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SCANNING ELECTRON, DIFFRACTION AND SPECTROMETER CHARACTERIZATION OF HA-ZrO_2 COMPOSITE FOR DENTAL APPLICATION

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Hydroxyapatite (HA-$Ca_{10}(PO_4)6(OH)$ are bioceramic material which mimic the natural bone substance. This experiment has been conducted to produce the composite of HA-ZrO_2 and to study its characteristics. In this experiment, hydroxyapatite has been synthesized by using precipitation method. The hydroxyapatite is mixed with commercial ytria stabilized zirconia. The effect of ratio percentage HA-ZrO_2 mixture has been investigated. Zirconia percentage are 40% and 60%. Also, the different time of milling process for all samples are being investigated. The samples obtained was analyzed at its chemical composition and morfological character. The analysis was conducted in the labs of Malaysian Nuclear Agency. The characterization of each samples was viewed by Scanning Electron Microscope integrated with Energy Dispersive X-Ray Spectroscopy (SEM-EDX and X-Ray Diffractometry (XRD) and Fourier Transform Infrared Spectroscopy (FTIR).

Key word; Composite, HA-ZrO_2, scanning Electron and Diffraction

INTRODUCTION

Hydroxyapatite (HA-$Ca_{10}(PO_4)_6(OH)_2$) type of bioceramic material of similar inert component as natural bone. This type of biomaterial is suited for medical applications such as bone augmentation or bone replacement (including the teeth) and thus applicable in dental implants application. According to Agata Dudek (2011), HA constitute a structure that contains 99% of calcium and 85% of phosphorus, while its crystals account for 77% of organic stroma the bones are made of. The structure and the composition of hydroxyapatite is similar to the mineral phase of bone and its bioactive and biocompatibility make it preferred to be used as bone graph. The ratio of calcium element to phosphate element for pure hydroxyapatite is 1.67 (Rey *.et al.* 1991). There are many methods that can be used to produce hydroxyapatite powder, such are precipitation method, solid-state synthesis, hydrolysis and hydrotermal and also sol-gel method (Kweh *et al.* 1999). However, precipitation method is the most often method to be used to produce hydroxyapatite powder (Asaoka *et al.* 1995). Among all methods that can be used to produce hydroxyapatite powder, two of the most polular method that already used are the reaction between diammonium hydrogen phosphate with calcium nitrate and the reaction between ortophosphoric acid and calcium hydroxide(Asaoka *et al.* 1995; Zhang&Gonsalves, 1997).

HA powder still has many weaknesses that need technologies to be improved, even though their properties and characteristics are quite ideal for medical field application (reference). One of the weaknesses is its fragile nature character. Many researches have attempted to improve mechanical strength and resistance to cracking through the introduction of the ZrO_2 modified with Y_2O_3 and CaO into HA. Currently, zirconia is widely used in biomaterial area as inert prosthetic material because of its good mechanical and chemical properties (reference). Thus, zirconia is a common biomaterial in restorative dentistry and dental implantology (reference). Usually, the crystal structure of zirconia is the mixed phase of monoclinic, cubic and tetragonal. Pure ZrO_2 melts at 2950 K, and has three zero-pressure phases: cubic above 2650 K, monoclinic below 1400 K, and tetragonal between. Under normal condition pure ZrO_2 should be monoclinic. Although mixtures of tetragonal and monoclinic phases have been observed in some of the nanocrystalline ZrO2 nanofibers at room temperature (reference), likely because of the structural constraints, the grains of fibers calcinated above 1200 K are uniformly monoclinic (C.Wang *et. al* 2010). Similar to other oxides, syntheses and characteristic evaluations of various nanostucture containing nanostucture materials that containing zirconia still being studied. Ytria-stabilized zirconia (YSZ) has been widely experimentally studied and used as the high-temperature corrosion-resistive and thermal barrier coating. The high melting point makes YSZ desirable in many industrial applications. According to Silva et al. (2001), the ytria-stabilized zirconia with the calcia can be used in bone phase application in zirconia-hydroxyapatite phase

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METHODS

To prepare hydroxyapatite powder, the titration method was applied. The chemical reaction occurred has been showed by followed equation:

$10Ca(NO_3)_2$+$6(NH_4)_2HPO_4$+$8NH_4OH$---
$Ca10(PO_4)_6(OH)_2$+$20NH_4NO_3$+ $6H_2O$

In the preparation process for hydroxyapatite powder, calcium nitrate and diammonium hydrogen phosphate were weighed and then dissolved in 1000L of distilled water to produce 1.0 mol calcium nitrate solution and 0.6 mol of diammonium hydrogen phosphate respectively. Both solution in individual beakers were magnetic stirrered for 20 minutes. Following which the diammonium hydrogen phosphate solution was titrated to the calcium nitrate solution. The rate of the titration process is 120drops per minutes. During the titration process, it is important to control the pH value of the solution is always more than pH9 (pH>9). This is to avoid the formation of tricalcium phosphate (TCP) to occur.

