U.S.A), left for 5 minutes to polymerize in air.

Group 4-SC : A modified laboratory tribochemical silica coating, was performed as follow: Airborne particle abrasion with 110 µm aluminum trioxide Al_2O_3 particles for 15 seconds followed by immersion in a saturated emulsion of Aluminum sulfate and Urea for one hour. The samples were introduced into a ceramic furnace (Jelrus v.i.b.300,USA) and heated to 95-98C^{o} for one hour for the purpose of beginning of calcinations (removal of water and beginning of ¥ alumina formation) . Although maturation is completed between 300-600C^{o}, this temperature was not applicable in this study to prevent the adverse effect of tetragonal phase transformation at high temperature. Fortunately, seeding of Al_2O_3 began at nearly 60C^{o}. In addition ,the proposed steps were believed to improve homogenization of alumina particles and increase attachment, binding of the particles together with the zirconia substrate [(28)], this step was followed by cleaning of the samples in ultrasonic water path to remove all of the loose Al_2O_3 particles. The following steps were blasting the surface with high purity aluminum trioxide particles,30 µm modified by silica (SiO_2) with blasting pressure of 2.8 bars for 15 seconds. Samples were then immersed in saturated solution of silicon oxide, prepared from solution of tetraethyl - orthosilicate in ethanol and ammonium hydroxide. Addition of predetermined drops Hcl to adjust the pH at 7[(29)] Samples were Introduced again into the furnace and heated to 100C^{o} for 15minutes, this step was done to enhance maturation and fixation of the silica layer to the under lying ceramic substrate [(30)] Samples were then, coated with 97.7 % 3-methacryloxy-propyltrimethoxysilane (MPS),(Alfa Aesar, Johnson Matthey Company, U.S.A), left for 5 minutes to polymerize in air.

The entire coated surface loses its smoothness gloss, due to silica deposition on the ceramic surface.

Group 5-AE: samples were immersed in the following laboratory prepared solution: 800ml ethanol, 200ml 37% conc. Hydrochloric acid Hcl, and 2g of ferric chloride $FeCl_3$.all of the chemical reagents are driven from BDH. chemically analar (high purity). The solution was heated in a Pyrex beaker till100 C^{o} and the beaker was then immersed in other larger beaker full with distilled water previously heated to boiling temperature 100 C^{o}.A thermostat was used to adjust the corresponding temperature. The zirconia samples were immersed for 15 minutes with continuous shaking with multi-wrist shaker,(Lab. Line instruments, Inc. USA), any drop in temperature was compensated with addition of boiled water to the external beaker. At the end of the predetermined time, the samples were removed from the etchant solution and washed under running water and dried with oil free air syringe and left in a desiccator, (Duran laboratory glassware, Germany).

2-4 Surface roughness measurements (Ra µm):

Randomly selected samples from each group were chosen to surface roughness study. The sample was attached by a special holder on the stainless steel table then the profilometer stylus (Surftest.SJ-201, Mitutoyo corp., and Kawasaki, Japan) scanned the whole sample surface longitudinally and horizontally, recording 10 readings in each axis. The final recorded figure is the mean of these 10 readings.

2-5 Atomic force microscopy topography study:

A nanoscope Auto-prope CP-Research,Thermo-microscobe AP-0100,Borregas Avenue Sunnyvale, California USA, of tapping mode was used to scan the surface of the samples, scanning speed was 1 Hz.The 3D photos was displayed on a computer screen with a soft ware,proscan1.8 and resolution of 256x 265 line and soft ware for image processing IP2.1. The surface roughness of the scanned area of each specimen has been evaluated as the root mean square (RMS) value, R_q,of the distribution of heights in the AFM topographical images was calculated in an area of 20x20 µm and for an area of 4x4 µm, according to the general surface roughness as viewed with the microscope before starting the scan i.e. if the surface characterized with high or sharp tops, the stylus propping the surface will not be able to move freely to record the whole depth and full heights of the surface, so the scanned area has to be reduced according to manufacturer instructions.

