RESEARCH AND EDUCATION

Incorporation of TiO$_2$ nanotubes in a polycrystalline zirconia: Synthesis of nanotubes, surface characterization, and bond strength

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Zirconia has been introduced into dentistry as a replacement for metal substructures[1] and has gained popularity because of its good optical and esthetic characteristics and its superior mechanical properties compared with those of other ceramics.[2] Furthermore, it offered chemical stability, low thermal conductivity, and biocompatibility, which expanded its application to monolithic restorations such as crowns, inlays, onlays, and implant abutments.[3,4]

Other ceramic materials such as glass-ceramics have high bond strength after etching with hydrofluoric acid and the application of a silane-coupling agent.[5] However, these treatments are not effective for zirconia because of resistance to etching with hydrofluoric acid and lack of silica.[6] Various methods have been proposed to increase the bond strength between zirconia and resin cements, including airborne

ABSTRACT

Statement of problem. Despite numerous advantages such as high strength, the bond of yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) to tooth structure requires improvement.

Purpose. The purpose of this in vitro study was to evaluate the incorporation of TiO$_2$ nanotubes into zirconia surfaces and the bond strength of resin cement to the modified ceramic.

Material and methods. TiO$_2$ nanotubes were produced by alkaline synthesis, mixed with isopropyl alcohol (50 wt%) and applied on presintered zirconia disks. The ceramics were sintered, and the surfaces were characterized by confocal laser microscopy, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) analysis. For bond strength, the following 6 groups (n=16) were evaluated: without TiO$_2$ and Single Bond Universal; with TiO$_2$ nanotubes and Single Bond Universal; without TiO$_2$ nanotubes and Z-prime; with TiO$_2$ nanotubes and Z-prime; without TiO$_2$ and Signum Zirconia Bond; with TiO$_2$ and Signum Zirconia Bond. After sintering, resin cement cylinders, diameter of 1.40 mm and 1 mm in height, were prepared and polymerized for 20 seconds. Specimens were stored in water at 37°C for 30 days and submitted to a shear test. Data were analyzed by 2-way ANOVA and Tukey honest significant difference (α=.05) tests.

Results. EDS analysis confirmed that nanoagglomerates were composed of TiO$_2$. The shear bond strength showed statistically significant differences among bonding agents (P<.001). No significant differences were found with the application of nanotubes, regardless of the group analyzed (P=.682). The interaction among the bonding agent factors and addition of nanotubes was significant (P=.025).

Conclusions. Nanotubes can be incorporated into zirconia surfaces. However, this incorporation did not improve bond strength. (J Prosthet Dent 2018;120:589-95)

particle abrasion with aluminum oxide and with silica-alumina followed by coupling agent application.[7,8] Nevertheless, the effectiveness of these methods is

Clinical Implications

The association of zirconia with nanostructures may improve the interaction between resin cement and Y-TZP ceramics at the adhesive interface.

unclear. Other attempts, such as laser application, roughening with diamond rotary instruments, selective acid infiltration, and low-fusing ceramic application to the zirconia surface, have also been described.[9-12] These methods have shown different percentages of martensitic transformation in the treated surface, leading to the initiation and propagation of cracks in the material and compromising the long-term durability of the zirconia restoration.[1,13,14]

The addition of phosphate monomers such as 10-methacryloyloxydecyl dihydrogen phosphate (MDP) in primers or cements can increase the bond strength to zirconia.[15-17] These monomers chemically interact through the phosphate (P) terminal group, which reacts with the hydroxyl (-OH) group on the zirconia surface to form chemical bonds between oxygen and zirconium (P-O-Zr).[18] Although materials that chemically interact with zirconia have shown promising results with regard to bond strength,[15] the bond strength tends to decrease after aging treatments.[19]

The authors are unaware of studies of the use TiO_2 nanostructures to promote bonding to zirconia. Reducing particle size from micrometer to nanometer scale has led to the appearance of a broad range of applications in different materials.[20] Nanoscale oxides such as TiO_2 may have unique physical and chemical properties because of their small size and high density of surface sites.[21] The particle size can influence the properties of the material, increasing the surface free energy by increasing the number of surface atoms and interfaces.[22] In particular, oxide nanotubes, such as TiO_2, are of interest mainly because of their large surface areas, which can originate strong interactions with the solid matrix in which they can be incorporated.[23] These characteristics may contribute to a better interaction and reaction with their environment.[24,25] Thus, TiO_2 nanotubes applied to the surface of zirconia such as yttrium-stabilized tetragonal zirconia polycrystal (Y-TZP) ceramics and linked to MDP monomers, which have an affinity with metallic oxides, may improve bond strength.

