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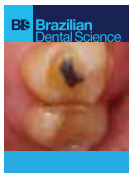

ORIGINAL ARTICLE

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# Sintering dental porcelain with $CO_2$ laser: porosity and mechanical characterization

Sinterização de porcelanas dentárias com o laser de $CO_2$: porosidade e caracterização mecânica

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## ABSTRACT

**Objective:** This study investigated $CO_2$ laser sintering of dental porcelain as an alternative to a conventional furnace by means of porosity, density, fracture toughness and microhardness tests. **Methods:** Two commercial veneering porcelains were chosen for this study: VM7 and VM9 (VITA Zahnfabrik). 25 porcelain green discs (4.1 mm dia. x 2.4 mm) of each commercial brand were confectioned and divided into 5 groups: a control group (oven-glazed specimens) and 4 groups of specimens sintered by continuous $CO_2$ laser (Coherent, USA – 35 W e $\lambda$= 10.6 $\mu$m) with different fluences: 6000, 6900, 12000 and 13800 J/cm$^2$. After sintering, the discs had one of their surfaces mirror polished until the final dimension of 3.5 mm x 2.0 mm was achieved. The amount of superficial pores (%) was assessed by the Image J software through images obtained from an optical microscope (Shimadzu - 100x). Apparent density was measured by the Archimedean's method. Microhardness and fracture toughness (Indentation Fracture - IF) were determined with a Vickers indenter (Shimadzu). **Results:** Porosity ranged between 4.0 to 5.9% for the irradiated specimens; the control group had 6.0 and 4.7% of porosity for porcelain VM7 and VM9, respectively. The density of the VM7 porcelain irradiated in 13800 J/cm$^2$ fluence was significantly higher than the control group. The microhardness and fracture toughness of the irradiated specimens were similar to the control. The indentation marks of some irradiated groups were not possible to achieve because the surface cracked during the test. **Conclusions:** Porcelain sintered with $CO_2$ laser in studied fluences produced a material with superficial porosity similar to that obtained in a conventional oven. Depending on the commercial brand and/or the laser fluence, the irradiated specimens presented a density, fracture toughness and microhardness results that differed from the control group.

## KEYWORDS

Dental materials; Lasers; Dental porcelain; Ceramics.

## RESUMO

**Objetivo:** Este estudo testou o laser de $CO_2$ como um agente de sinterização de porcelanas dentárias e o comparou ao forno convencional por meio das seguintes caracterizações: porosidade, densidade, tenacidade à fratura e microdureza. **Materiais e métodos:** Duas porcelanas comerciais foram escolhidas para o estudo: VM7 e VM9 (VITA Zahnfabrik). 25 discos (4,1 mm dia. x 2,4 mm) de cada porcelana foram confeccionados e divididos em 5 grupos: 1 grupo controle (espécimes sinterizados no forno) e 4 grupos de espécimes sinterizados pelo laser de $CO_2$ de forma contínua (Coherent, USA – 35 W e $\lambda$= 10,6 $\mu$m) em diferentes fluências: 6000, 6900, 12000 e 13800 J/cm$^2$. Após a sinterização, os discos tiveram uma de suas faces polidas. A dimensão final dos espécimes foi de 3,5 x 2,0 mm. A contagem de poros superficiais (%) foi feita pelo programa Image J (domínio público) através de imagens obtidas em um microscópio óptico (Shimadzu - 100x). A densidade aparente foi medida por Arquimedes. A microdureza e a tenacidade à fratura (método IF - Indentation Fracture) foram determinadas por um indentador Vickers (Shimadzu). **Resultados:** A porosidade variou entre 4,0 e 5,9% para os espécimes irradiados; o grupo controle apresentou a porosidade de 6,0 e 4,7% para o grupo controle das porcelanas VM7 e VM9, respectivamente. A densidade da porcelana VM7 irradiada na fluência de 13800 J/cm$^2$ foi significantemente maior do que a observada no grupo controle. A microdureza e a tenacidade à fratura dos espécimes irradiados foram similares ao grupo controle, porém em alguns grupos não foi possível se obter as marcas de indentação devido ao trincamento da superfície, o que inviabilizou o teste. **Conclusões:** A sinterização com o laser de $CO_2$ produziu uma porcelana com porosidade superficial semelhante àquela obtida em forno convencional. Dependendo da marca comercial ou da fluência do laser, os resultados de densidade, tenacidade à fratura e microdureza diferiram dos do grupo controle.

