

# Strengthening and Toughening of Dental Porcelain by the Inclusion of an Yttria-Stabilized Zirconia Reinforcing Phase

Bruno Henriques, Rafaela Santos, Mihaela Buciumeanu, Júlio Matias de Souza, Filipe Silva, Rubens Nascimento, Márcio Fredel

**Abstract**—Dental porcelain composites reinforced and toughened by 20 wt.% tetragonal zirconia (3Y-TZP) were processed by hot pressing at 1000°C. Two types of particles were tested: yttria-stabilized zirconia ( $ZrO_2-3\%Y_2O_3$ ) agglomerates and pre-sintered yttria-stabilized zirconia ( $ZrO_2-3\%Y_2O_3$ ) particles. The composites as well as the reinforcing particles were analyzed by the means of optical and Scanning Electron Microscopy (SEM), Energy Dispersion Spectroscopy (EDS) and X-Ray Diffraction (XRD). The mechanical properties were obtained by the transverse rupture strength test. Wear tests were also performed on the composites and monolithic porcelain. The best mechanical results were displayed by the porcelain reinforced with the pre-sintered  $ZrO_2-3\%Y_2O_3$  agglomerates.

**Keywords**—Composite, dental restoration, porcelain, strengthening, toughening, wear, zirconia.

## I. INTRODUCTION

THE use of ceramics in dentistry is nowadays the mainstream in aesthetical restorative dentistry. Zirconia is in the forefront of this trend due to its biocompatibility, aesthetics [1], corrosion resistance [2] and good mechanical properties relative to alternative materials. Zirconia-based restorations comprise a strong and thought zirconia substructure that is veneered with a weaker compatible porcelain that is used to mimic the color of real teeth and eventually to reduce the wear of the dental restoration with the opposite teeth.

Zirconia is a polymorphic ceramic with different crystal structure at different temperatures, but keeping the same

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chemistry. Zirconia can be found in three crystalline forms: monolithic; tetragonal and cubic. Pure zirconia is stable in monoclinic phase at room temperature. At 1173°C it undergoes a phase transformation from monoclinic to tetragonal and then to cubic at 2370°C. Above 2690°C zirconia melts. These transformations are reversible upon cooling with the tetragonal to monoclinic (t-m) transformation imparting compressive stresses to the material due to the volume expansion of 4-5% that occurs with the transformation. It is possible to fully or partially stabilize zirconia in its tetragonal or cubic form at room temperature by alloying it with other cubic oxides termed as “stabilizers”. Calcia, magnesia, ceria, alumina or yttria are used for that end. Zirconia is said to be partially stabilized (Partially Stabilized Zirconia – PSZ) when a multiphase form coexists in the material: cubic as the major phase and monoclinic and tetragonal zirconia precipitates, as the minor phase. To date, the best properties are exhibited by zirconia stabilized with  $Y_2O_3$  (yttria), where the whole material is constituted by transformable t-zirconia grains and called Tetragonal Zirconia Polycrystals (TZP). The addition of 2-3 mol% yttrium oxide ( $Y_2O_3$ ) as stabilizing agent results in a fully tetragonal fine-grained zirconia ceramic material with 100% small metastable tetragonal grains (Y-TZP). This is the type of zirconia that has been extensively used in the production of dental frameworks for all-ceramic restorations. Partially stabilized zirconia displays a toughening mechanism that uses the t-m transformation to arrest the crack propagation, and is therefore termed transformation toughening. When a crack arises in zirconia, the stress field generated at the crack tip cause a local phase transformation from the metastable tetragonal phase to monoclinic phase. This transformation is accompanied to a volume increase of the crystals, constrained by surrounding ones, and a compressive stress field is generated at the crack surfaces near the crack tip that tend to pinch the crack shut, thereby hindering its propagation.

Dental porcelains, as well as other several glass-ceramics used in biomedical applications lack in mechanical properties that allow them to be employed in load-bearing applications. Therefore, some authors addressed their efforts to toughen these materials by adding a second high-strength biocompatible phase [3]-[8].