2-6: Teeth preparation:

Freshly extracted posterior second molars were used in this study. The teeth were stored in glycerin and ethanol until use (not more than one weak to preserve the tooth structure elasticity, and not to affect the bonding). The occlusal surface of the teeth was cut immediately before cementation with sharp diamond disc under copious water irrigation. The resultant cut tooth surface ensures exposure of the deep dentin surface. Flattening of the resultant dentin surface is performed carefully with size 4 diamond disc. Before cutting the occlusal surface of the teeth, they were invested from the root side into self cure acrylic resin blocks.

2-7 Cementation of zirconia discs to the tooth structure:

Rely X Unicem, 3M ESPE St. Paul, USA, self adhesive cement (Aplicap capsules) was used in this study. Immediately prior to bonding procedures, occlusal surface of samples underwent 600-grit silicon-carbide disc cutting to create fresh smear layer. The samples were cemented to the dentin as follows : equal volume of base and catalyze pastes were mixed on a paper pad, for 10 s, application of the cement by a suitable instrument which was spreaded on the ceramic sample and the dentin surface as well,the sample was fixed on the tooth with gentle finger pressure for 20 seconds,removal of excess cement with suitable instrument then, curing with light emitting diode LED(Ortholux ^{TM} LED 3M, Unitec, USA)of intensity of up to 1000mw/cm^2 for 40 s(groups 1, 2).For gps. 3,and 4and 5, application of silane(97.7% 3-methacryloxy-propyltrimethoxysilane (Alfa Aesar, Johnson Matthey Company, U.S.A) on the ceramic samples and left to air dry for 5 minutes, prior to application of adhesive cement according to manufacturer instructions.

2-8 Aging of samples:

The samples of each group were stored in a distilled water at room temperature for 21 days then subjected to thermo-cycling(at 5-55C for 5000cycles,(Porto-Tech;version2.1A,Portland,Ore) according to (ISO Standard 10477).[(31)]

2-9 Shear bond strength:

The bond strengths of the samples after thermo-cycling were assessed by shear bond strength testing. Specimens were mounted in a jig of the computer controlled universal testing machine (Lloyd LRX; Lloyd Instruments, Fareham, UK) and shear force was applied by a mono-beveled chisel at a crosshead speed of 1.0mm/min, at the adhesive interface until failure occurred. The load was recorded in Newton then divided by the interfacial area of bonding (radius of the disc) to express the bond strength in MPa.

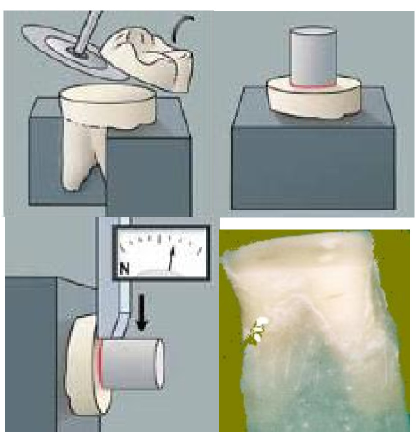

Figure1: SBS. Set up test (pamphlet of RelyX Unicem) + experimentally prepared tooth.

Statistical Analysis:

The results of surface roughness and shear bond strength were statistically analyzed using SPSS version 17,comparison between groups was done with one way Anova ,multiple comparisons to test the inter-relation between groups to determine which group that affect the results using Post Hoc and Tuky-t-test at confidence level of 95%.

3-Results:

Table 1 shows the different values of surface roughness and the shear bond strength of all groups ,superscript of the same letters indicating statistically not significant values,*$p<0.05$*. The surface roughness of group5 (acid etching) was 54.5±6.8 which is doubled nearly25 times more than control group samples (2.3±1.4). Table2 shows the Anova statistical test between the groups and within the groups, F value is significant for, shear bond strength and surface roughness values. Surface treatments had a strong effect on surface roughness of the groups as well as on shear bond strength, but to a lesser extent.

