EGYPTIAN
DENTAL JOURNAL
www.eda-egypt.org

Vol. 70, 1489:1502, April, 2024

Print ISSN 0070-9484 • Online ISSN 2090-2360

Fixed Prosthodontics and Dental Materials

Submit Date : 25-12-2023 • Accept Date : 01-02-2024 • Available online: 10-04-2024 • DOI : 10.21608/EDJ.2024.256718.2846

THE EFFECT OF HEAT TREATMENT AND SURFACE ENERGY ALTERATION ON CONTROLLING THE LONG TERM STABILITY OF THE ZIRCONIA-RESIN BOND

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ABSTRACT

Purpose: To evaluate the proper curing and surface energy alteration protocol for the MDP primed zirconia and to assess the bond stability before and after aging.

Materials and methods: Zirconia samples (n=50) were cut using an Isomet 4000® and sintered into a standardized dimension of (8x8x4mm), then they were divided into 10 groups of 5 and assorted according to the surface treatment they received. The groups of comparison were, silica coating (gp 1&6)/ silica coating + MDP primer "Z-prime plus" (gp2&7)/ silica coating + MDP + heat ttt (gp 3&8)/ silica coating + MDP + hydrophobic coating (gp 4&9)/ silica coating + MDP+ hydrophobic coating + heat treatment X2 (gp 5&10). The µSBS of the groups was tested using an INSTRON® universal testing machine and the bonding surfaces were scanned with an electronic microscope under magnification of X40 pre and post aging (5000 cycles at 5-50°C).

Results: The study showed that there is a significant difference between the mean SBS of the groups pre and post aging (P=0.001). There was a positive correlation (with no significance) between applying heat treatment to the MDP treated groups and achieving higher SBS both pre and post aging. The heat treated groups came superior pre and post aging followed by the MDP treated group with no heat treatment. After aging the groups with the highest number of (mixed failure) were the ones that received heat treatment.

Conclusions: Aging affects the SBS of the Zr-resin bond negatively. Applying an MDP primer significantly improved the SBS of the bond in comparison to the non-treated samples (pre and post aging). Exposing the MDP treated samples to heat treatment had a positive correlation to improving the SBS pre and post aging. Heat treatment protected the bond from water degradation as the heat treated groups had the highest numbers of samples with mixed failure in the post aging groups. Applying a hydrophobic coating didn't improve the SBS.

KEYWORDS: zirconia, silica coating, MDP, zirconia primer, heat treatment, hydrophobic coating, aging, µSBS test.

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INTRODUCTION

In recent years, yttrium-stabilized polycrystalline tetragonal zirconia (Y-TZP) has been attracting the interest of many researchers and dentists due to its superior mechanical properties, bio-compatibility, dimension stability and superior flexure strength. [1,2]

But the success of a restoration doesn't only depend on the properties of the material.

Maintaining a strong bond to the substructure and maintaining a proper marginal integrity are key factors in determining the success of such restorations [3,4] .

Many systematic reviews and meta analyses concluded that a considerable rate of Y-TZP restorations would de-bond, shedding the light on the importance of different surface treatments and their effects on bond durability.[5–14]

Different surface treatments showed success in improving the bond of Y-TZP to resin cements, with tribochemical silica coating showing better results when compared to other surface treatments such as air abrasion and acid etching.[7,15–18]

Several researches showed that the use of an MDP primer would have a positive impact on the initial shear bond strength (SBS) of the bonded zirconia samples.[7,11,14,16,17,19–25]

Although a high initial shear bond strength was achieved using a combination of surface treatments, priming agents and cements was successfully achieved[7,8,14–16,26,27] , deterioration of the bond and significant decrease in the SBS was also noticed[7,8,14,23,25,28]

Hence the need for testing different methods to maintain the original SBS or decrease the bond deterioration after aging was needed.

The purpose of this research is to study the effect of heat treatment and change of surface hydrophilicity on controlling the long term stability of the zirconia-resin bond in tribochemical silica-coated / MDP treated zirconia samples.

The hypothesis of this research is that the use of heat treatment +/- a hydrophobic coating will significantly improve the strength and longevity and decrease the hydrolysis of the zirconia-resin bond.

