Bioengineered and Biocompatible Zirconia based Ceramics for Tissue Engineering Applications

G. Sankar, S. Meenaloshini, R. Dinesh

Abstract*: This research work explains the densification behavior, mechanical properties, and microstructure of high-purity titanium oxide (TiO_2) and tricalcium phosphate (TCP)-doped Y-TZP where different weight percentage of TiO_2 varied from 0 to 10wt% and a fixed percentage of 15wt% for tricalcium phosphate were used in this research work. The preparation of the samples was done by uniaxially pressing the samples at 200MPa into circular discs and rectangular bars and pressureless-sintered at temperatures ranging between 1200˚C to 1400˚C for 90 minutes holding time. The microstructure of the samples was characterized using the scanning electron microscope (SEM). The obtained results were analyzed for mechanical properties i.e bulk density, compressive strength, and Vickers hardness respectively. The results had shown significant improvement in terms of mechanical properties with the addition of dopants to the pure Y-TZP powder. In addition to that, the dopants have reinforced and toughened the samples. The results obtained for the mechanical properties of the TiO_2 and TCP-doped Y-TZP ceramics were 4.89Mgm^{-3} and 10.67GPa for density, and Vickers hardness, respectively, for the composition of 10wt% TiO_2/15wt% TCP and 75wt% ZrO_3 sintered at 1400˚C with 90 minutes holding time.

***Index Terms*: Titanium Oxide, Tricalcium phosphate, Zirconia Mechanical Properties, Microstructure**

I. INTRODUCTION

Bioceramics are widely used for biomedical applications in the recent era, as this bring lesser harm to the human body. However, the production of scaffolds is a challenge in the technology of biomaterials [1-4]. These biomaterials have tremendous uses in different areas, like for medical applications, specifically for orthopedics implants and dental implants [5]. For the past years, Tricalcium Phosphate (TCP) has been known as the most valuable implant material that is being used to repair bone defects. On a contrary, the use of TCP for biomedical implants has some limitations as their mechanical properties make the material brittle and poor fatigue resistance [6-7]. Generally, the mechanical properties of tricalcium phosphate, hinders the load-carrying applications [8].

Inert ceramic oxides like zirconia have high tribological properties [9]. This being the reason, zirconia has drawn attention as its possibility to obtain a nanograined bulk ceramic and a controllable microstructure. In addition to that, zirconia possesses other intrinsic physical and chemical properties like hardness, wear resistance, low coefficient of friction, elastic modulus, chemical inertness, ionic conductivity, electrical properties, low thermal conductivity, and high melting temperature [9]. Hence, zirconia can be mixed with tricalcium phosphate to make bioceramics composites, which would combine the biocompatibility of the tricalcium phosphate and high tribological properties of zirconia. The addition of TCP in zirconia matrix increases the mechanical properties and partially prevents the inverse allotropic transformation of zirconia [10]. However, there is tendency of poor mechanical properties of zirconia and TCP composites due to the allotropic transformation of zirconia from the tetragonal to monoclinic phase [11].

In order to retain the biocompatibility and mechanical properties, it is necessary to introduce a reinforcing agent like ceramic oxides that would contribute towards the enhancement of mechanical properties. In comparison to ceramic oxide agents, Titanium Oxide (TiO_2) has been used widely in orthopedics applications especially, because of its excellent biocompatibility and its chemical stability in aqueous environments and chemical inertness [12-16]. Due to this property, TiO_2 has been chosen as the agent of reinforcement in this research work. It would be discussed in this paper the influence of titania on the densification, hardness, and microstructures. The titania content would vary from 0wt%, to 10wt%. The samples were sintered at 1200˚C, 1250˚C, 1300˚C, 1350˚C and 1400˚C with a holding time of 60 minutes, 90 minutes and 120 minutes.