Figures 2, and 3 illustrate that group5 (acid etching) has very high surface roughness value compared to the other groups (54.5±6.8) and also the highest recorded shear bond strength (24.3±3.2). From these figures, it is clear that when the surface roughness was doubled 25 times, the bond strength doubled nearly 8 times.

Table (1): statistical analysis of surface roughness and the corresponding shear bond strength values.

		surface roughness	shear bond strength(MPa)	P value
control	Mean	2.3000 (a)	3.054(s)	
	Std. Deviation	1.41803	1.99403	
Grinding tool	Mean	3.671(a)	4.431(s)	*P< 0.05*
	Std. Deviation	1.17149	2.36731	
group3	Mean	7.5043 (b)	8.4371(E)	
	Std. Deviation	3.2531	2.84825	
group4	Mean	12.750 (c)	13.4286(E)	
	Std. Deviation	4.25979	4.54994	
group5	Mean	54.5 (d)	24.300 (M)	
	Std. Deviation	6.86339	3.21388	

Table (2): statistical results of all groups, one way Anova

		Sum of Squares	df	Mean Square	F	Sig.
surface roughness	Between Groups	26056.947	4	6514.237	326.714	.000
	Within Groups	598.160	30	19.939		
	Total	26655.107	34			
shear bond strength	Between Groups	441.180	4	110.295	85.123	.000
	Within Groups	38.871	30	1.296		
	Total	480.051	34			

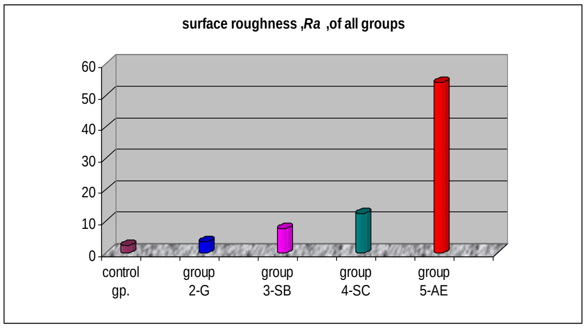

Figure 2: Surface roughness Ra, after surface treatment for all groups.

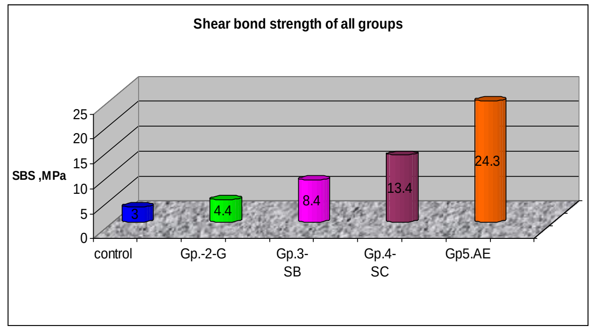

Figure3: Shear bond strength MPa, of all groups

3-2 Results of atomic force microscopy AFM:

Figures 4,and 5 shows the surface topography as traced by the AFM, the roughness of the scanned area,20μm., the surface appeared smooth except some sharpness which was interpreted as attached powder, or dust from the laboratory fabrication procedures, and for gp2-G very minute sharpness and scratches appeared. Generally the recorded average roughness, in small scanned area, 20μm, Ra was402 nm, for control group while for group2, the recorded Ra was600nm. The recorded highest peak area in the histogram is not statistically different compared with the control.

Figures 6and 7 showing the roughness resulted from sand blasting (group3) and modified tribochemical coating, it is clear that surface roughness increased, as much more peaks of sharp irregularities corresponds to the coated alumina modified silica particles which remains well attached to the surface even after ultrasonic washing.The recorded roughness peak in the histogram in group3 was 890nm,while it was 1.4μm in group4 with much more thickness in z- plane axis.

In group5, fig 8, the surface is full of deep, wide valleys and concavities as well as sharp tops, irregularities with the highest recorded surface roughness histogram, within the scanned area, 2.84μm, as well as increased thickness in z-plane axis. Acid etching procedure yielded a wide surface area available for the bonding cement to penetrate and interlocked within the rough surface.