In this work, two types of zirconia particles were used as reinforcing phase in the pressure assisted (hot pressed) sintered composites: yttria-stabilized zirconia ( $ZrO_2-3\%Y_2O_3$ )

agglomerates and pre-sintered yttria-stabilized zirconia ( $ZrO_2-3\%Y_2O_3$ ) particles. The influence of these two types of reinforcing phases in terms of mechanical and wear properties was investigated. Results were compared with monolithic porcelain obtained under the same processing conditions.

## II. MATERIALS AND METHODS

The zirconia ( $ZrO_2-3\%Y_2O_3$ ) agglomerates (named as ZA from now on) were used as received by the manufacturer (Innovnano, Portugal) and blended with the porcelain powders (Vita VM9, Vita) in a rotation machine during 24h. The zirconia content in all mixtures was 20%, vol.%. Porcelain powders are named PORC from now on.

The pre-sintered zirconia powders (named ZP from now on) were obtained out of the sintered agglomerates provided by the supplier. Zirconia agglomerates were sintered in a furnace at 1500°C for 2h. Afterwards, powder mixtures (pure porcelain and zirconia) were ball milled to reduce agglomeration and to enhance mixing, respectively.

Specimens were hot pressed in vacuum, at 970°C for two minutes. The mechanical properties were assessed by the means of a 3-point bending flexural test. The crosshead speed was 0.5 mm/s and the load cell used had 25kN of capacity. The microstructure and fractured surfaces were inspected by SEM/EDS.

The wear tests were applied to the different samples, using the Artificial Saliva (AS) [9] at 37°C (the oral cavity temperature), which chemical composition is given in Table I and a reciprocating ball-on-plate tribometer (CETR-UMT-2) for to evaluate wear characteristics of samples contact pairs (10 mm diameter alumina ball, Goodfellow). These tests consisted in a load applied of 3N in the center of sample, at a frequency of 1Hz and the total stroke length 3mm, during 30 min.

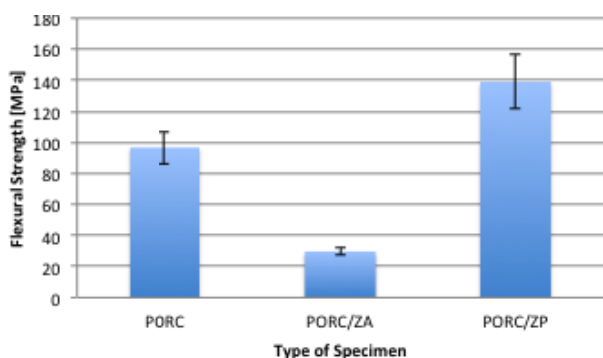


Fig. 1 Flexural strength of the porcelain reinforced composites with zirconia agglomerates (PORC/ZA) and zirconia particles (PORC/ZP)

## III. RESULTS

Fig. 1 shows the flexural strength of the composites PORC/ZA and PORC/ZP when compared to the monolithic porcelain (PORC). The zirconia agglomerates (ZA) showed to produce a detrimental effect on the strength of the composites relative to pure porcelain. On the other hand, the pre-sintered zirconia particles (ZP) showed to improve significantly the

flexural strength of the composite relative to pure porcelain (PORC).