MATERIALS AND METHODS

Materials used in this study:

Y-TZP blocks, zirconia primer, hydrophobic adhesive, dual cured resin cement, alumina sand, silica coated alumina sand (table 1)

Specimen preparation:

A total of 50 zirconia specimens were cut out of the main zirconia blank (ceraMotion®Z Dentaurum - Germany) with the final (post sintering) dimensions of (8X8X4mm), using (Isomet 4000 BUEHLER-Germany). The specimens were sintered following the manufacturer's instructions using (TABEO MihmVogt- Germany) at 1550˚C for 12 hours. The bonding free surfaces were marked to prevent mishandling. The bonding surfaces were sand blasted with 110µm alumina sand (Korox® BEGO-Germany) at a pressure of 4 bar, a distance of 10mm and an angel of 45˚ for 20 seconds/sample. After cleaning the samples with air, they all received a silica coating surface treatment (CoSil® 30µm) using (Aquacare air abrasion device Velopex – UK) at a pressure of 2.8 bar and a distance of 10 mm for 15 seconds.

The samples were then randomly assigned to 10 groups (n=5) receiving different surface treatments as follows:

Group (1) & (6): silica coating only "no chemical treatment"

Group (2) & (7): received 2 coats of Zr primer (Z-Prime Plus-BISCO) and were allowed to air dry for 15 minutes.

Group (3) & (8): received 2 coats of Zr primer then were heat at 82˚C for 3 minutes.

Table (1): Description of the materials used

	Material	Manufacturer	Main composition
1	ceraMotion®Z	Dentaurum - Germany	-ZrO2+HfO2+Y2O3 >99.0% -Y2O3 4.5-6% -Al2O3 < 0.5% -further oxides < 0.5%
2	Z-Prime Plus	BISCO –USA	-ethanol 75-85% -bisphenol A Diglycidylmethacrylate 5-10% -2-hydroxyethyl methacrylate 5-10% -proprietary 1-5% -MDP 1-5% **
3	Heliobond	Ivoclar	-Bis-GMA 59.5% BW -triethylenglycole dimethacrylate 39.7% BW -stabilizers and catalysts 0.8% BW
4	DUO LINK UNIVERSAL	BISCO-USA	-Ytterbium Fluoride 10-20% - bisphenol A Diglycidylmethacrylate 10-30% -urethane Dimethacrylate 10-30% -ytterbium Oxide-Silica 1-5% -tetrahydrofurfuryl Mrthacrylate 1-5% -trimethylolpropane Trimethacrylate 1-5% **
5	Korox® alumina sand 110µm	BEGO-Germany	-aluminum oxide 99.6%
6	CoSil® silica coated alumina sand 30µm	Aquacare lab series – velopex-UK	-silica coated alumina abrasive sand 30 µm

*****As mentioned in the product's safety data sheet*** ***BW: by weight.***

Group (4) & (9): received 2 coated of Zr primer, then they were left to air dry for 15 minutes, then received 1 coat of a hydrophobic coating (Heliobond-ivoclar) which then was light cured for 10 seconds according to the manufacturer's instruction

Group (5) & (10) : received 2 coats of Zr primer then were heat treated at 82˚C for 3 minutes, then were allowed to cool to room temperature, then received 1 coat of a hydrophobic coating (Heliobond-ivoclar), then received another cycle of heat treatment at 60˚C for 1 minute and then was light cured for 10 seconds according to the manufacturer's instructions.

After finishing the different surface treatments of all samples "50 samples", cylindrical transparent silicone dies were positioned on the bonding surface of the blocks (fig.1), then the resin cement was manipulated according to the manufacturer's instructions, and inserted into the cylinders using auto-mix tips with intra-canal extensions (fig.2)

The resin cement was cured for 3 seconds /surface according to the manufacturer's instructions, and then the silicone dies were removed after 24 hours using a size 24 scalpel blade.

Groups (1,2,3,4,5) were subjected to shear test directly.

To measure the long term bond stability, the sample groups (6,7,8 9,10) were aged, subjecting them to thermal cycling of (5-55˚C) for 5000 cycles.

Shear (µ SBS) test: machine and mechanism

An INSTRON® universal testing machine model 3345 (fig.3) was used to apply force on the samples till failure.