## PALAVRAS-CHAVE

Materiais dentários; Lasers; Porcelana dental; Cerâmica.

## INTRODUCTION

In modern dentistry, ceramics are an important material to the patient and professional when considering an esthetic procedure. Within this context, ceramics, especially the veneering porcelain, are highlight materials responsible for reproducing dental color and translucency [1]. Researchers look forward to new ceramic materials and manufacturing procedures that offer esthetic characteristics combined with sufficient mechanical properties to support the chewing efforts [2].

Ceramic processing quality is determined by many factors, such as powder composition, morphology (surface area, particle size and shape), agglutination process and the firing cycle [3]. Considering the fire cycle, sintering is the final stage of ceramic manufacturing and may be described, in general, as a process in which a compacted powder is thermal activated to generate a solid. Thus, all the aspects of this process are commonly studied, like pressure conditions, atmosphere and heating rates [4]. Beyond the conventional furnace firing, there are many other sintering techniques that include hot pressing, microwave, electrical discharge and laser [5-7].

In 2005, Macedo, ZS and Hernandes, AC [7] sintered a ceramic material (bismuth titanate - Bi4Ti3O12) using a continuous $CO_2$ laser as the main heat source. Compared to conventional sintering in an electrical furnace, both techniques resulted in similar density of the material, regardless of some microstructural differences that were found. Laser sintering was 10 times faster than the conventional process and reached 99% density at lower temperatures.

Recently, literature has focused on the laser-assisted prototyping process of ceramic materials [8-11]. Shortening the production time of small ceramic parts was the great advantage related to this process. This methodology uses a scanning laser system (usually YAG laser; $\lambda = 1.064$ $\mu$m) to produce small porcelain pieces with the same density than a conventional sintered one, despite a slight reduction in mechanical strength [10, 12]. In 2005, Li and Shaw studied the microstructure of a dental porcelain sintered in a $CO_2$ laser-assisted prototyping process [13]. The authors estimated the temperature distribution and the leucite content in the laser-densified porcelain, but no mechanical characterization was conducted.

The use of $CO_2$ laser for dental ceramic sintering may emerge as an alternative to resistive furnace and can provide high densification of reduced thickness restorations. Nevertheless, there is a lack in the dental literature about the use of laser sintering porcelain pieces. This study tested the continuous $CO_2$ laser as an alternative heat source to porcelain sintering. The hypothesis tested was that porcelain specimens sintered by $CO_2$ laser are similar to oven-sintered specimens regarding porosity, density, fracture toughness and microhardness.

## MATERIALS AND METHODS

### Preliminary tests

There was not a methodology developed for laser processing of dental porcelains in the literature. Thereby, some attempts were made to define a methodology with fewer interfering factors.

A $CO_2$ laser device (Coherent, USA) with a nominal power of 35 W and wavelength of 10.6 $\mu$m was used in this study. The laser spot was set at 0.8 cm of diameter (optical table assembly is shown in figure 1). Veneering dental porcelain VM9 (Vita Zahnfabrik) was tested. A metallic device was used for the specimens' confection; the dimensions of the green disks were 2.4 mm high by 4.1 mm diam.