II. MATERIALS AND METHODS

The TiO2 and TCP doped zirconia (Y-TZP), with different TiO2 and TCP contents were synthesized through co-precipitation method. The different weight percentages of TiO2 and TCP were mixed evenly with Y-TZP in ethanol solution using an ultrasonic machine. Then after, to ensure homogenous mixture, ball milling operation was performed for 1 hour. Then, the slurry was dried at 60°C in an oven for 12 hours. Upon drying in the oven, the dried sample was then sieved using a 212µm mesh stainless steel sieve to obtain a TiO2-TCP-YTZP powder, that was later used to press the bar and disc samples. The mixed powder was pressed in a hardened steel circular (20 mm in diameter) and rectangular

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(80 x 50 x 8mm) mold and die set under a hydraulic pressure of 500 MPa. The samples were subsequently subjected to cold isostatic pressing (CIP) at a pressure of 200MPa with a holding time of 5 minutes.

In order to further harden the samples, the pressing process was followed by sintering the samples by ambient pressure using a heating furnace (ModuTemp). The sintering temperatures were ranging from 1200˚C to 1400˚C. Some sintering parameters were set in the furnace. The samples were sintered at a ramp-rate of 10˚C/min for both heating and cooling and holding time of 1, 1.5 and 2 hours prior to cooling to room temperature. Then all samples were polished using SiC papers (120, 240, 600, 800). These grades indicate the polishing done using coarse to rough papers. The samples were also diamond paste-polished to 6µm, in order to obtain an optical reflective surface.

Scanning Electron Microscope (Philips XL30 ESEM) was used to investigate the microstructure and morphology of the powders of the sintered samples.

Archimedes' principle using an electronic balance retrofitted with a density determination kit (Mettler Toledo, Switzerland) was used to determine the bulk density of the sintered samples.

Vickers indentation method was used to obtain the Vickers hardness measurements (Future Tech., Japan). This test was conducted on polished samples. The indentation load was kept constant at 98.1 N for a loading time of 10 s. The values of KIc were computed using the equation derived by Niihara et al. [17].

III. RESULTS

A. Bulk Density

Fig. 1 shows the densification behavior of various compositions and sintering temperatures on the bulk density of zirconia for 1.5h holding time. The densification behavior of the zirconia composites with the addition of TCP and TiO_2 in terms of bulk density was studied and observed for various sintering temperatures. Higher density values were obtained at a relatively higher sintering temperatures ranging from 1300˚C to 1400˚C. The density values show a result ranging from 4.63 to 4.9 g/cm^3. Based on these temperatures, the 10wt% TiO_2/15wt% TCP and 75wt % ZrO_3 samples achieved the highest bulk density, approximately 4.89 g/cm^3. The density value obtained is approximately 98% of the minimum theoretical density value of 5.0 g/cm^3 for zirconia. Sintering at a high temperature i.e 1400˚C with 90 minutes holding time shows increase in bulk density for all compositions. Thus, it can be determined that the optimum sintering temperature is 1400˚C. The sintering temperature has been the most significant contributor towards the increase in the overall bulk density, where it would have reduced the porosity of the samples during the sintering process. This results show a similar comparison with Alumina-10wt% TCP composites sintered with different amount of titanium oxide (2.5 wt% to 10 wt%) at various temperatures 1500˚C to 1600˚C for 1 hour, where an optimum densification was obtained at 1600˚C with 5wt% TiO_2 [18].

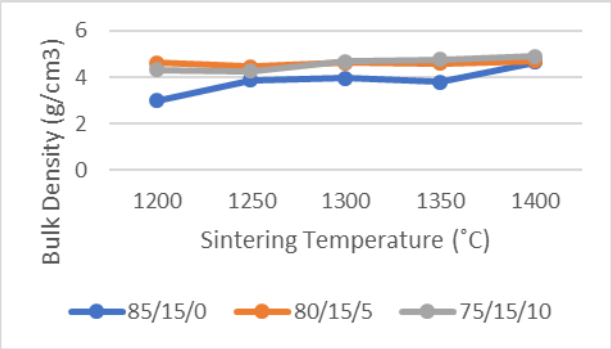

Fig. 1 The effect of various compositions and sintering temperatures on the bulk density of zirconia for 1.5h holding time