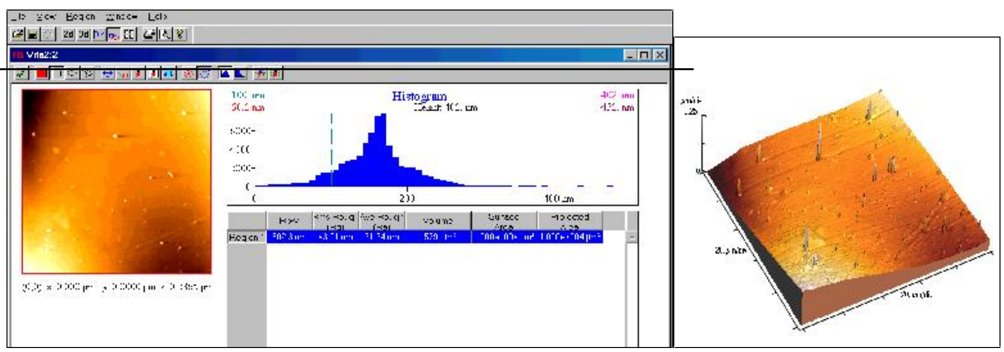

Figure4: Surface roughness parameters as recorded from AFM, 2D and 3D AFM photo of control group

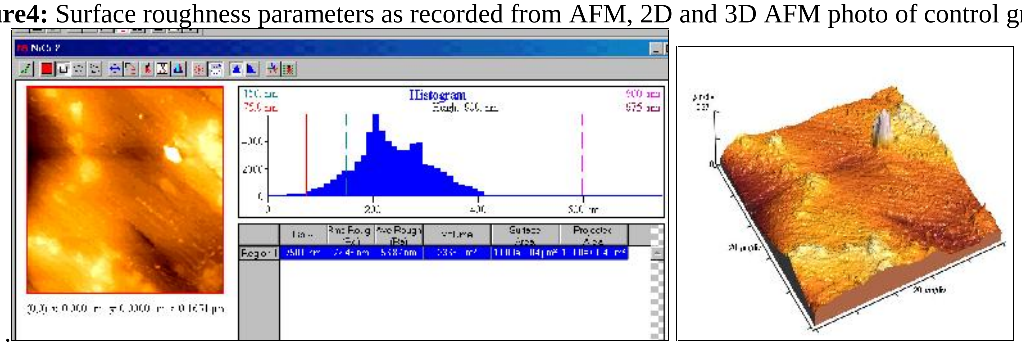

Figure 5: Surface roughness parameters as recorded from AFM, 2D and 3D AFM photo of group 2-G

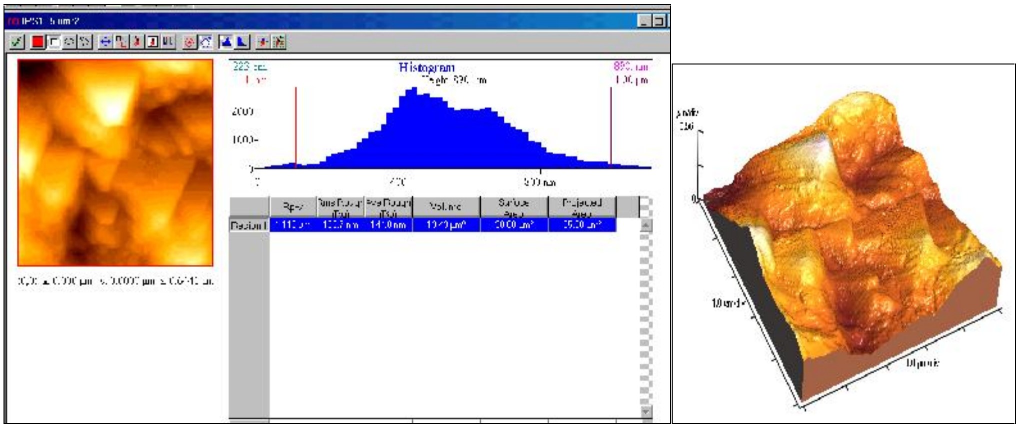

Figure 6: Surface roughness parameters as recorded from AFM, 2D and 3D AFM photo of group3-SB (sand blasting)