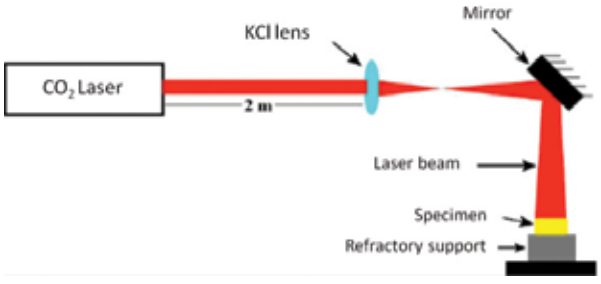


**Figure 1** – Schematic representation of optical table.

Polyvinyl alcohol (PVA) was first used as a binder as described in a previous study [7]. During the manufacturing of the green body, specimens were pressed with a load of 14.7 KN for 10 s in a mechanical press. After sintering, the specimens were mirror polished (Ecomet 4, Buehler) with diamond suspensions (45, 15, 6 and 1 $\mu$m), analyzed in an optical microscope (100X) and photographed. Pores were identified in micrographs with the aid of a computer program (Photoshop 8, Adobe) and the fraction of pores was calculated by the Image J (public domain) software (Figure 2).

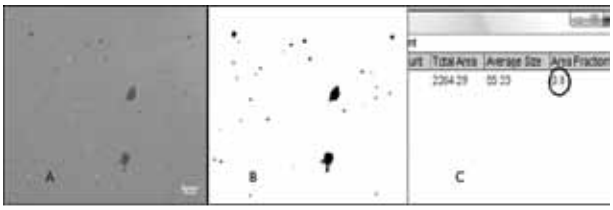


**Figure 2** – Surface porosity determination. A – image of porcelain specimen obtained by optical microscope; B – adjustment of micrograph's contrast and brightness (Photoshop 8) highlighting the pores; C – The fraction of pores determined by the Image J Software.

Specimens were sintered using 4 laser irradiances (17, 18, 20 and 23 W/cm$^2$) and 6 exposition time intervals (40, 60, 80, 120, 300 and 600 s), totaling 24 experimental conditions (n = 3). Fluence ranged from 680 to 13800 J/cm$^2$.

The control group consisted of discs sintered in a conventional oven (Kerampress – Kota), following the porcelains manufacturer's instructions (table 1).

This methodology produced specimens with a high amount of superficial pores (up to 18%) compared to other previous studies [14] and to the control group (3.2 %).

Nevertheless, this previous analysis based on superficial porosity, allowed for defining the best laser irradiance/time correlation (20 and 23 W/cm$^2$ for 5 and 10 min). It corresponded to fluences of 6000, 6900, 12000 and 13800 J/cm$^2$.

The temperature variation on the porcelain surface was measured by a thermocouple probe and pointed to a maximum temperature of 950 °C (20 W/cm$^2$) and 1100 °C (23 W/cm$^2$), achieved after approximately one and a half min of laser exposition. After achieving the maximum, the temperature suffered little variation until the laser incidence was completed.

**Table 1** – Sintering cycles of studied porcelains

| | VM7 | VM9 |
|---|---|---|
| Pre-drying (min) | 6 | 6 |
| Start temp (°C) | 500 | 500 |
| Heating rate (°C/min) | 55 | 55 |
| End temp (°C) | 910 | 910 |
| Hold time (min) | 1 | 1.5 |
| Cooling time (min) | 6 | 6 |

## Applied methodology

The adopted methodology for this study was based on the preliminary tests described above.

Two commercial porcelains were analyzed: VM7 and VM9 (VITA Zahnfabrik). Distilled water was used as a binder due to the previous negative experience with PVA. The agglutination of porcelain and water was similar in technique to that used in prosthetic laboratories. The green specimens were not pressed. The irradiance and times tested were 20 and 23 W/cm$^2$ for 5 and 10 min. Then, five experimental conditions, for each commercial porcelain, were tested (n = 5): the laser fluences of 6000, 6900, 12000 and 13800 J/cm$^2$ and the control group (oven sintered – sintering cycles are described in table 1).

These specimens were also mirror polished and characterized as described in the last topic regarding superficial porosity. The final specimen configuration (after polishing) was 2.0 mm in thickness and 3.5 mm in diameter.

The density of the sintered specimens was calculated by the Archimedean's method. The specimens' mass were measured on an analytical balance in two forms: dry (mass air) and water immersed (mass water). The specimen's density ($\rho$) was calculated by the following equation:

$$(1)\quad \rho = \left( \frac{mass_{air}}{mass_{air} - mass_{water}} \right) \cdot \rho_{water}$$

where $\rho_{water}$ is the water density at room temperature.