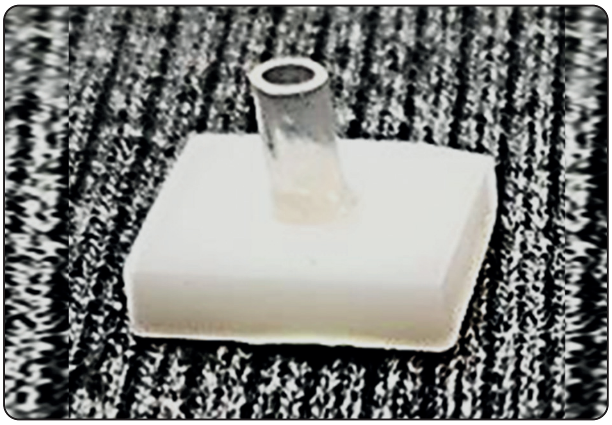

Fig. (1) An empty die fixed to the Zr. Sample surface

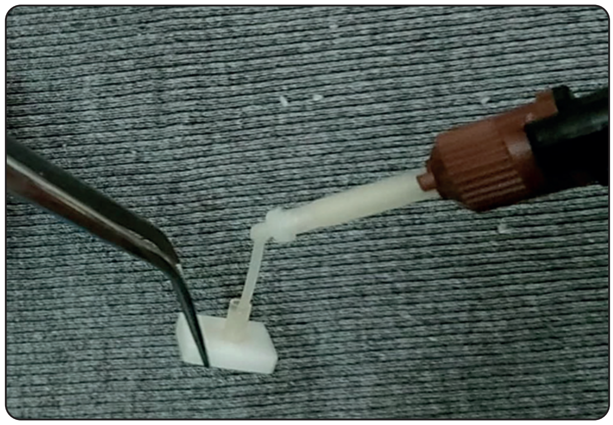

Fig. (2) Delivering the resin cement inside the silicone die using an "intra-canal" resin cement extension

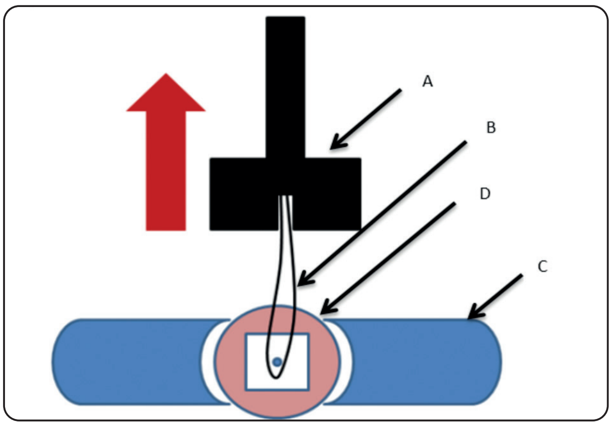

Fig. (3) INSTRON® universal testing machine parts: A) Cross head B) Load string C) The grips D) Resin housing with zirconia sample attached to a resin cement cylinder cast (resin rod).

The INSTRON® universal testing machine works by applying different types of forces to the testing samples till failure, utilizing different shapes of heads.

At this test, the samples were invested in self-cured acrylic resin to simplify sample handling and mounting to the machine grips, due to the small cross-section of the resin cement casts, a wire attachment was used (load string) to apply forces on the samples till failure, as the wire was put around the resin rods and pulled up till the resin rod separates from the treated zirconia surface. Then the data was collected and calculated using BlueHill universal INSTRON England®, and reported for statistical analysis.

Statistical analysis:

The data was analyzed using: Data analysis package SPSS version 21. Quantitative data was presented by mean, standard deviation, minimum and maximum (range) Tests of significance was done (one sample t test, paired t test, One way ANOVA and post hoc turkey test for the quantitative parametric data), level of significance was set at P equal or below 0.05.

Mode of failure analysis

The failure modes of the tested samples were observed using a digital microscope (Gloptics digital microscope) under 40X magnification (Fig. 5,6,7,8) and classified according to the mode of failure to: (table 11)

a) Mainly adhesive failure

b) Mainly cohesive failure in the ceramic

c) Mainly cohesive failure in the cement

d) Mixed failure (mainly adhesive)

e) Mixed failure (mainly cohesive)

RESULTS

When checking the mean SBS before aging (Thermo-cycling) the SBS values of groups (1-5) was gp 3 > gp 2> gp 4 > gp 5> gp 1, with gp 3 (MDP+ heat ttt) coming first followed by MDP only group (table 2)