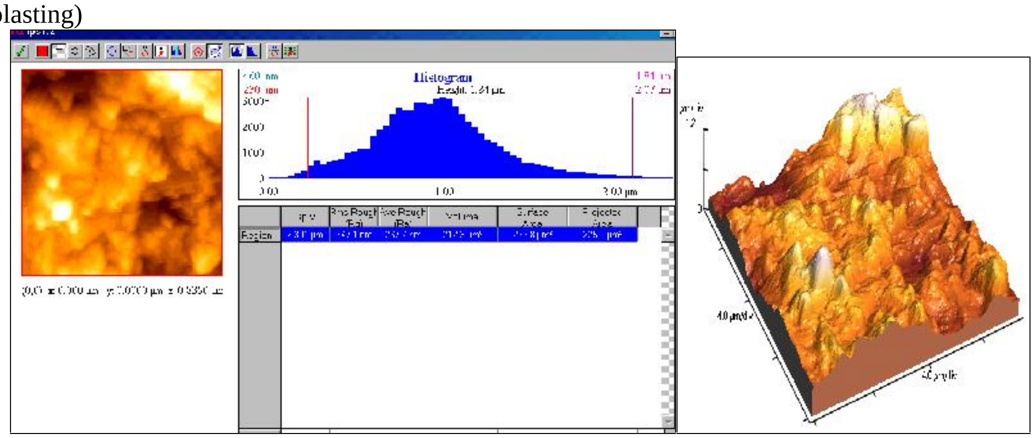

Figure 7: Surface roughness parameters as recorded from AFM, 2D and 3D AFM photo of group 4-SC (modified tribochemical technique).

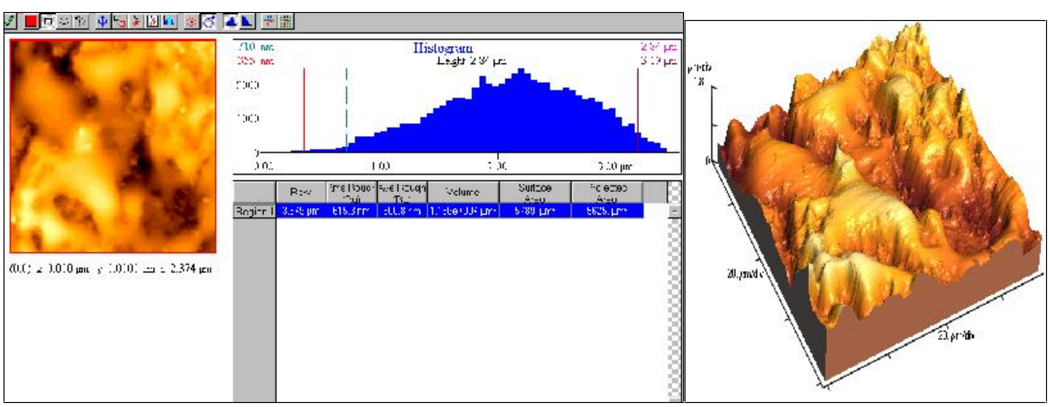

Figure 8: Surface roughness parameters as recorded from AFM, 2D and 3D AFM photo of group 5-AE (acid etching).

4-Disscusion:

Non-silicate ceramics, especially zirconia, have become a topic of great interest in the field of prosthetic and implant dentistry. Although its mechanical properties are superior than other available ceramics, problems with use of zirconia-based ceramics in achieving suitable adhesion with tooth structure always arises, especially in stress areas of the oral cavity.