For the mechanical characterization, the microhardness and fracture toughness (indentation fracture test - IF) of the materials were determined. Two Vickers indentations (2 Kgf load, 20 s) were made over the polished specimens' surface (MVK-H-3 microhardness tester – Mitutoyo).

Radial cracks were used to measure the fracture toughness, according to the following equation:

$$(2)\quad K_{lc} = 0.016(E/H)^{0.5}(P/c^{1.5})$$

where P is the applied load, c is the radial crack length, E is the elastic modulus of porcelain and H is the Vickers Hardness Number found.

All results were submitted to one-way ANOVA and a Tukey's post-hoc testing ($p < 0.05$).

## RESULTS

### Porosity

Table 2 presents the superficial pore percentage observed in the VM7 and VM9 porcelain specimens.

There were no statistically significant differences between the amount of pores obtained by a traditional porcelain oven and laser sintering for both porcelains.

**Table 2** – Means of porosity (%) and standard deviations ( ) for studied porcelains

| Irradiance (W/cm²) | Time (min) | Pores % * | |
|---|---|---|---|
| | | VM7 | VM9 |
| 20 | 5 | 5.6(2.3) | 5.9(1.2) |
| | 10 | 5.5(1.4) | 5.7(1.3) |
| 23 | 5 | 4.0(2.0) | 4.8(1.1) |
| | 10 | 5.8(1.4) | 5.2(0.8) |
| Oven | - | 6.0 (2.8) | 4.7 (2.5) |

*There were no statistically significant differences between groups.

### Density

Figure 3 shows the density observed in the VM7 and VM9 specimens.

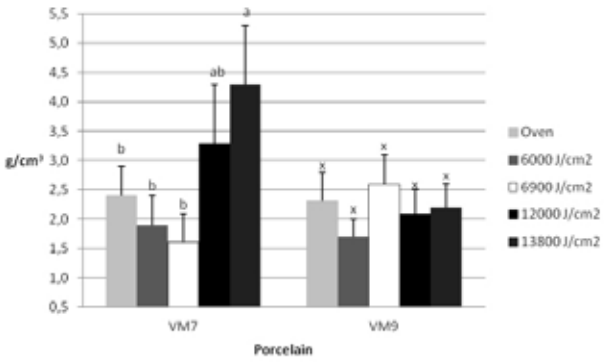


**Figure 3** – Means of density for porcelains according to treatment. Same letters correspond to similar results (statistical analysis was proposed for each material separately).

The VM7 porcelain that was irradiated for 10 min showed an increase in densification compared to the other conditions. The laser sintered VM9 showed similar density to that obtained in the furnace group, independently of the irradiation conditions.

### Microhardness and fracture toughness

Both microhardness and fracture toughness test results revealed no statistically significant difference between the conventional sintering and the $CO_2$ laser methodology (table 3). Some results were not listed in the table because the VM9 specimens irradiated for 5 min and the VM7 specimens irradiated for 10 min presented irregular marks after indentation, not allowing for the correct measurement.

**Table 3** – Means and standard deviations of Vickers Hardness (VH) and fracture toughness (KIC) for porcelains according to treatment

| Irradiance (W/cm²) | | 20 | | 23 | | Oven |
|---|---|---|---|---|---|---|
| Time (min) | | 5 | 10 | 5 | 10 | - |
| VM7 | $K_{IC}$(MPa.m$^{1/2}$) | 1.2(0.1) | - | 1.4(0.2) | - | 1.1(0.1) |
| | VH (GPa) | 4.9(0.4) | - | 4.6(0.2) | - | 5.3(0.5) |
| VM9 | $K_{IC}$(MPa.m$^{1/2}$) | - | 1.0(0.1) | - | 1.1(0.1) | 1.0(0.1) |
| | VH (GPa) | - | 4.8(0.4) | - | 4.7(0.3) | 5.3(0.3) |

## DISCUSSION

The hypothesis of this study was partially accepted because despite the fact that the porosity did not differ among the studied conditions, the density and the mechanical properties of some irradiated groups differed from the control group.