The purpose of this in vitro study was to evaluate the infiltration of TiO_2 nanotubes into the surface of a Y-TZP ceramic and to determine whether the bond strength of a resin cement to the infiltrated ceramics may be improved. The null hypotheses tested were that no infiltration would be detected, the addition of TiO_2 nanotubes would not influence the shear bond strength, and no differences

would be found between commercially available bonding agents used in bond strength evaluation.

MATERIAL AND METHODS

This study was divided into 2 stages: the first stage consisted of synthesis of TiO_2 nanotubes and characterization of ceramic surfaces by using confocal laser microscopy, scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) analysis. The second stage consisted of evaluation of shear bond strength with resin cement and different zirconia bonding agents.

The commercially available materials used in this study are presented in Table 1. The TiO_2 nanotubes were synthesized from 10 g of a commercial mixture of TiO_2 anatase powder (titanium dioxide; Sigma-Aldrich, Inc) and 120 mL of alkaline solution of NaOH (10 M), as described by Arruda et al.[23] The mixture was kept at 120°C for 24 hours in a polytetrafluoroethylene (Teflon) open container. This container was heated in a glycerin bath. The entire process of synthesis was carried out at ambient atmospheric pressure. After the alkaline treatment, the mixture was repeatedly washed with 0.1 M hydrochloric acid (HCl) and deionized water to remove the sodium ions and until the pH was neutralized (pH 7.0). Finally, the solution passed through a drying process at 200°C for 24 hours in atmospheric air to eliminate the liquid part and obtain the final powder and nanotubes with a diameter of approximately 10 nm and length of approximately 200 nm.

Slices were obtained from Y-TZP blocks (IPS e.max Zircad; Ivoclar Vivadent AG) by sectioning under water irrigation with a double-faced diamond disk (Wafer blade, 5 inch × 0.15 inch × 0.15 inch; Extec) in a cutting machine (IsoMet 1000; Buehler) to obtain 1.5-mm-thick specimens that were finished with #800 and #1200 silicon carbide papers (Carbimet; Buehler) and polished with 1-μm diamond solution (MetaDi water based suspension; Buehler) on fine-grained felt disks. The specimens were cleaned in an ultrasonic bath, using deionized water (USC 750; Unique Group) for 5 minutes.

The TiO_2 nanotubes were mixed with isopropyl alcohol (Synyh) at a 50 wt% to obtain a paste. This paste was actively applied by rubbing the surface of the ceramic specimen with a microbrush to obtain a uniform, thin layer. The alcohol was then evaporated with light jets of air at a distance of 15 cm. Excess nanotubes were removed by using a dry microbrush. No nanotubes were applied to the control group. The ceramics were sintered in a furnace (inFire HTC Speed; Dentsply Sirona) by following the cycle recommended by the manufacturer. After sintering, the surface was analyzed. Two zirconia specimens, with and without application of nanotubes, were used. Confocal microscopy (Leica DCM 3D; Leica