B. Hardness

Fig. 2 shows the mechanical properties of the sintered composites based on Vickers hardness relative to the dopant content and sintering temperatures. The effect of TiO_2 and TCP additions on the Vickers hardness of zirconia sintered from 1200˚C to 1400˚C has shown a substantial result. The Vickers hardness values of the compositions varied in a quite similar pattern as compared to bulk density values. Samples sintered at higher temperatures i.e 1300˚C to 1400˚C displayed hardness values ranging from 9.436GPa to 10.67GPa. The highest hardness value, 10.67GPa was achieved when the samples were sintered at 1400˚C with the composition of 10wt% TiO_2/15wt% TCP and 75wt %ZrO_3. In addition to that, composites of 5wt% TiO_2/15wt% TCP and 80wt %ZrO_3 also showed a relatively high Vickers hardness value, 9.93 GPa. The results obtained show, that the additives were playing a major role in contributing towards the hardness of zirconia sintered at high temperatures ranging from 1300˚C to 1400˚C. Moreover, the bulk density values and Vickers hardness values are directly proportional with each other, which is in accordance to theoretical findings based on literature reviews.

Hence, based on the results of bulk density and Vickers hardness, as shown in Fig. 1 and 2, there is a similar increasing trend in bulk and hardness for composition of 10wt% TiO_2/15wt% TCP and 75wt % ZrO_3. The increase in density in the composites may prove stronger bonding between the grains in the sintered composites, which suggests that they can achieve greater hardness and material strength. The significant improvement of the characteristic of 15wt% TCP and 10wt% TiO_2 compositions also can be explained due to the liquid phase between tricalcium phosphate and titanium oxide that has been formed. This will lead to the contribution towards better densification and Vickers hardness [19].

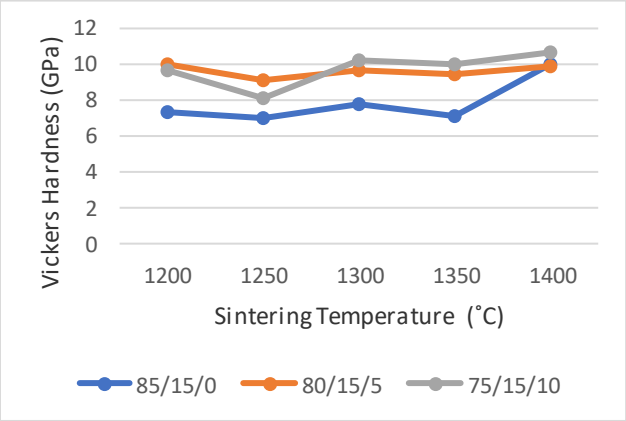

Fig. 2 The effect of various compositions and sintering temperatures on the Vickers hardness of zirconia for 1.5h holding time

C. Compressive Strength

Figure 3 shows the effect TiO_2 and TCP additions and the sintering temperatures on the compressive strength in zirconia. The influence of sintering temperatures quite obviously show that all samples sintered at high temperatures, regardless of percentage of dopant, displayed a high compressive strength value. A similar trend was observed in Fig. 1 and Fig. 2 for bulk density and Vickers hardness. The highest compressive strength was observed for the composition of 10wt% TiO_2/15wt% TCP and 75wt% ZrO3, where about 4100MPa of strength achieved at the highest sintering temperature, 1400˚C. Referring to Fig. 3, it can be said that the addition of TiO_2 contributed to the improvement in strength, as the results show higher compressive strength for higher amount of TiO_2 dopant content.

This clearly indicates that the samples containing higher amount of TiO_2 yielded higher mechanical properties. Generally, the strength of ceramic is mostly dependent on the porosity and microstructural appearance i.e. grain size that lie within the sample. Samples with a higher porosity rate tend to have lower mechanical properties as well as density as there are voids between particles of the samples. Thus, this phenomenon may cause formation of crack since there are no particles to stop the crack from propagating further [20]. By subjecting the samples to optimum sintering conditions, the sintering temperature, holding time and TiO_2 dopant content, the mechanical properties have shown significant results, due to the decrease in porosity. Based on Fig. 1, Fig. 2 and Fig. 3, the optimum sintering temperature would be 1400˚C, as this has produced the best mechanical property results.