And after aging (Thermo-cycling) the mean SBS values of groups (6-10) was gp 8 > gp 7 > gp 10> gp9> gp 6 again with (MDP+ heat ttt) coming first followed by MDP only group (table 3) With (MDP+ heat ttt) taking the first place in both instances

The statistical analysis showed that there was a significant difference between the mean SBS from the (collective) groups pre and post aging (table 4) and that there was a significant difference between the results of each treatment when compared to the rest of the treatments in both the pre and the post aging group comparisons (table 5,6,7,8) (fig.4) and when analyzing the data with post hoc Tuckey test all samples at both pre and post aging groups had significant differences except groups (2 vs 3) and (7 vs 8) (table 10,11) .

-The electronic microscope at magnification X40 showed the different modes of failure of the samples (table 11) and found that the group with the highest number of samples with mixed failure was gp 8 (MDP+ heat ttt+ aging) (fig.6,7), And that the only group with a sample achieving cohesive failure (1 sample) belonged to gp 5 (MDP+ hydrophobic coating + heat ttt X2) (fig.5)

Means:

TABLE (2) Mean SBS groups (1-5) (pre aging)

Group number	Mean SBS in MPa	**S.D**
Gp 1	4.46692 MPa	1.96243
Gp 2	31.83686 MPa	7.14727
Gp 3	34.40175 MPa	7.41387
Gp 4	27.93586 MPa	5.50820
Gp 5	22.58833 MPa	12.73396

Before aging the mean SBS of groups was gp 3 > gp 2> gp 4 > gp 5> gp 1

TABLE (3) Mean SBS groups (6-10) (post aging)

Group number	Mean SBS in MPa	S.D.
Gp 6	0.0*	0.0*
Gp 7	19.45479 MPa	2.52046
Gp 8	19.74368 MPa	5.54398
Gp 9	5.80995 MPa	2.67795
Gp 10	8.27599 MPa	1.94472

After aging the mean SBS of groups was gp 8 > gp 7 > gp 10> gp9> gp 6

****all samples of (Gp 6) detached from the zirconia surface after thermo-cycling***

TABLE (4) Comparing mean shear stress PRE and POST AGING:

	Groups	**Mean**	**N**	**Std. deviation**	**Std. error mean**	**P value**	**95% CL**
SBS	Gp (1-5)	24.2440	5	2.31789	1.03659	0.001	9.89:17.28
	Gp (6-10)	10.6552	5	1.41043	.63076		

Comparing mean shear stress [MPA] among all groups before heat treatment was statistically significant higher before heat treatment compared to post treatment mean (P=0.001).

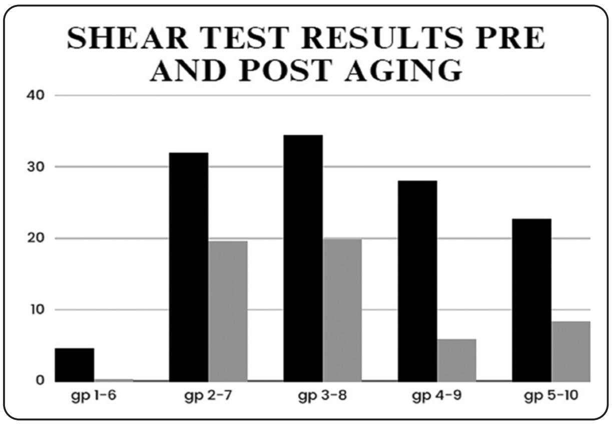

Fig. (4) Mean SBS pre and post aging

TABLE (5) Comparing the SBS in MPa of each group to the rest of the groups (gp 1 to 5):

SBS	N	Mean	Std. Deviation	Minimum	Maximum	P value	95% CI
Group 1	5	4.4620	1.96152	3.01	7.89	0.007	2.02:6.89
Group 2	5	31.8320	7.14615	24.98	40.59	0.001	22.95:40.70
Group 3	5	34.3980	7.41251	27.46	43.90	0.000	25.19:43.60
Group 4	5	27.9380	5.50899	24.89	37.63	0.000	21.09:34.77
Group 5	5	22.5900	12.73340	9.24	39.42	0.017	6.77:38.04

There is statistical significant difference in mean shear stress between groups before heat treatment. Group 1 (p=0.007), group 2 (p=0.001), group 3 (p<0.001), group 4 (p<0.001) & group 5 (p=0.017).