This study tested dental porcelain sintering by the use of $CO_2$ laser irradiation. This technique significantly differs from the traditional furnace method, in terms of heating/cooling rates and thermal gradient. The literature suggests that different heating rates (10 °C to 50 °C/min) for leucite-based porcelains is not that critical, since it may not affect its densification [15]. Nevertheless, when using laser, the heating rate is highly increased. This situation may lead to the formation of distinct zones on the porcelain's body with different microstructure and densification taxes [16].

VM9, a leucite-based porcelain presented the same Archimedean's density for both conventional and laser sintering methods. The apparent density of the VM7 porcelain showed a significant increase when a fluence of 13800 J/cm$^2$ was applied. What distinguishes the VM7 from the VM9 porcelain is its microstructure. VM7 does not present a crystalline content [17]. A possible explanation for this remarkable densification of the VM7 porcelain, when exposed to laser, could be a free diffusion of entrapped gases all over the amorphous matrix without a crystallization movement occurring simultaneously.

The temperature achieved by laser on the specimen's surface (950 – 1100 °C) was higher than the sintering temperature (910 °C) of the studied porcelains, as well as the holding time (1 min in furnace). The reduction in porosity of porcelain is expected to be more sensitive to temperature than to sintering time. A higher $CO_2$ laser irradiance maintained for an extended time should favor the diffusion of entrapped gases through the matrix as the viscosity of the material decreases [18,19], but the effect of temperatures maintained above the specified by manufacturers is uncertain. [15].

Regarding superficial porosity, this study showed that it is possible to keep higher temperatures for prolonged periods without an increase in the volume of pores.

Total porosity found in oven sintered porcelains, determined in a previous study, was lower (~3.5%) [14]. This difference may be explained in terms of the known sensitivity of the porcelain manufacture to operator. Another remarkable aspect is that no vacuum was needed for the laser sintering; nevertheless the fraction of pores observed was near the ones obtained in conventional oven sintering.

Hardness and fracture toughness numerical changes could point to microstructural modification in the studied materials but the values did not change. The values of hardness and fracture toughness found in the groups where indentation marks were possible to achieve are consistent with the literature [20-22].

VM7 specimens irradiated for 10 min and VM9 specimens irradiated for 5 min had at least three failures during indentation, which excluded them from comparison with others. Gaussian distribution of the laser beam generates

a radial temperature gradient, with the highest temperature at the center of the laser beam [9,16]. The gradient problem was avoided using a laser spot 50% higher than the specimen diameter, but differences in the distinct specimen's areas may have occurred anyway. Thereby, temperature differences on top of the specimen and its base could have led to the generation of cracks or stress concentration within the material and thus cause the failure after indentation. This gradient problem was emphasized by the Li and Shaw study, that observed that in laser irradiated specimens there is a formation of heterogeneous zones with different leucite content all over the specimen [13].

Another explanation for the impossibility of measuring indentation diagonals would be the entrapped gases situated sub-superficially. The abrupt increase in temperature when the laser was fired may have produced a superficial glassy layer and also may have precluded the gradual loss of the binder to the atmosphere. This condition could have resulted in a large amount of pores situated sub-superficially [23].

More studies must be carried forward analyzing other aspects of irradiated porcelain such as color, biaxial flexural strength and microstructure. Nevertheless, this study is the first to evaluate the mechanical implications of laser sintering of dental porcelains and its results suggest that some adjustments in technique for each material individually may lead to better results. The studied laser irradiances produced specimens with hardness, fracture toughness and superficial porosity similar to those obtained by the conventional oven sintering but with a reduced sintering time.

## CONCLUSIONS

In relation to porosity and density the results observed after $CO_2$ laser sintering were similar to those achieved in traditional oven sintering of dental porcelain.

Mechanical properties of the irradiated porcelain remains uncertain, since some irradiated specimens failed after indentation. It suggests the necessity of a deeper microstructural analysis of the dental porcelain submitted to this sintering technique.

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