Traditional adhesive techniques used with silica-based ceramics do not work effectively with zirconia, because of their lack of silica and glass phase, the responsible elements in providing good bond strength in traditional silicate ceramics. Several investigations are being utilized clinically to solve this problem, and other approaches are under investigation. Most focus on surface modification of the inert surfaces of zirconia.

Zirconium is an inert element, 3d, 4S,and 4b orbital are completely filled, and 4d orbital is of high energy level and not involved in common reaction at ordinary chemical condition.[30] The ability to chemically functionalize or activate the surface of zirconia appears to be critical in achieving adhesive bonding. Some literatures suggest the use of air abrasion or tribochemical coating prior to adhesive cementation, the effect of those surface treatments on the mechanical properties of Y-TZP materials is controversial, and both positive and negative results have been described in the literature [32, 33].

In most of the previous studies the bond strength of adhesive resin materials to Y-TZP ceramics was studied. Shear and tensile bond strength tests were the methods most frequently used in those investigations.[34-36] In both methods, the specimens had only one adhesive interface to be tested, that is, between the ceramic and resin-based materials. However, in the clinical situation, both interfaces between the ceramic and adhesive restorative material and between the adhesive restorative material and tooth structure are present.

Thus, the performance of the complex tooth structure- adhesive resin—zirconia ceramic must be tested, as there are much complicated factors to affect the bonding strength to the tooth structure. Therefore the results which did not include the important tooth-restoration interface may be not clinically reliable.

In this study, hot iso-static pressed (HIP) yttrium-oxide-partially-stabilized zirconia poly crystal blocks machinery fabricated were used. The effect of several methods to modify the surface of zirconia to improve bonding with dentin namely, grinding surface with carbide disc,air abrasion technique with Al_2O_3, modified protocol of the tribochemical technique,and acid etching with solution of 27% Hcl and ferric chloride.

The selected cement ,a self adhesive cement, RelyX Unicem, which was used to decrease the sensitive steps of bonding procedures. Self-adhesive resin cements, do not require tooth pre-treatment, therefore simplifying the clinical steps during the cementation procedures of crowns/fixed partial dentures. The cement paste is very acidic and has hydrophilic properties. Therefore it shows a higher moisture tolerance than multi-step composite cements. During setting of the cement, a strongly cross-linked cement matrix with hydrophobic properties develops through the cross linkage polymerization reaction. A low linear expansion and low solubility are the results and lead to the long-term stability which plays a central role especially for all-ceramic restorations. Additional advantages of these products are the decrease or elimination of post-operative sensibility, as well as lesser susceptibility to moisture, as reported by **Mazzitelli et al. 2008)** [37]**.** By elimination of other influencing bonding variables related to etching and or priming of dentin, the results of bonding strength were confined to proposed surface treatments only, with no other influencing factors.

The results of this study showed that no significant difference in shear bond strength between control group with no surface treatment and the use of grinding tool ,as there was no difference in surface topography, and the resulted roughness was incapable of providing the adequate micromechanical bonding with the cement and tooth structure. The results were in accordance with other researchers who reported that surface grinding techniques, using conventional grinding tools and bonding with resin cements, have no significant effect on increasing the bond strength of zirconia to resin cements, The low surface energy and inertness of zirconia surface provide very low bond strength with tooth structure after 5000thermo-cycling and storage in water**.** [20,21,25]

Silane coupling agents (silanes) are well-known to form covalent chemical bonds between dissimilar matrices, i.e glassy ceramics (oxides) and organo-functional monomers in the adhesive cement. [38]

In this study, the silane monomer with the methacrylate functionality, 3-methacryloyxpropytrimethoxy silane, which is widely used in dentistry, was selected in treatment of samples of group 3 and 4. Also in group 5 to improve wettability of the etched zirconia surface, in addition after etching, there will be an ionized free components and oxides of trace elements which could share in bonding process. However, silanes cannot react directly with the chemically inert zirconia. Silanes are also believed to promote surface wetting, which enhances potential micromechanical retention with low viscosity resin cements [39, 40].