Table 1. Materials and composition

Material (Manufacturer)	Composition*	Instructions
Single Bond Universal (3M ESPE)	MDP phosphate monomer, dimethacrylate resins, HEMA, Vitrebond copolymer, filler, ethanol, water, initiators, silane	(a) Clean surface with alcohol and dry with compressed air; (b) apply with microbrush to surface for 20 seconds; (c) apply compressed free oil air for 5 seconds; (d) polymerize for 10 seconds
Signum Zirconia Bond (Kulzer GmbH)	Signum zirconia bond I: acetone, 10-MDP, acetic acid. Signum zirconia bond II: methyl methacrylate, diphenyl (2,4,6- trimethylbenzoyl) phosphine oxide.	(a) Clean surface with alcohol and dry with compressed air; (b) Dispense Signum Zirconia bond I and apply with suitable brush to entire surface, air dry for 5 seconds; (c) Apply Signum Zirconia bond II, polymerize for 40 seconds
Z-Prime Plus (Bisco)	Biphenyl dimethacrylate, MDP, ethanol	(a) Clean intaglio surface of restoration; rinse and air dry; (b) apply 1 to 2 coats of Z-Prime Plus, uniformly wetting bonded surface; (c) dry with air syringe for 3 to 5 seconds
RelyX Ultimate (3M ESPE)	Base paste: silane-treated glass powder, 2-propenoic acid, 2-methyl-, 1,1′-[1-(hydroxymethyl)-1,2- ethanediyl] ester, reaction products with 2-hydroxy-1,3- propanediyl dimethacrylate and phosphorus oxide, triethylene glycol dimethacrylate (TEGDMA), silane treated silica, oxide glass chemicals, sodium persulfate, tert-butyl peroxy-3,5, 5-trimethylhexanoate, copper (ii) acetate monohydrate Catalyst paste; silane-treated glass powder, substituted dimethacrylate, 1,12-dodecane, dimethacrylate, silane treated sílica, 1-benzyl-5-phenyl-barbic-acid calcium salt, sodium p-toluenesulfinate, 2-propenoic acid, 2-methyl-, [(3-methoxypropyl)imino]di-2,1- ethanediyl ester, calcium hydroxide, titanium dioxide	(a) Mix base paste and catalyst paste for 20 seconds with spatula to obtain homogeneous mixture; (b) avoid incorporation of air bubbles

HEMA, 2-hydroxyethyl methacrylate; MDP, 10-methacryloyloxydecyl dihydrogen phosphate.   *According to manufacturer information.

Microsystems) was used to make average surface roughness measurements (Ra), with 3 readings made at different locations on each specimen at ×50 magnification. SEM images were made at various pressures (EVO LS15; Zeiss), and the surface atomic compositions of the specimens were evaluated by EDS analysis.

For shear bond strength, 2 factors were analyzed: bonding agents (at 3 levels) and application of TiO_2 nanotubes (at 2 levels). The bonding agents were combined with and without the application of TiO_2 nanotubes for a total of the following 6 groups: without application of TiO_2 nanotubes and Single Bond Universal; with the application of TiO_2 nanotubes before ceramic sintering and Single Bond Universal; without the application of TiO_2 nanotubes and Z-prime; with the application of TiO_2 nanotubes and Z-prime; without the application of TiO_2 nanotubes and Signum Zirconia Bond; and with the application of TiO_2 nanotubes and Signum Zirconia Bond.

Specimens were fixed in 10-mm-high 19 mm polyvinyl chloride tubes with acrylic resin (Jet; Dental Articles Classic), and bonding agents were applied according to the groups previously described by following each manufacturer's recommendations and polymerized by a light-emitting diode device (Valo Cordless; Ultradent Products, Inc) with irradiance of 1000 mW/cm^2. Surgical catheters with an inner diameter of 1.40 mm and a height of 1 mm were used to produce resin cement cylinders (RelyX Ultimate; 3M ESPE). Four cylinders were made from each ceramic specimen, (n=16 per group). The cement was handled according to the manufacturer's recommendations and polymerized for 20 seconds with the light-emitting diode device. After 10 minutes, the surgical catheters were removed with #12 scalpel blades to expose the resin cement cylinders. Specimens were then stored in 37°C deionized water for 30 days. After 30 days of water aging, the prepared specimens were submitted to shear testing in a universal testing machine (Instron 3342; Illinois Tool Works). The measurement of the force during the test was made by using a 500-N-load cell. The specimens were subjected to shear bond strength evaluation by using a 0.2-mm wire loop at a crosshead speed of 0.5 mm per minute. After completion of the shear test, the surfaces of the specimens were analyzed by using a stereomicroscope (Modular Stereomicroscope Leica MZ6; Leica Microsystems) to determine the failure type involved. Failures were classified as adhesive, cohesive, or mixed.

Statistical analysis was performed by using software (Statistica 10; Stat Soft Inc). Shear bond strength data were submitted to the Bartlet test to check the homogeneity of variations. When the homogeneity had been verified, the data were analyzed by using 2-way ANOVA, considering the bonding agents and the addition of nanotubes as an independent variable and shear bond strength (in MPa) as a dependent variable. Multiple comparisons were performed by using the Tukey honestly significant difference (HSD) test (α=.05 for all tests).