TABLE (6) Comparing the SBS in MPa of each group to the rest of the groups (gp 6 to 10) :

SBS	N	Mean	Std. Deviation	Minimum	Maximum	P value	95% CI
Group 6	5	.0000	.00000	0.00	0.00	-	-
Group 7	5	19.4540	2.52323	16.19	22.73	0.000	16.32:22.59
Group 8	5	19.7400	5.54515	14.84	25.79	0.001	12.85:26.62
Group 9	5	5.8080	2.67782	1.56	8.74	0.008	2.48:9.13
Group 10	5	8.2740	1.94272	6.69	11.44	0.001	5.86:10.688

There is statistical significant difference in mean shear stress between groups after heat treatment. Group 6 (p=N/A), group 7 (p<0.001), group 8 (p=0.001), group 9 (p=0.008) & group 10 (p=0.001).

TABLE (7) One way ANOVA groups (1-5)

Source	sum of squares SS	degrees of freedom ν	mean square MS	F statistic	p-value
treatment	2,792.6838	4	698.1710	12.7582	2.5628e-05
Error	1,094.4698	20	54.7235		
Total	3,887.1536	24			

The p-value corresponding to the F-statistic of one-way ANOVA is lower than 0.05, suggesting that the one or more treatments are significantly different.

TABLE (8) One way ANOVA groups (6-10)

Source	sum of squares SS	degrees of freedom ν	mean square MS	F statistic	p-value
treatment	1,395.2908	4	348.8227	34.4994	1.8114e-08
Error	192.1088	19	10.1110		
Total	1,587.3996	23			

The p-value corresponding to the F-statistic of one-way ANOVA is lower than 0.05, suggesting that the one or more treatments are significantly different.

TABLE (9) Post hoc Tukey groups (1-5)

treatments pairs	Tukey HSD p-value	Tukey HSD inference
Gp 1 Vs Gp 2	0.0010053	** p<0.01
Gp 1 Vs Gp 3	0.0010053	** p<0.01
Gp 1 Vs Gp 4	0.0010053	** p<0.01
Gp 1 Vs Gp 5	0.0010053	** p<0.01
Go 2 Vs Gp 3	0.3095770	Insignificant
Gp 2 Vs Gp 4	0.0010053	** p<0.01
Gp 2 Vs Gp 5	0.0010053	** p<0.01
Gp 3vs Gp 4	0.0010053	** p<0.01
Gp 3 Vs Gp 5	0.0010053	** p<0.01
Gp 4 Vs Gp 5	0.0435975	* p<0.05

TABLE (10) Post hoc Tukey groups (6-10)

treatments pairs	Tukey HSD p-value	Tukey HSD inference
Gp 6 Vs Gp 7	0.0010053	** p<0.01
Gp 6 Vs Gp 8	0.0010053	** p<0.01
Gp 6 Vs Gp 9	0.0010053	** p<0.01
Gp 6 Vs Gp 10	0.0010053	** p<0.01
Gp 7 Vs Gp 8	0.8999947	Insignificant
Gp 7 Vs Gp 9	0.0010053	** p<0.01
Gp 7 Vs Gp 10	0.0010053	** p<0.01
Gp 8 Vs Gp 9	0.0010053	** p<0.01
Gp 8 Vs Gp 10	0.0010053	** p<0.01
Gp 9 Vs Gp 10	0.0010053	** p<0.01

Table (11) Mode of failure analysis:

	Number of samples + Mode of failure					
Group	**a)**	**b)**	**c)**	**d)**	**e)**	**d+e (mixed)**
Group 1	5	0	0	0	0	0
Group 2	1	0	0	2	2	4
Group 3	3	0	0	1	1	2
Group 4	4	0	0	1	0	1
Group 5	3	0	*1	0	1	1
Group 6	5	0	0	0	0	0
Group 7	2	0	0	1	2	3
Group 8	0	0	0	1	4	**5
Group 9	3	0	0	2	0	2
Group 10	1	0	0	3	1	***4