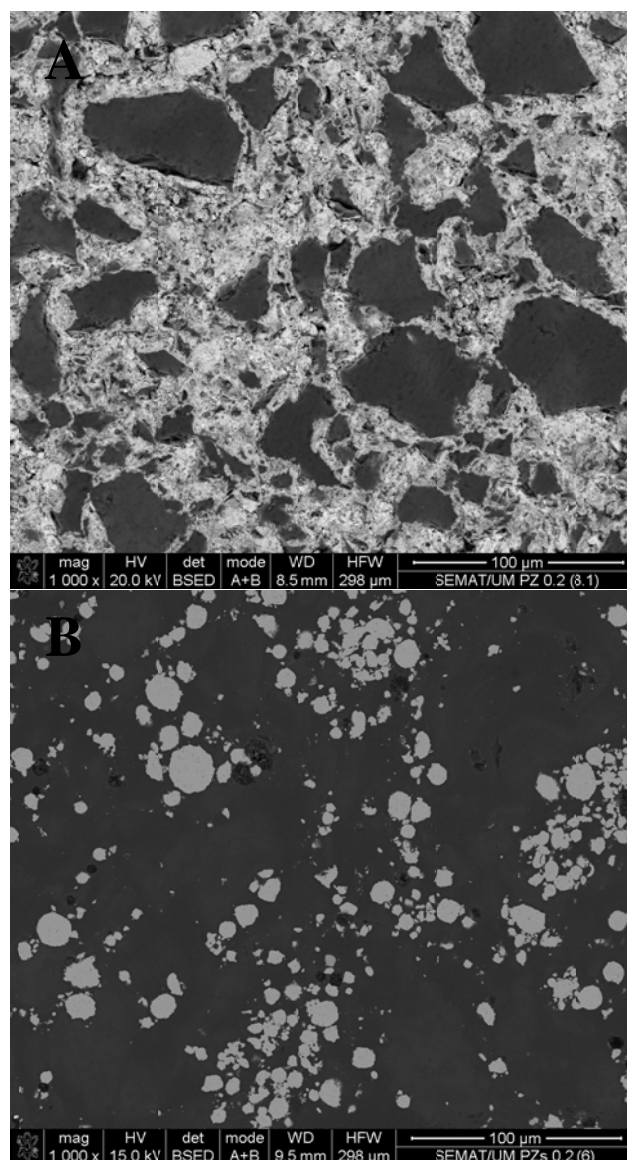


Fig. 2 Micrographs of the porcelain composites reinforced with zirconia agglomerates (PORC/ZA) (A - on the top) and zirconia particles (PORC/ZP) (B - on the bottom). Zirconia appears as white phase and porcelain as dark phase)

TABLE I  
 CHEMICAL COMPOSITION OF THE ARTIFICIAL SALIVA (AS)

Symbol	Quantify (g/L)
NaCl	0,4
KCl	0,4
CaCl <sub>2</sub> .2H <sub>2</sub> O	0,795
Na <sub>2</sub> S.9H <sub>2</sub> O	0,005
NaH <sub>2</sub> PO <sub>4</sub> .2H <sub>2</sub> O	0,69
Urea	1

Fig. 2 shows the micrographs of the zirconia reinforced porcelain composites, PORC/ZA and PORC/ZP. The two microstructures produced are significantly different from each

other, which might indicate different sintering behaviors.

In PORC/ZA samples it is not visible the zirconia agglomerates, suggesting that they were destroyed during the mixing procedure. The white phase in Fig. 2 is the pulverized zirconia powder that covered the porcelain powders and negatively impacted the sintering of the composite.

On the other hand, in PORC/ZP it is possible to see round zirconia particles spread through the porcelain matrix. Few pores can be detected within the porcelain matrix of PORC/ZP samples and they are preferentially located at the vicinities of the ZPs rather than in the porcelain matrix.

In Fig. 3, the detail of the interface between the reinforcing ZP phase and the matrix is presented in high resolution. It shows a good bonding between the ZP and the matrix and a complete infiltration of the matrix inside the topological details of the ZPs.

Fig. 4 shows a plot of the wear result obtained for the different specimens. Porcelain (PORC) specimens exhibited the lowest mass loss followed by the PORC/ZP and then by PORC/ZA specimens.

#### IV. DISCUSSION

The mechanical properties and wear of the composites were strongly influenced by the type of reinforcing phase that was used in each composite: zirconia agglomerates (PORC/ZA) and zirconia particles (PORC/ZP).

The low strength observed in the PORC/ZA composites was due to the destruction of the zirconia agglomerates during the powders mixing process. This produced a fragmentation of the powders in micrometric and nanometric powders that covered the powders of porcelain and did not allowed the fused porcelain powders to bond with each other. Most of the porcelain powders were covered by fine zirconia particles that sinters at 1500°C and not at 970°C as happens with porcelain. The work of [10] suggests that if the zirconia agglomerates were maintained in the powder mixture without being destroyed (switch the ball mill of powders by steering suspension of the mixture in alcohol until complete evaporation) the mechanical strength could be even increased. The mechanism was explained by the infiltration of the porcelain phase into the zirconia agglomerates, leading to a partial spreading of each particle into agglomerates of small zirconia grains (about 1 μm size).