Ammonium hydroxide solution is added to control the solution. The titration process has been conducted in fume hood. After the titration process is completed, the solution mixture is stirred with magnetic stirrer for 24 hours at room temperature (pH>9 for aging process. After aging process, the mixture solution are filtered by using vacuum filtration. The cake gel obtained from the first titration is washed with 2000 L of distilled water and repeat 3x to rinse. This is to ensure that only hydroxyapatite is harvested from the experiment

Table 2 Total volume percentage for mixing HA-ZrO_2

Sample	Hydroxyapatite (%)	Ytria stabilized zirconia (%)	Total percentage (%)
A	40	60	100
B	60	40	100

The cake obtained from the filtration process were dried in a hot oven (Memmert Modell 600) at temperature 50-60 °C for 24 hours. The dried hydroxyapatite is crushed by using agate mortar and pestles to get the smaller particle size. The powder of hydroxyapatite is then being mixed with zirconia powder. Table below shows the percentage of mixture hydroxyapatite with ytria stabilized zirconia commercial.

The ratio of hydroxyapatite and ytria stabilized zirconia was calculated by using density formulary. In this experiment, the white powder of 3(% mol) YSZ with 15-25 nm average size has been used. Both of sample A and B are added with 1000 L of distilled water in beaker. Each of them are added with 2 g of dispersants agent.

The slurry of mixture of hydroxyapatite-zirconia for sample A and sample B undergo milling process at 350 rpm . After that, the samples are dried in oven and grind to get the smaller particle size, <20 μm using zirconia grinding ball machine (Pulverisette 6) .The samples A & B are then will undergo an additional 2 hours milling time, and additional 4 hours milling time. All of samples are spray dried . The powder of the mixture of hydroxyapatite-zirconia is then obtained

RESULTS AND DISCUSSION

Several analysis have been conducted on types of sample. The samples are HA-ZrO_2(40:60) with 2hours additional milling time , HA-ZrO_2(40:60) with 4hours additional milling time and also HA-ZrO_2(60:40) with 2 hours additional milling time followed by spray dry. For sample A [HA-ZrO_2(40:60) 2hrs milling time] green body, the mean value is 3.525 μm with standard deviation 2.320 μm. The range is from 0.265 μm to 18.50 μm. For sample B green body [HA-ZrO_2(40:60) 4hrs milling time], the mean value is 7.681 μm with standard deviation 6.301 μm. The range is from 0.315 μm to 74.00 μm. For sample C green body [HA-ZrO_2(60:40) 2hrs milling time], the mean value is 3.811 μm with standard deviation 2.366 μm. The range is from 0.630 μm to 15.56 μm. Sample A and Sample B have the same ratio of HA-ZrO_2 (40:60) but had undergoes different time of milling time during the process.

Sample	Diameter	Volume	Std. deviation
HA-ZrO2(40:60) 2hrs Milling	4.176 1.233	67% 33%	2.320
HA-ZrO2(60:40) 2hrs Milling	3.934 1.187	82% 18%	2.366
HA-ZrO2(40:60) 4hrs Milling	8.632 1.228	60% 40%	6.301

From observation, it can be seen that the peak of phosphorus group [$(PO4)^{-3}$] bending is higher for HA-ZrO_2 with a ratio of 40:60 (range from 1025.97cm^{-1} to 1033.21cm^{-1}) as compared to HA-ZrO_2 with a ratio of 60:40 (range from 1024.59cm^{-1} to 1026.26cm^{-1}). This showed that the presence of phosphorus group in HA-ZrO_2 (60:40) green body is higher. The same result was also obtained from experiment conducted by Silva and Lameiras (2000). This might due to the presence of higher ratio of zirconia phase in the mixture, which may effected on the nature phase of hydroxyapatite (Silva & Lameiras, 2000). Fig. 3.19 shows the spectrum for sample C, HA-ZrO$_2$ (60:40). All of the samples are sintered at 1200°C. The XRD pattern showed a sharp and slimindicating a highly crystalline structure. From the obtained micrograph at 1000X and 10,000X, it can be clearly seen that the sizes of the mixed powder HA-ZrO$_2$ are homogenous and in sphere sized. This is because of the use of spray dried technique to obtain the said powder.