**** Cohesive failure in the cement only happened in group 5***

***** Group 8 is the only group with all 5 samples having mixed failure "mainly mixed-cohesive"***

****** Group 10 is the second group with most samples having mixed failure "mainly mixed-adhesive***

Fig. (5) Cohesive failure in the cement

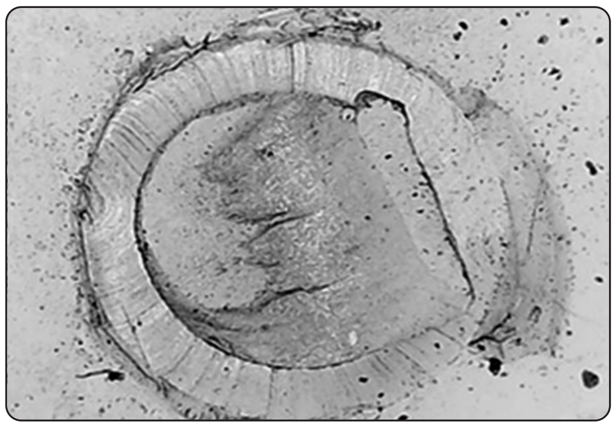

Fig. (6) Mixed failure (mainly cohesive)

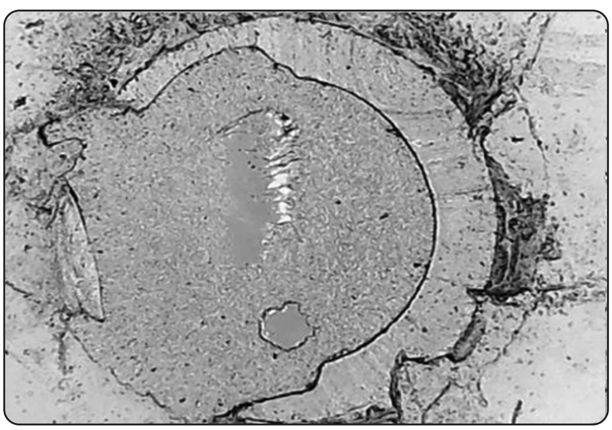

Fig. (7) Mixed failure (mainly adhesive)

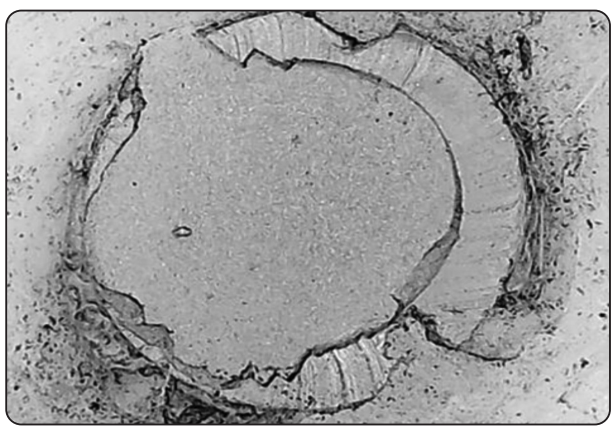

Fig. (8) Adhesive failure

DISCUSSION

This study aims at finding out the effects of changing of the surface hydrophilicity and surface energy of the MDP treated zirconia samples on the stability of the bond after aging.

It has been stablished that applying an MDP primer to a topographically altered Zirconia surface would significantly improve the Zr-resin bond strength.[21,25,27,30]

It was also noticed that after aging (thermo-cycling) the bonds weaken regardless of the surface treatment received.[7,23,68]

A finding that was confirmed by *Eduardo M. da Silva et a.l* after testing MDP containing primer vs MDP free primer and found that the deterioration of the bond was inevitable regardless the primer used.[5]

For the purpose of this study a meticulous protocol was designed, to try and detect the -expected to be-slight differences between the comparison groups.

The zirconia sample material of choice was ceraMotion®Z HT White, which is a 3Y-TZP with a composition of (>99% ZrO2+Hfo2+y2O3)

3Y-TZP is the basic form of zirconia that is used in dentistry, with a high flexure strength of almost 1200 MPa, many new modifications were introduced to Y-TZP to try and improve its optical properties, either by changing the composition to 4Y-TZP or 5Y-TZP or by adding different modifiers or crystals (e.g. Lithium silicate), changing the mechanical properties of the material along with its physical properties, for standardization purposes a basic 3Y-TZP (ceraMotion®Z HT White) was chosen.[31,32]

Tribochemical silica coating was selected as the topographic surface treatment as it was proven to be an effective way of achieving the desired change in the surface (changing the topography and increasing the reactivity of the said surface).[2,7,33]

Following the silica coating step, all samples except the two control groups (pre and post aging) received an MDP primer (to achieve a chemical bond to the resin cement).