RESULTS

The SEM images of the sintered zirconia specimens with and without the application of nanotubes showed that the nanotubes were incorporated into the zirconia surface (Fig. 1). The EDS analysis confirmed that the nanoagglomerates were composed of TiO_2 (Fig. 2,
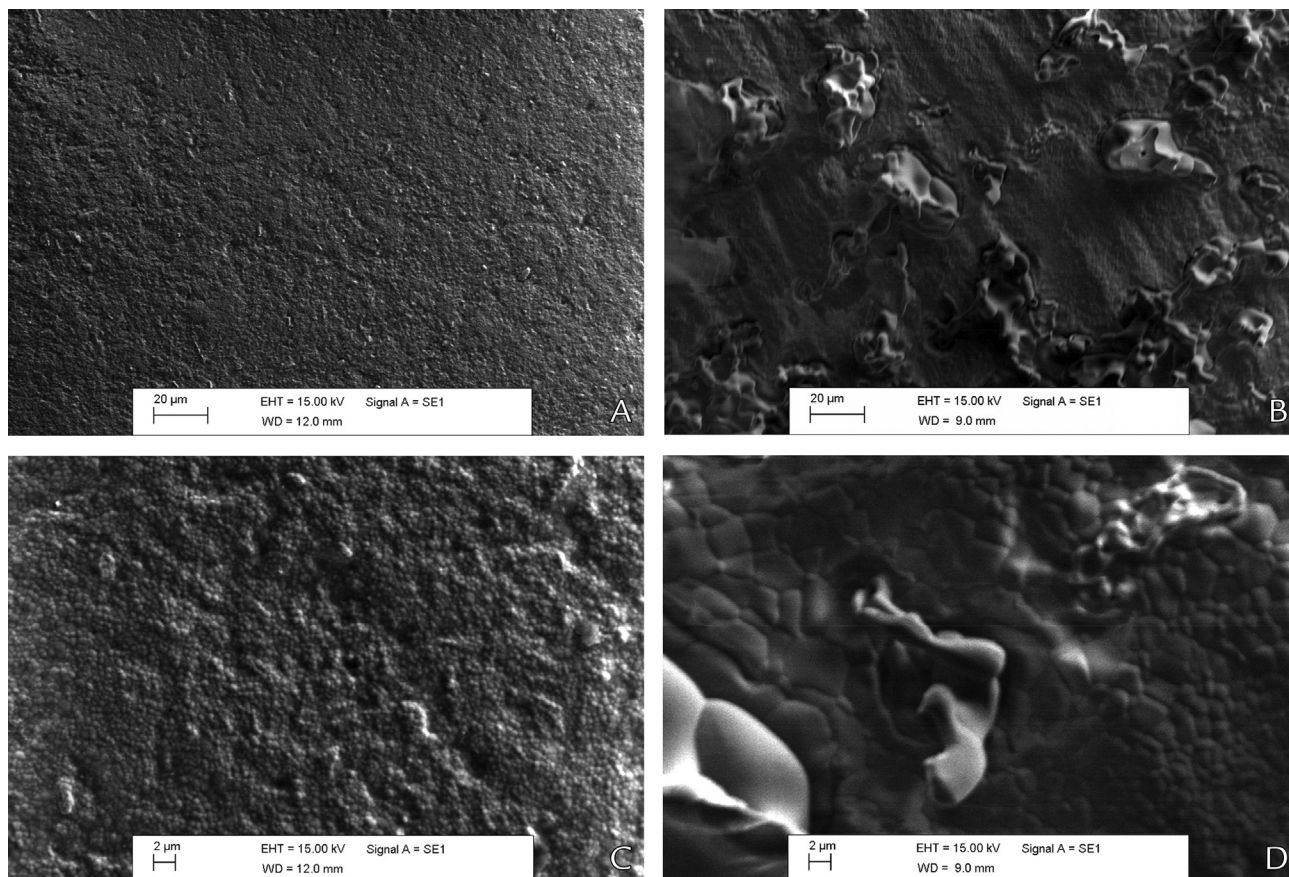
Figure 1. Scanning electron microscopy images of Y-TZP before and after addition of TiO$_2$. A, Y-TZP surface without TiO$_2$ nanotubes (original magnification ×1000). B, Y-TZP surface with addition of TiO$_2$ nanotubes (original magnification ×1000). C, Y-TZP surface without TiO$_2$ nanotubes (original magnification ×4000). D, Y-TZP surface with addition of TiO$_2$ nanotubes. (original magnification ×4000.) Y-TZP, yttria-stabilized tetragonal zirconia polycrystal.
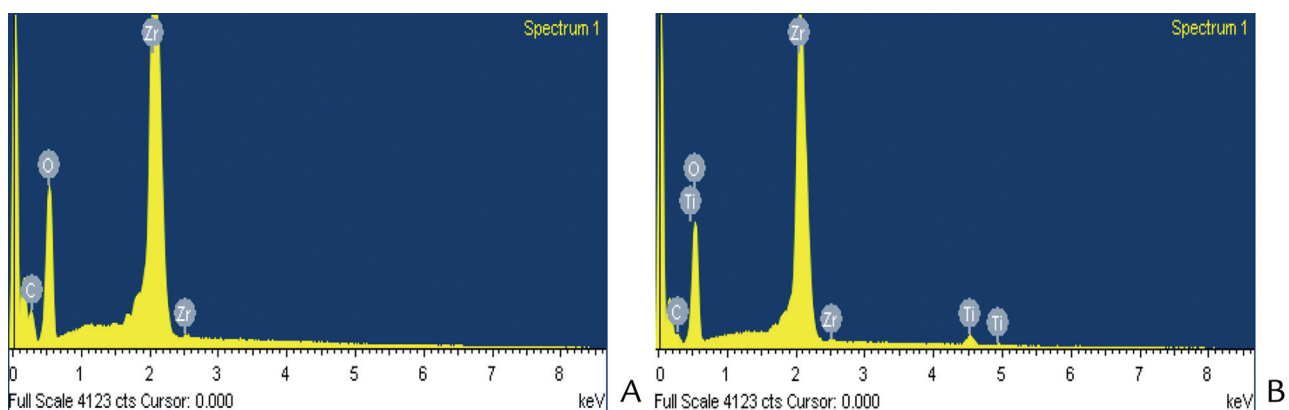
Figure 2. Atomic composition evaluated by EDS analysis. A, Y-TZP without TiO$_2$ nanotubes. B, Y-TZP with TiO$_2$ nanotubes. Selected area of reading: 700 µm^2 and ×200. EDS, energy-dispersive X-ray spectroscopy; Y-TZP, yttria-stabilized tetragonal zirconia polycrystal.