In group 3, sand blasting with Al_2O_3 increased the bond strength significantly 8.4 ± 2.8 in comparison to the control group. Airborne-particle abrasion has been shown to be a good method for cleaning and roughening the zirconia surface after clinical try-in procedures, since the contamination with saliva is known to decrease the bond strength. **Yang et al., 2008; Yang et al., 2007**[41,42]. stated that airborne particle abrasion with alumina creates surface roughening and significantly improved Zirconia-resin bond strength

Un-fortunately, these techniques can create surface microcracks [43, 44]. That may act as crack initiation sites that can decrease strength .Moreover, surface grinding also results in a tetragonal to monoclinic phase transformation on the surface of zirconia. This can theoretically produce a compressive stress layer that counteracts the flaw-induced reduction in strength [43, 44]. Work by **Guazzato *et al*' 2004)** [6]. showed that sandblasting produced the most effective tetragonal to monoclinic phase change when compared to fine polishing, grinding with an abrasive wheel, or grinding using a diamond bur It was determined that sandblasting was able to induce transformation at low temperature (room temperature) [44,45]. In the literatures, there are a controversial information about the minimum accepted clinical bond strength, while it was mentioned that minimum of 5 MPa set by the International Organization for Standardization [21], Thurmond et al., and Piwowarczyk et al.,[46,47] stated that it must not be less than 10-12 MPa to survive in the oral cavity, and of course it varies according to location in the oral cavity and the type of occlusion. However, the bond strength yielded from sand blasting with alumina followed by silan coupling agent, failed to reach the minimum accepted bond strength (10-12Mpa) needed for clinical service in the oral cavity[46,47]

The fourth proposed surface treatment was application of the tribochemical chemistry in coating the zirconia surface with silica modified alumina particles then silanization of the surface before application of the adhesive cement.

Tribochemical method that has shown to be quite effective in increasing bond strength to zirconia based ceramics is the technique of silica coating followed by silane application is a simple and effective technique that uses silica-coated 30mm aluminum trioxide particles, followed by the application of silane. According to the manufacturer, sandblasting with this material uses impact energy to apply a silica coating to the target surface [48]. Other literatures denies these claims, as it is unlikely, that in the case of high toughness alumina or zirconia materials, there is actual embedding of silica coated particles because of the intrinsic hardness of the target material.[49,50]

Modification of the technique was proposed to enhance the bond strength with cement through increasing the surface roughness of zirconia via homogenization between Alumina particles and Alumina modified Silica particles. In addition, it was reported that conventional blasting procedure, yielded a layer which is loosely attached to the ceramic substrate, therefore bonding to this lose layer impair formation of a durable zirconia/cement bond strength [51]

The EDXS analysis and SEM studies showed that the coating silica on Zirconia surface could be cleaned away by ultrasonic washing in water or pressurized water spray, indicating that no stable chemical bond was formed between silica and zirconia. The silica was probably deposited on the Zirconia surface *via* weak physical force, such as vander- Waals forces, which might not be strong and stable enough in a clinical situation. (**Chen *et al*., 2011a), Nishigawa *et al*., 2008;** [49,50]

The proposed additional steps of immersion in saturated solution of alumina and silica then heat tempering at 100C^{o} was postulated to improve coalescence and bonding between silica and alumina particles and the surface of zirconia. In addition, it is well known that heating the surface increases its surface energy, improves wettability and removes any oily substances or dirt waste coming from handling the samples. Also immersion in the saturated solution of silica and alumina, and subsequent heat treatment may increase the concentration of fresh active elements available for chemical bonding with applied silane and thereafter, the adhesive cement.

Internal research at Bisco Dental Products with tribo-chemical bonding (Cojet/Rocatec) showed that it did not offer improved bonding and could be prone to degradation. [52].

It was reported in a previous study conducted by ÖZCAN ***et al* (2008)**[51] that bond strength after tribochemical surface treatment with Rocatec system of Y-ZTP Lava™ samples and thermocycling for 6000 cycle, samples were bonded with Panavia F resin cement, the reported shear bond was 8.23 3.8 MPa with no significant difference between air abrasion with 110µ Al_2O_3 and Rocatec system.