Z-Prime plus was found to be among the most successful MDP zirconia primers, achieving a higher SBS to all comparison groups in multiple studies.[9,20,23,27]

The groups receiving heat treatment targeting the MDP primer were then heat treated at 82˚C for 3 minutes. As this temperature is expected to cure the 2-HEMA resin.[29]

Although success with light curing was achieved previously with MDP primer (Z-prime plus)[23], in this study the heat treatment method was preferred for hydrophilicity modification, as success was achieved using this method by P Zhuang et al.[34], specially that no (photo initiator) was mentioned as a part of the chemical composition of the Z-Prime Plus® MDP primer that was used in this study. (*Z-prime plus safety data sheet*). Improper polymerization , and leaving behind un-polymerized resinous material can increase the solubility and decrease the bond stability[35]. The extent of the enzymatic degradation is probably related to the extent of curing of the resin, because ester groups may be more available for attack in more loosely crosslinked networks as stated by *Saurabh K Gupta et al*.[36] As it was mentioned in the *(Z-prime plus safety data sheet)* and also published in a study in 2019 [37] that the composition of the Z-Prime plus zirconia primer is (10-20%) resinous (Bis-GMA, 2-HEMA and carboxylic acid monomer BPDM), no photo initiator nor an instruction for the use of any curing method was advised by the manufacturer, although an instruction about the sensitivity of the material to UV light was mentioned. Also a higher bond stability was achieved when an MDP-bond treated tribochemical silica coated zirconia samples were heat treated.[13] The issue of residual solvent also presents itself here, When Putting in mind that MDP primers are monomer/solvent mixtures, e.g. Z-prime plus "MDP Primer" is 75-85% ethanol *(Z-prime plus safety data sheet)*, ensuring proper solvent evaporations seems to be of prime importance.

It was found in the literature that applying a hydrophobic coating would help protect the bond from water degradation after aging.[38,39]

When choosing the bonding agent that is to be used as a hydrophobic coating, it was important to choose a bond with no hydrophilic monomers in its composition (not self-etch) as these bonds are designed to interact with the moist surface of dentine, and hence aren't suitable for the application on Zr surface, as their hydrophilicity will not be fully exhausted by any reaction, making them keep their acidity and hence hydrophilicity which in turn increase their risk of hydrolysis, leading to hydrolytic degradation of the bond.[40,41]

So for the groups that are to receive a hydrophobic coating Heliobond (Ivoclar Vivadent) was chosen as it is a part of a total etch bonding system and contains no hydrophilic monomers nor acids.[34]

The same concept was previously tested by applying a layer of hydrophobic resin over the hydrophilic dentine bonding agent, and although no significant difference was initially noticed, when the samples were tested 6 months later "after aging", adding a hydrophobic coat proved itself to be effective.[38,39]

A second round of heat treatment at 60˚C was decided to increase the degree of conversion of the hydrophobic bond layer without affecting the efficiency of the photo-initiator.[42]

After preparing all the sample surfaces, silicon dies were fixed to them to allow for the resin cement to be applied in a uniform diameter, affecting the same surface area, for higher accuracy upon testing.

DUO LINK UNIVERSAL® was the selected resin cement (adhesive needing) to avoid the problem of hydrophilic/acidic monomers that exists in self-adhesive products.

All materials were handled according to the manufacturer's instructions, to achieve the highest level of accuracy.

After performing the experiment, the findings of this study concurred with the results of some of the mentioned studies, and came in contradiction to some other.