Table 2). Confocal laser microscopy analysis showed an increase in Ra with the application of nanotubes from 532.7 to 689.1 nm (Fig. 3).

Mean values, standard deviations, and statistical differences among the 6 groups for shear bond strength test results are shown in Table 3. Significant differences were found between bonding agents ($P<.001$) but not for the application of nanotubes ($P=.682$). The interaction between bonding agent and addition of nanotubes was significant ($P=.025$). In the groups without the application

Table 2. Atomic composition evaluated by EDS analysis for Y-TZP with and without TiO$_2$ nanotubes

Y-TZP	Element	Weight %	Atomic %
Without nanotubes	C	15.1	32.1
	O	33.6	53.6
	Zr	51.3	14.3
	Totals	100	100
With nanotubes	C	7.7	17.9
	O	37	64.6
	Zr	53.4	16.4
	Ti	1.9	1.1
	Totals	100	100

EDS, energy-dispersive X-ray spectroscopy; Y-TZP, yttrium-stabilized tetragonal zirconia polycrystal.

of nanotubes, significant differences were found among the bonding agents ($P<.001$), with the bond strength varying according to the following sequence: Signum Zirconia Bond > Single Bond Universal > Z-prime ($P<.001$). In the groups with the application of the nanotubes, significant differences were found among the bonding agents ($P<.001$), with no significant differences between Single Bond Universal and Z-prime. The Signum Zirconia Bond group with nanotubes showed the highest bond strength results (20.1 ±3.6 MPa), and the Z-prime group without nanotubes showed the lowest values (6.2 ±4.5 MPa). SEM images after shear bond strength testing showed the presence of TiO$_2$ nanoagglomerates (Fig. 4). Failure modes were adhesive in almost all specimens (97.9%). Mixed failures occurred in 2 specimens (2.1%).

DISCUSSION

The null hypothesis that no TiO$_2$ infiltration would be detected was rejected. The second null hypothesis, however, was accepted, because no statistically significant differences were found between the application or not of TiO$_2$ nanotubes. The third null hypothesis was rejected, because significant differences were found between commercially available bonding agents.