Hence, the results obtained for the compressive strength in this research was relatively high for 10wt% TiO_2/ 15wt% TCP and 75wt% ZrO_3 composition sintered at 1400˚C is an excellent contribution factor towards mechanical properties of biomedical applications.

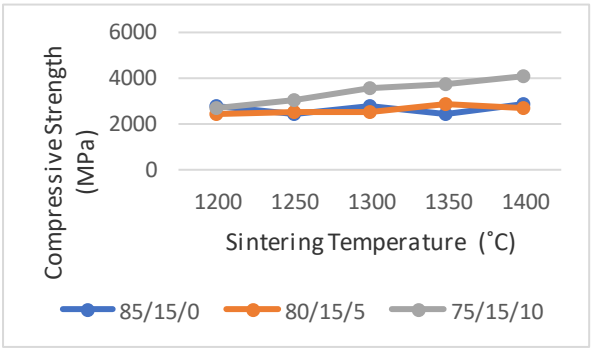

Fig. 3 The effect of various compositions and sintering temperatures on the compressive strength of zirconia for 1.5h holding time

D. Microstructure Evaluation

Fig. 4 shows the SEM image for 10wt% TiO_2/15wt% TCP and 75wt% ZrO_3. This test was done to study the grain size of the composition. The addition of TiO_2 contributed towards the transformation toughening mechanism of the composition. Thus, the microstructure and the morphology of the samples were evaluated using Scanning Electron Microscope (SEM). In order to prevent the occurrence of charging, the samples were coated with a layer of platinum before the SEM imaging was carried out. The parameters used for the SEM imaging was a voltage of 15 kV, a spot size of 3.0 and a magnification of 15000. The morphology and grain size of the best composition was investigated.

Based on the SEM evaluation results, the composition 10wt% TiO_2/15wt% TCP and 75wt% ZrO_3 exhibited an average grain size value of about 549.28nm. This shows there is not any significant phase transformation from tetragonal to monoclinic [21]. Generally, a larger grain size could have been formed due to microcracks of the intergranular boundaries caused by sintering at a higher temperature [22], but the results for this research shows there isn't large grain size that are causing microcracks on higher sintering temperature. In addition to that, the addition of TiO_2 has in fact made the microstructure stronger.

However, a higher amount of TiO_2 content which is about 50wt% naturally hinders the mechanical property performances. This originated from small expansion and grain growth, which lead towards excessive grain shown seemingly in the micrograph [20]. Therefore, it is also significant that, higher content of TiO_2 would promote grain growth which would indirectly reduce the mechanical properties achievements.

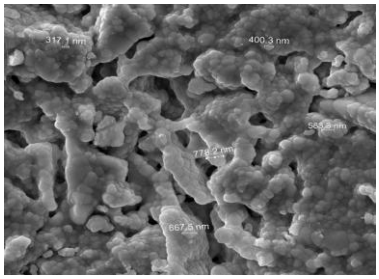

Fig. 4 The SEM image for 10wt% TiO_2/15wt% TCP and 75wt %ZrO_3

IV. CONCLUSION

This research work investigated the effect of TiO_2 and TCP additions to improve the mechanical properties and microstructural behavior of zirconia. The results show that the properties were significantly enhanced by additions of 10wt% TiO_2/ 15wt% TCP and 75wt% ZrO_3. The highest value of density obtained was about 4.89 g/cm^3, approximately 80% of the theoretical density value (6.10 g/cm^3). The Vickers hardness and compressive strength achieved were 10.67GPa and 4100MPa respectively. Sintering at high temperatures, i.e at 1350˚C and 1400˚C was seen to be the best temperature to achieve the optimum mechanical properties. The microstructure evaluation also showed a smaller grain size achievement.

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