In this study, the bond strength of group4 samples, has improved and the proposed modified tribochemical method yielded much more stable silica/alumina layer which reflected on the durable bond strength even after aging procedure, taking into consideration that there was a good bond strength to dentin surface interface which was not considered in most of other studies. The surface roughness (12.7±4.2) and bond strength (13.4±4.5) increased significantly and the bond strength exceeded that value set by ISO standards for accepted clinical bond strength [21].

Zirconia is a very tough material and the HF acid etching suitable for application in silicate based ceramics are not suitable to induce etching in surface of Y-ZTP.On the other hand, considering the metallic nature of pure zirconium, it can be predicted that acids or etching solutions originally performed for conditioning alloys may works well for etching zirconium dioxide crowns or bridge frameworks. A hot chemical solution has been proposed to etch the wings of Maryland bridges, roughening the surface and promoting retention[(53)].

25% conc. Hydrochloric acid is considered as a corrosive solution for most of alloys and tough material. The addition of ferric chloride to Hcl increases its ability to etch the preferential boundaries of the superficial grains of Y-ZTP. Ferric chloride is an octahedral, highly symmetric complex ion. It can form complexes with the weakest metal ions on the surface of the substrate (Y-ZTP). The resultant new complex ions dissolve in water and leads to the observed etching –corrosion procedure. The legating nature of this solution make it suitable to produce widening between the densely arranged grains of Y-ZTP ,created a surface roughness recorded in this study which exceeded all other surface treatments ever described in a relevant literatures (54.5±6.8), after 15 minutes application period. The advantage of this solution is that its evaporation does not significantly vary its composition during use. In addition, the preparation of the solution is not a technique sensitive [(54)]. The action of the hot etching solution is basically a corrosion-controlled process. It selectively etches the zirconia,[(55)] enabling for micro-retentions by modifying the grain boundaries through preferential removal of the less arranged, high energy peripheral atoms the created micro spaces that would optimize the overall bonding mechanism. The shear bond strength results of acid etching group was 24.2±3.2 MPa. The bond strength doubled nearly 8 times. Once resin cement systems penetrate the inter-grain spaces forming micromechanical interlocks with the substrate, a superior strength would be necessary to debond it.

This method of inducing surface roughness had the advantage of removing the inter facial layer (whether Alumina or Silica) and the cement penetrates through the created inter-grains spaces. It is well known that the weakest link in any adhesion process is always the inter mediate layer where cracks and de-bonding may occur[(56)]. So by removing this inherent weak layer, bond strength doubled 8 times.

Acid etching technique was the least sensitive and in-expensive method for functionalizing surface of Y-ZTP dental ceramics, as the modified tribochemical technique proposed in this study has a prolonged time to be performed, and further investigation are needed to reduce the described steps and therefore facilitate its application in dental labs.

More investigations are also needed to find out other more suitable etching solutions, to improve acid etching techniques, and make it more suitable for application in dental clinics at room temperature, instead of being in the labs, as the hot temperature of the etching solution is not applicable in clinics.

5- Conclusions:

1-Although it needed much time to be performed, yet, proposed modified tribochemical technique was a valid method in increasing Y-ZTP /dentin bond strength and recommended to be applied rather than conventional tribochemical method. 2- The use of hot etching solution of Hcl and ferric chloride $FeCl_3$ is recommended as an effective and simple method and could be performed easily in labs to modify surface of zirconia chemically and mechanically, so that, enhance bonding to dentin surface even after water storage and thermo-cycling.3-Self adhesive cement RelyX Unicem, produced a comparable results to resin cement with the advantage of reduced time and elimination of sensitive steps of resin bonding cements which requires a separate etching and bonding agents.

Corresponding author
Manal R. Abu-Eittah
Fixed Prosthodontics Department, Faculty of Dentistry, Minia University, Minia,Egypt.
manalrafei@yahoo.com

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