On the other hand, the improvement in the flexural strength of the composite PORC/ZP relative to pure porcelain is explained by the action of the uniformly distributed dense zirconia particles (pre-sintered agglomerates). The zirconia particles act as a second phase that is more rigid than the porcelain matrix, allowing the load transfer reinforcing mechanism to occur from matrix to the reinforcing phase.

Besides the improvement noticed in flexural strength of the PORC/ZA it is also expected an improvement in the toughness behavior relative to pure porcelain [10]. The toughening mechanism is based on the crack deflection around the zirconia particles.

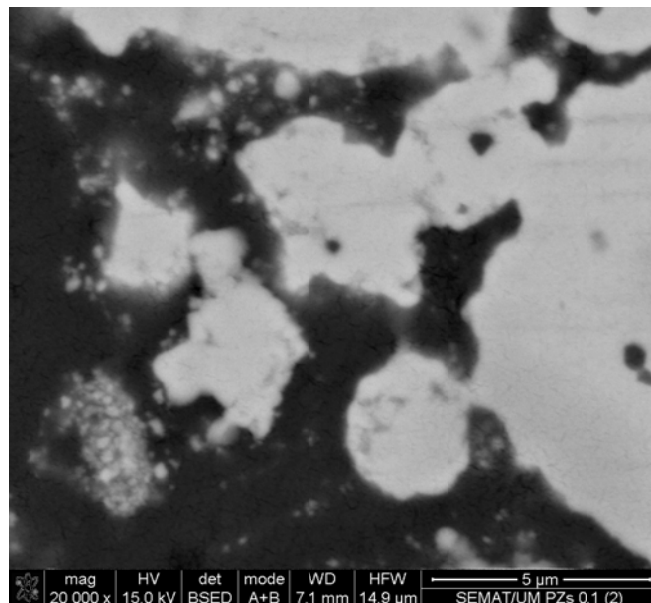


Fig. 3 Detail of the interface between the zirconia particle ZP (white phase) and the porcelain (dark phase)

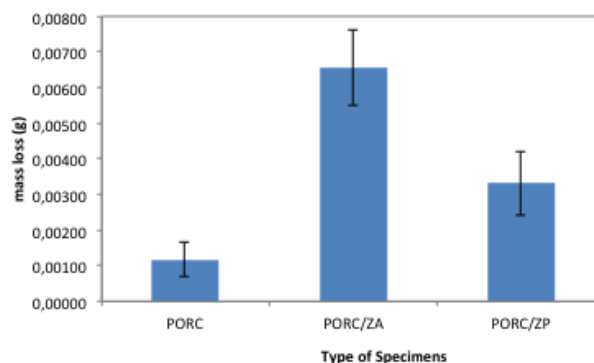


Fig. 4 Wear results, expressed in terms of loss of mass (g), of the following specimens: pure porcelain (PORC), porcelain composites reinforced with zirconia agglomerates (PORC/ZA) and zirconia particles (PORC/ZP)

The low wear properties exhibited by the PORC/ZA specimens are related to the insufficient sintering level of these specimens, underlined by their low flexural strength. The lower mass loss showed by the PORC specimens relative to the PORC/ZP will need further investigation to be fully explained. Nevertheless, it might be close related to the pullout of the zirconia particles (ZP) from the matrix due to the sliding action of the alumina ball during wear tests.

#### V. CONCLUSION

Two types of dental porcelain based composites reinforced by zirconia agglomerates (PORC/ZA) and zirconia powders (PORC/ZP) were produced by pressure assisted sintering. The best mechanical properties were found for PORC/ZP samples due to a good dispersion and good bonding between the reinforcing zirconia phase and the matrix of porcelain. A deterioration in the wear resistance was though observed for these specimens relative to PORC. The pulverization of the

zirconia micro/nano particles during the blending process of the porcelain powders-zirconia agglomerates showed to impart problems to the sintering and densification of PORC/ZA composites, reducing dramatically the strength of the composite and the wear properties. Monolithic porcelain (PORC) showed the best wear properties among the tested specimens.

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