Zirconia has a very dense structure, which prevents the penetration of nanometric structures. For this reason, in the present study, a thin layer of the TiO$_2$ nanotubes was applied to the surface of the Y-TZP before sintering so that the 2 materials could be fused during the high-temperature melting process. SEM revealed that without the application of the nanotubes the surface showed only the typical microstructural characteristics of the zirconia, but after application, nanostructures were present between the zirconia crystals (Fig. 1). The nanotubes were incorporated into the surface of the material but not in a uniform way. Some areas had a higher concentration of nanoagglomerates than others, and some regions lacked the nanoagglomerates. In those regions, the nanotubes could have been removed during the manual process of removing excess. Additionally, the nanotubes might have melted during the sintering process, losing their tubular conformation, and then agglomerated while cooling.

Obtaining homogeneity with the application of nanotubes on the surface of Y-TZP with the method used in the present study was difficult because it was an attempt to mix 2 solid state materials at room temperature. The nanotubes were applied in this way because of the ease of incorporating it into the laboratory process, in which a layer of the paste containing the nanotubes could be applied to the zirconia restorations after machining. The nanotube powder was not mixed with the zirconia powder and subsequently pressed because the purpose of the study was not to modify the material, which already has excellent mechanical properties, but to propose a surface treatment that could improve its interaction with other materials.

Mixing nanotubes with resin-based materials can improve their properties.[23,25] This suggests that TiO$_2$ nanotubes attached to Y-TZP surfaces may lead to improvements in bond strength to resin cements. However, in the present study, the nanoagglomerates incorporated
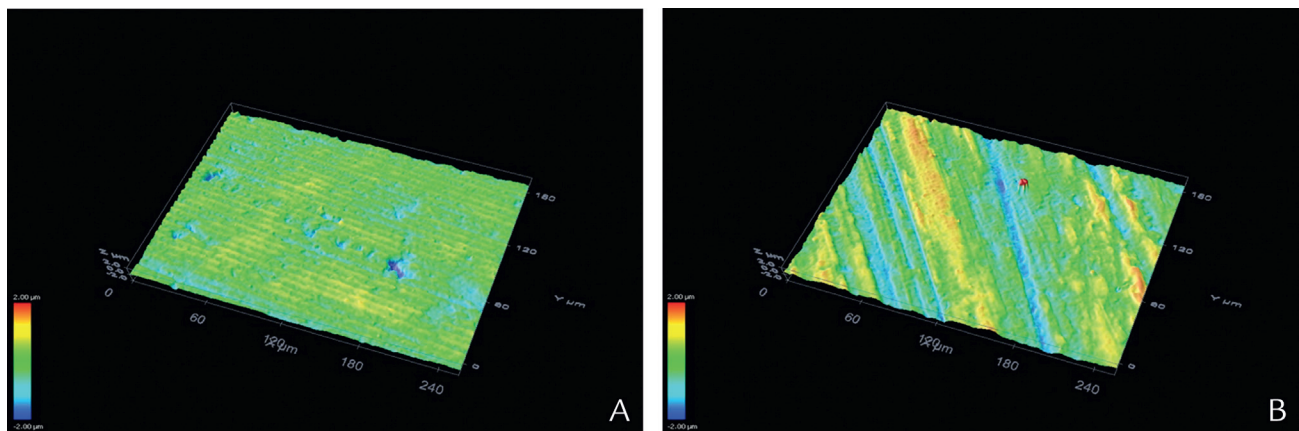
Figure 3. 3D confocal microscopy images. A, Y-TZP without application of TiO$_2$ nanotubes. B, Y-TZP after application of TiO$_2$ nanotubes. Increased roughness represented by red (valleys) and blue (peaks). 3D, 3-dimension; Y-TZP, yttria-stabilized tetragonal zirconia polycrystal.

Table 3. Mean ±SD shear bond strength and number of specimen losses

| Adhesive	Nanotubes	Shear Bond Strength (MPa)	Specimen Losses (%)
Single bond Universal	Without	11.4 ±5.8[b]	1 (6)
Single bond Universal	With	7.5 ±3.5[cb]	1 (6.3)
Signum Zirconia Bond	Without	18.7 ±3.2[a]	0 (0)
Signum Zirconia Bond	With	20.1 ±3.6[a]	0 (0)
Z-Prime Plus	Without	6.2 ±4.5[c]	3 (18.9)
Z-Prime Plus	With	7.6 ±5.1[cb]	3 (18.9)

Different superscript letters indicate statistically significant differences (*P*<.05).

into the Y-TZP surface were not removed (Fig. 4). Nevertheless, despite the limitations of the technique of applying nanotubes to the Y-TZP surface, when incorporated, they remained on its surface even after shear bond strength evaluation.

