# Effect of Short Pulse Laser Patterning on Adhesion of Resin-Matrix Cements to Zirconia

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*Keywords*: *3Y-TZP, DLW (Direct Laser Structuring), Bonding, Adhesion, Surface treatment*

## Introduction

Yttria-stabilized tetragonal zirconia polycrytsal (Y-TZP) owing to its excellent mechanical properties, high degree of biocompatibility and attractive aesthetic properties have emerged as a popular dental biomaterial[1]–[4] Out of all zirconia system 3mol% yttria stabilized zirconia (3Y-TZP) have been used for monolithic crowns, inlays, onlays, dental posts and several other types of indirect restorations[5]. However zirconia is chemically inert and demands surface modification for strong bonding to its underlying substrate[6]–[11] It is highly crystalline in structure and is not readily etched with mineral acids. Several surface modification strategies have been employed so far for increasing adhesion of zirconia to its underlying substrate[12]–[14]. However there is so far no gold standard have been established for adhesion to zirconia. It also have weak adhesion when resin-matrix cements are used for bonding restorations. Air particle abrasion using Alumina ($Al_2O_3$) and Silica($SiO_2$) coated particles are popularly used for surface roughening and increasing bond strength. However they produces surface flaws and can be detrimental to longevity of restorations[14]–[16] Photo machining by the application of LASER (Light Amplification by Stimulated Emission of Radiation) offers an alternative due to its simplicity, flexibility, precision, and reproducibility and relatively low cost for increasing surface roughness and improving adhesion to zirconia[17]–[20] Therefore this study employed Nd:YAG laser for surface structuring and compared with conventional surface modification methods such as alumina blasting and compared the surface qualitatively as well as the resulting bond strengths are also compared.

## Experimental Procedure (or Computational Procedure)

**Green Zirconia Disk:** A 3 mol% yttria-stabilized zirconia spray-dried powder (TZ-3YSB-E, Tosoh Corporation, Japan), was poured into a steel mold (10 mm Diameter, 30 mm Height) of cylindrical shape, a pressure of 200 MPa was applied for 30s and Green zirconia compact disk produced having 10 mm of diameter and 2.32 mm thickness. **Surface Treatments:**
Alumina blasting(ALB): One group was treated with 50 µm alumina($Al_2O_3$) sand for 20 s, at 2.5 bar pressure, nozzle distance 10 mm, at an angle of 45º. The Alumina particle blasting was done with already sintered samples. Laser Groups: The Laser texturing was done on the green zirconia compact disks before sintering for this study a Nd:YAG laser (OEM Plus, SISMA, Italy), (Output Power: 6 W, Pulse width: 35 ns (approximately), spot size: 3 µm, fundamental wavelength: 1.064 µm, maximum pulse energy: 0.3 mJ/Pulse) was used. The laser surface treatment were carried under atmospheric pressure and one air jet stream was used not to allow deposition of powder and debris produced during the texturing process. The two laser textured groups were done as per the parameters given in table 1.

Table1: Laser Parameters used for two laser textured groups.

| **Groups** | **Scanning Speed (mm/s)** | **Number of Scans** | **Power(W)** |
|---|---|---|---|
| D10P1V256(LD10) | 256 | 1 | 0.06 |
| D35P10V128(LD35) | 128 | 1 | 0.6 |

The two laser textured groups are named as per the texturing strategy employed to the Green Zirconia Disk surfaces, LD10: In this groups a squared lines (Grid pattern) was used with each lines crossing at 10 µm distance. Similarly LD35 groups were textured with squared lines (Grid pattern) and each lines crossing each other at 35µm distances and for both the groups the laser parameters are as given in table 1. The sintering was done using a high temperature furnace (Zirkonofen 700, Zirkonzahn, Italy) with a sintering temperature of 1500 °C, a heating and cooling rate of 8 °C/min and 2 h of holding time. After all the surface modification, all the samples were cleaned ultrasonically in IPA(isopropyl alcohol) for 10 min and then in distilled water for 10 minutes to get rid of any grease or contamination from the surface of the samples.