The Aging process, thermo-cycling for (5000 cycles) significantly affected the SBS (P=0.001). which concurs with the findings of *Pitta João et al*. back in 2018 when they studied the effects of artificial aging on different primer/cement combinations[9], and also with the results of many other studies.[7,10,12,68]

Zhao Li et al. also reached the same conclusion in 2016 when subjecting the treated samples to artificial aging.[8]

Which is expected to be due to hydrolysis rather than phase transformation.[5,10]

-In agreement with almost all of the studies checked, applying an MDP surface treatment did in fact significantly improve the SBS compared to the non-treated samples (tribochemical silica coated only). It was proven that the addition of MDP primers would improve the SBS, and that this was concentration dependent and that continuous application "up to 3 layers" would improve the SBS of the tested bonds.[7,11,27,30,43,13,14,16–18,24–26]

-On the front of heat treatment, many studies stated the benefits of applying heat treatment to MDP primers or bond prior to applying the resin cement in the process of bonding Zirconia.[44,45]

Dal Piva et al. confirmed this hypothesis in 2019 by testing the effect of heat treatment when applied to MDP treated Zr samples in combination with several resin cements, both pre and post aging.[13]

In the experiment in hand the results showed that applying heat treatment (82˚C for 3 minutes) had an influence on the SBS as this group gave the highest mean SBS in both pre and post aging comparisons.

Although the difference between the MDP treated/heat treated group vs the MDP treated groups was non-significant pre and post aging, the fact that the heat treated groups had a higher SBS can't be denied.

The authors also suspect that the heat treatment of the samples that received (MDP only) or (MDP+ a hydrophobic coating) resulted in some protection of the Zr-resin bond from water degradation after aging, which was proved by the study in hand as the best performance in both the pre and the post aging groups was achieved by the (MDP+ heat ttt) groups.

On the mode of failure test, the groups that received heat treatment had the highest number of samples with (mixed failure)

Although, when comparing the chemically treated samples, the samples that received a (*hydrophobic coating*) came inferior in SBS to the samples that didn't, when comparing the groups that received (*a hydrophobic coating*) to the groups that received (*a hydrophobic coating+ heat ttt*), the ones with heat treatment came superior, and the heat treated groups post aging had again the highest number of samples with (mixed failure).

After checking the evidence provided by many papers on the effects of applying a hydrophobic coating on the strength of the resin bond[38,39,4623], a great improvement in the SBS of the (hydrophobic coating) treated groups was expected as they mentioned that applying a hydrophobic coating would eliminate the effects of the surface hydrophilicity and prevent water degradation of the bond.

On the contrary to the study hypothesis and to previous researches, the results of the current study showed that the samples treated with a hydrophobic coating, (+/-) heat treatment and (+/-) aging, had a SBS inferior to that of the samples that were treated with MDP only (+/-) heat treat treatment and (+/-) aging, and came superior only to the samples that received silica coating alone and no chemical surface treatment.

The authors attributed that to the possibility of a less than desirable curing of the hydrophobic coating that could have been caused by a shorter than needed curing time (the manufacturer's instructions for curing the hydrophobic bonding agent weren't enough (light curing for 10 seconds)), or that some adjunct curing method was needed (extended air drying (+/-) heat), to ensure full curing of the bonding agent resulting in higher resistance to water degradation.[42]

According to the results of this study, the null hypothesis stating that applying MDP primer won't improve the SBS of the zirconia-resin bond was rejected.

But the null hypothesis that applying heat treatment to MDP treated samples won't improve the SBS of the Zr-resin bond was only partially rejected, as although the difference between the heat treated vs the heat treatment free groups was non-significant, the heat treated groups had a higher SBS pre and post aging and there was a positive correlation between subjecting the samples to heat and gaining a higher SBS for both pre and post comparison groups.

The null hypothesis that heat treatment won't protect the bond from water degradation was rejected, as the highest number of samples with mixed-cohesive failure was found in the heat treated groups.

Whereas the null hypothesis that applying a hydrophobic coating won't improve the SBS was accepted, as the group that received a hydrophobic coat came only superior to the group that received no chemical surface treatment, and inferior to all the rest of the comparison groups.

CONCLUSIONS

This study concluded that:

1. Aging of the Zirconia ceramics had a significant negative effect on the SBS.
2. There was a positive correlation (with no significance) between applying heat treatment

to the MDP treated groups and achieving higher SBS, the heat treated groups came superior pre and post aging followed by the MDP treated group with no heat treatment.

3) Heat treatment protected the bond from water degradation as the heat treated groups had the highest numbers of samples with mixed failure in the post aging group.

4) Applying a hydrophobic coating didn't improve the SBS.

RECOMMENDATIONS

For further research the authors recommend the study of:

- The extended drying time of MDP.
- The extended heat exposure of MDP treated samples.
- The extended curing time of the hydrophobic bond.
- Increasing the number of samples per comparison group to avoid the possibility of a statistical type 1 error.

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