After being heated, the structure of the nanotubes changed from tubular to amorphous but remained on the nanometric scale, retaining their chemical stability and large surface area.[24] All the coupling agents evaluated in the present study contained monomers of MDP. Because they can chemically bond to metal oxides, MDP monomers could also bind to TiO_2 nanoagglomerates, forming bonds with the oxygen of these structures as well as with oxygen on the surface of zirconia.

Two methods have been used to evaluate bond strength: shear bond strength and tensile bond strength.[26] In the present study, shear bond strength was measured. This method, however, has limitations because it may not provide actual bond strength results due to the nonhomogeneous stress distribution at the adhesive interface.[27] The small bonding area (less than 2.0 mm²) used in the present study reduces this problem.[26] The choice of the type of shear test and its assembly, as well as the distance between the load application and adhesive interface, affect stress distribution. The farther away the load is applied from the bonded area, the greater the tensile stresses generated at the adhesive interface region.[26] In shear testing, tensile stresses are greater than shear stresses, suggesting that tensile forces are responsible for the initial bond failure.[26,28] The wire loop test used in the current study has been shown to have better stress distribution at the edge of the bond area.[29] Nevertheless, despite these criticisms, the shear test is still used for the preliminary evaluation of bonding because it is more straightforward and faster than tensile testing.

The results of the present study have shown that after aging the Single Bond Universal adhesive with nanotubes and Z-Prime with and without nanotubes have lower bond strength values. This is consistent with other studies that showed that the effectiveness of chemical bonds between MDP and zirconia decreases after periods of aging, suggesting that the bonding may undergo hydrolytic degradation.[17,19] In the groups that contained the
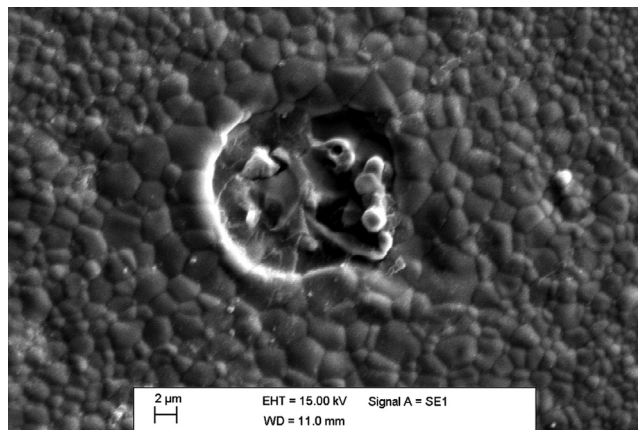
Figure 4. Scanning electron microscopy image after shear bond strength test, showing presence of TiO_2 nanoagglomerates (original magnification ×2000).

Signum Zirconia Bond adhesive, the results showed higher values of bond strength even after aging, which agrees with other studies. These high-bond strength values may be related to the presence of methyl methacrylate in its composition that establishes primary bonds with the methacrylate present in the resin cements, thus improving the bond strength.[16]

The zirconia surface was not pretreated in the current study because the purpose was to evaluate the bond strength of a resin cement to zirconia with different bonding agents with and without the application of nanotubes. Additionally, the Y-TZP specimens were polished to a 1-μm diamond paste before sintering, which might have made the incorporation of nanotubes more difficult.

The bond strength test was conducted with 30-day water storage. The results might have been different if long-term water storage, thermocycling, or mechanical cycling had been used instead.

Although SEM images showed that the incorporation of nanotubes was not uniform, a denser and thicker layer of nanotubes may be applied on the surface of the zirconia in future studies. Moreover, new types of nanometric structures can be tested, and the adhesive interface placed under cyclic mechanical–thermal stress before the bond strength evaluation.

CONCLUSIONS

Based on the findings of this in vitro study, the following conclusions were drawn:

1. For the shear bond strength test, a significant difference was found between the bonding agents evaluated.
2. The application of TiO_2 nanotubes on the zirconia surface had no significant effect on bond strength.

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