**Roughness Analysis:**

The surface roughness of all the groups were performed using a contact profilometer (Surftest SJ 201, Mitutoyo, Tokyo, Japan) consisting of a diamond stylus with a 2 µm diameter. Three measurements were carried out in three different axis, with speed of 0.5 mm/s and the average roughness (Ra) was obtained.

**Wettability test:** To determine the effect of all surface modification methods on surface wettability, contact angle measurement were carried out using optical goniometer OCA 15 plus (Dataphysics, Germany) using sessile drop method. For the experiment freshly prepared ultrapure deionized water (18.2 Ω) with a dosing
volume of 5 µL at a dosing rate of 2.5 µL were dispensed from a micrometric syringe and the reading was taken after the stabilization of the drop**.**

**Results and Discuss**

Objective: To evaluate the effect Nd:YAG based short pulse laser patterning on green dental zirconia (3Y-TZP) for improving adhesion of resin-matrix cement.

Methods: Yttria-tetragonal zirconia polycrystalline (3Y-TZP) specimens were randomly divided into four groups: As sintered (CTL), Alumina particle blasting (ALB), and two short pulse laser patterns: LD10-Laser structured squared lines (10 µm apart), LD35-Laser structured pyramidal lines (35 µm apart). Surface roughness and contact angle(wettability) and SEM(Scanning Electron Microscope) in each group were evaluated. Specimens of each group were cemented to self-cure resin-matrix cement using 10-Methacryloyloxydecyl dihydrogen phosphate (MDP) containing adhesive and stored in distilled water for 24 h (37°C). Subsequently, shear bond strength (SBS) was measured in a universal testing machine.

Results: All groups with surface modification showed increased surface roughness (CTL: 0.21 ± 0.01µm, ALB: 2.75 ± 0.09, LD10:1.12 ± 0.03 µm, LD35: 2.09 ± 0.03 µm), and wettability (CTL: 46.32 ± 2.97º, ALB: 24.8 ± 3, LD10:19.1 ± 7.4º, LD35: 9.2 ± 2.0º) in comparison to control group as shown in table 2. All surface modified groups significantly increased SBS(CTL: 0.98 ± 1.26 MPa, ALB: 9.69 ± 3.92 MPa, LD10: 9.15 ± 1.54 MPa, LD35: 8.88 ± 2.18MPa) compared to the control group as shown in figure 3.

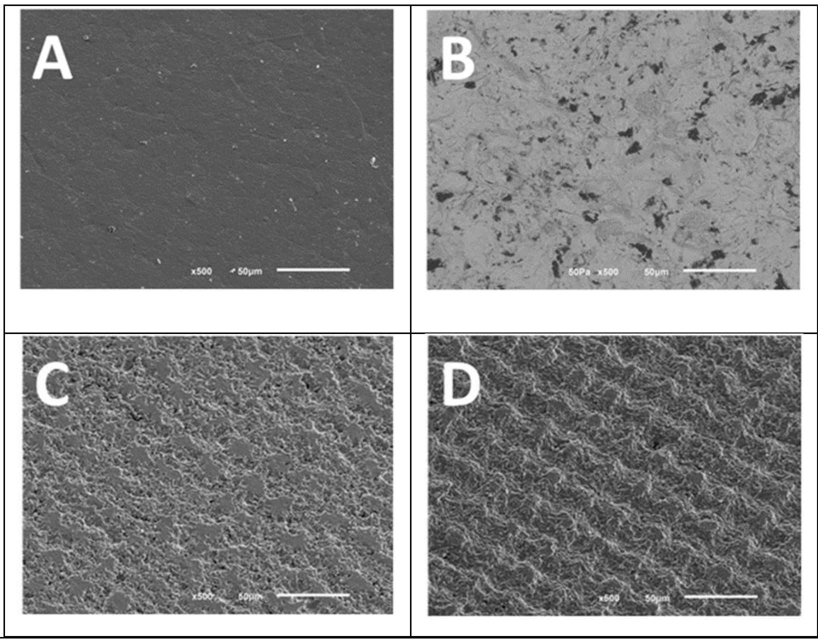


Fig1. SEM micrographs for different surface treatments; A: As sintered (Control Group), B: Alumina particle blasted, C:Laser structured D10P1V256(LD10), D: Laser structured D35P10V128(LD35).