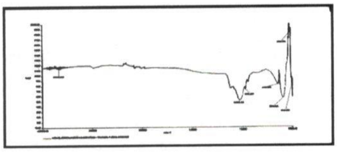

Fig. 3.1. FTIR analysis of HA-ZrO$_2$(40:60) (a) green body and (b) sintered at 1200°C

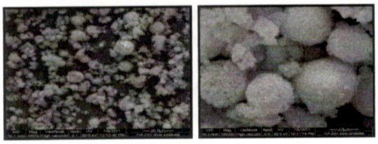

Fig.3.10. HA-ZrO$_2$(40:60), 4hours milling time, and spay dried and sintered 1200°C at (k) magnification-1000X and (l) magnification-10,000X

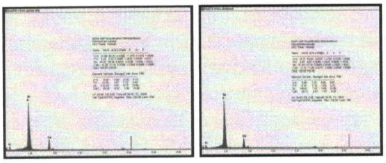

Fig.3.11. EDX analysis of HA-ZrO$_2$(40:60) which (a) undergoes 4 hours additional milling time and (n) sintered at 1200°C

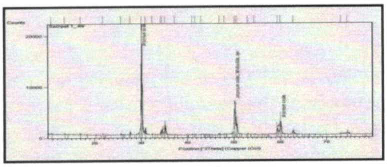

Fig.3.12. XRD analysis of HA-ZrO$_2$(40:60) past 4 hours additional milling time.

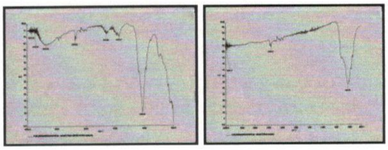

Fig.3.14. i) FTIR analysis of HA-ZrO$_2$(60:40) gren body ii) FTIR analysis of HA-ZrO$_2$(60:40) sintered 1200°C

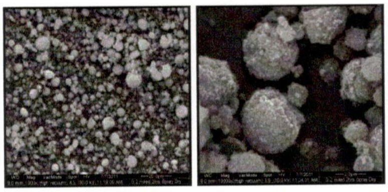

Fig.3.16. HA-ZrO$_2$(60:40), 2hours milling time, and spay dried at (o) magnification-1000X and (p) magnification-10,000X

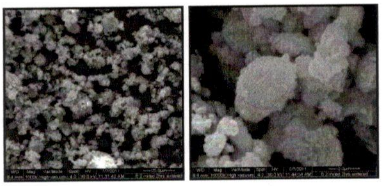

Fig.3.17. HA-ZrO$_2$(60:40), 2hours milling time, and spay dried and sintered 1200°C at (q) magnification-1000X and (r) magnification-10,000X

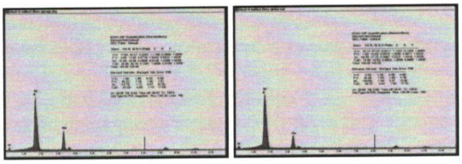

Fig.3.18. EDX analysis of HA-ZrO2(60:40) which (s) undergoes 2 hours additional milling time and (t) sintered at 1200°C

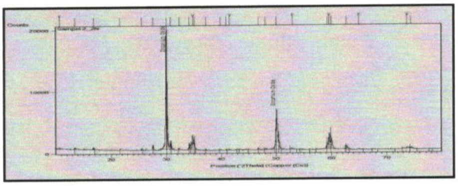

Fig.3.19. XRD analysis of HA-ZrO$_2$(60:40) which undergoes 2 hours additional milling time

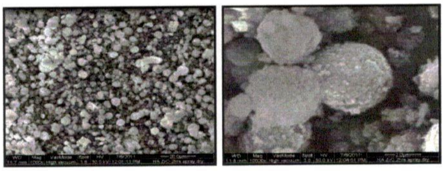

Fig.3.2. HA-ZrO$_2$(40:60), 2hours milling time, and spay dried at (c) magnification-1000X and (d) magnification-10,000X

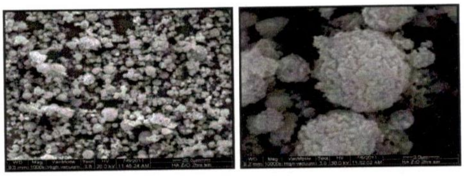

Fig.3.3. HA-ZrO_2(40:60), 2hours milling time, and spay dried and sintered 1200°C at (e) magnification-1000X and (f) magnification-10,000X

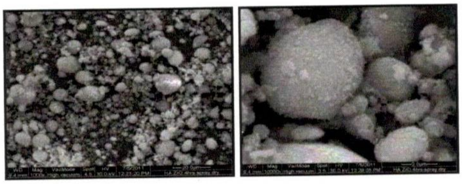

Fig.3.9. HA-ZrO_2(40:60), 4hours milling time, and spay dry at (i) magnification-1000X and (j) magnification-10,000X

CONCLUSION

This is a potential technology apply to produce of HA-ZrO_2 by using precipitation method variables. From the result, it can be concluded that the milling processing time may effect the particle size. When the time taken is long, heat may produce. This might cause the particle of HA agglomerate to form the bigger particle size. As the result, the particle size of HA for Sample B is bigger than the Sample A. These are two different sample with different ration of HA-ZrO_2 but had undergoes the same process- 2 hours milling time. From the result it can be concluded that the sizes of distribution size average is same due to the same milling hours. It is important to ensure of HA- ZrO_2 is in nano size for dental application, especially for teeth implantation management. The used of spray dried technique is thus very successful to produce HA/ZrO_2

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