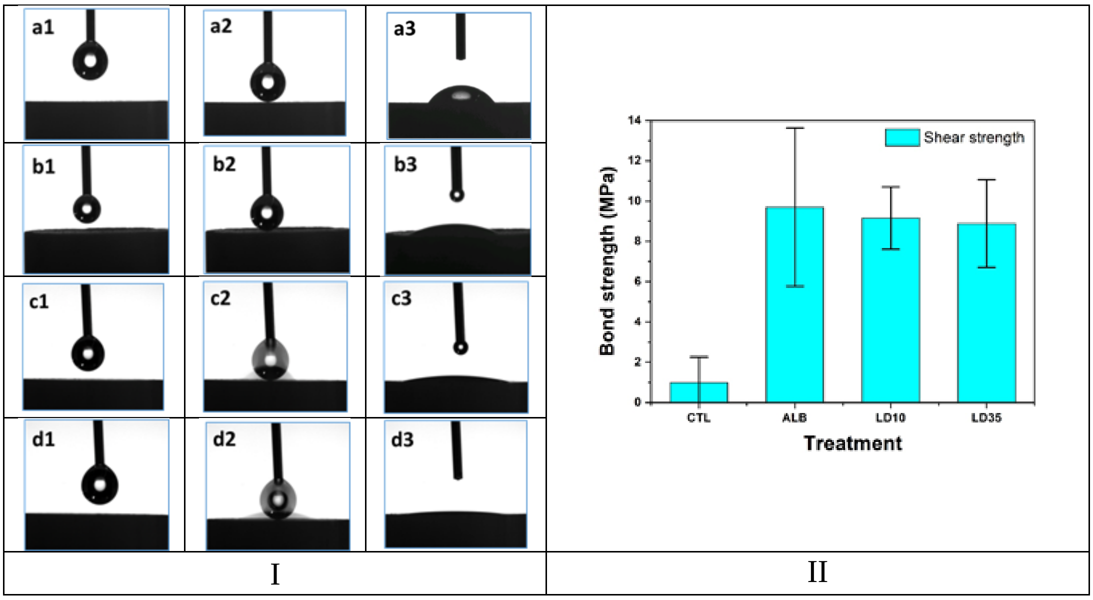


*Fig2(I). Water contact angle for different surface treatments; where the subcript represents the position of the water droplet 1: Start, 2: Touch 3: a1 and a2 and a3: CTL(As sintered), b1 and b2 and b3:ALB( Alumina particle blasted), C1 and c2 and c3: LD10 Laser texured group1. D1 and d2 and d3:LD35 laser Textured group2.*
*Fig2(II): Fig3: Shear Bond Strength(SBS) results of All Surface treated groups of Zirconia with resin-matrix cement.*

## Conclusions:

Under the limitation of this study it can be concluded that Nd:YAG based short pulse laser patterning improved surface morphology, roughness and wettability and yielded to higher shear bond strength of resin cement to zirconia without structural damage to the surface. Although highest SBS value was observed in ALB group, nevertheless the impact surface damage and its effect on the longevity of restoration needs to be studied, moreover the SBS value under thermocycling condition also need to be analyzed in future study for all surface treatments groups.

**Acknowledgments**

This study was supported by FCT national funds, under the national support to R&D units grant, through the reference project UIDB/04436/2020 and UIDP/04436/2020. Additionally, this work was supported by POCI-01-0145-FEDER-031035_LaserMULTICER, CNPq-Brazil (CNPq/UNIVERSAL/421229/2018-7) and CAPES-HUMBOLDT Program (Grant number: 88881.197684/2018-01).

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