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Synthesis and Characterization of Hydroxyapatite-Zirconia Composites for Dental Applications

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ABSTRACT

Hydroxyapatite (HA)-zirconia composite was prepared by mixing synthesized HA with Yttria-Stabilized Zirconia (YSZ) nanopowder. Composites with 20, 40, 60 and 80 wt% YSZ were prepared and sintered over the temperature range of 1100-1300°C for 2 h. The composite with 20 wt% zirconia exhibited the best mechanical property with a hardness and compression strength of 5.2 and 1.7 GPa, respectively. The phases of the composites were analyzed by using X-ray Diffraction (XRD) and the morphologies of the samples were observed by Field Emission Scanning Electron Microscopy (FESEM). The decomposition of HA into tricalcium phosphate was increased by the addition of zirconia, thus increasing the porosity of the sample. The findings of the XRD coincided with the results of FESEM.

Key words: Hydroxyapatite, yttria-stabilized zirconia, composite

INTRODUCTION

Hydroxyapatite (HA) $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ is the main inorganic component in human bones and teeth. HA is extensively used in the biomedical (Ramli *et al.*, 2011), medical (Murugan and Ramakrishna, 2005) and dental fields (Serraj *et al.*, 2002) for its excellent biocompatibility and osteoconductivity. However, the application of HA is limited to non-load-bearing applications because of its inferior mechanical properties (Zhao *et al.*, 2006). To address this problem, additives or hybrid materials, such as Yttria-Stabilized Zirconia (YSZ) (Nayak *et al.*, 2008), have been introduced to enhance the mechanical properties of HA.

Zirconia or zirconium dioxide (ZrO_2) exhibits superior mechanical properties, such as stress-induced phase transformation which enhances the properties of brittle materials (Sung and Kim, 2003). Stabilized zirconia is preferred over pure zirconia because the latter undergoes phase transformation at 1150°C, thus leading to the sudden failure of the material after the zirconia cools down (Heuer *et al.*, 1986). Stabilized zirconia is formed by mixing zirconia with metallic oxides, such as yttria (Y_2O_3), Magnesium Oxide (MgO), or Calcium Oxide (CaO). Stabilized zirconia with 3 mol% Y_2O_3 is commonly used in biomedical applications (Picconi and Maccauro, 1999).

Prabakaran *et al.* (2005) and Sung *et al.* (2007) found that the combination of HA and zirconia could produce a composite with superior mechanical properties. By producing a HA-zirconia composite via., co-precipitation, Sung *et al.* (2007) found that the addition of 25 wt% zirconia increased the strength and fracture toughness of the composite by 31 and 121%, respectively. Chiu *et al.* (2007) found that the addition of zirconia in HA produced a composite with a finer grain structure than monolithic HA. However, the mixture of HA with YSZ nanopowder has not yet been investigated. This study aims to determine the effect of zirconia nanopowder on the mechanical properties of HA. Compact HA-zirconia composites were produced and characterized by using X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and microhardness and compression tests.

MATERIALS AND METHODS

The HA-zirconia composite was formed by preparing HA powder, mixing the HA with zirconia powder and forming the sample via., uniaxial pressing, sintering and characterization. Laboratory-grade HA powder was produced via., wet chemical precipitation with calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$). Ammonium was added to the solution during titration to maintain the pH level of the solution above 9.5 and to maximize the HA yield (Liu *et al.*, 2003). Thereafter, the $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_2\text{HPO}_4$ mixture was stirred and aged for 24 h while maintaining the pH level above 9.5. Ammonia was filtered from the mixture by using a grade 4 filter paper. The filtrates were then dried in an oven (Mettler UFE 600, United State) from 50-60°C for 24 h. The dried sample was crushed by using a mortar and then milled at 350 rpm for 8 h by using a planetary ball-milling machine (Fritsch Pulverisette 6, Germany). The synthesized HA powder was mixed with 20, 40, 60 and 80 wt% YSZ (ZrO_2 -3 mol% Y_2O_3) powder ($D_{0.5} = 15$ nm). Samples with pure HA were also used as controls to determine the effects of zirconia on HA.

HA and zirconia were mixed via., wet ball milling (Fritsch Pulverisette 6, Germany) with ethanol as the milling medium. The resultant mixture was dried at 70°C for 24 h and was then crushed into fine powder. Pellet-shaped green bodies were produced via., uniaxial pressing and were sintered at 1100, 1200 and 1300°C in a high-temperature furnace (Nabertherm, Germany) at 2.5°C min⁻¹. The samples were soaked for 2 h and cooled in the furnace. The density of the sintered sample was measured by using a densitometer (Mettler Toledo NewClassic MS Analytical, United State). The measured density was then used to obtain the relative density (Williams, 1993).

Microhardness was measured by using a microhardness tester (Shimadzu HMV, Japan) with a 500 g applied load and a 15 sec holding time. A compression test was performed by following the ASTM standard test method for compressive strength of fired whiteware materials (ASTM C 733-88). The phase stability and morphology of the sample were also measured by using XRD (Bruker D8 Advance, United State) and FESEM (Leo Supra 55VP, United State).

RESULTS AND DISCUSSION

X-ray diffraction analysis: Figure 1 shows the XRD results of the HA-zirconia composites that were sintered at 1300°C. Samples sintered at 1300°C were analyzed by using XRD because these samples exhibited desirable mechanical properties. The XRD analysis was performed at an angle range of 10°<θ<80° to determine the phases and compounds present in the samples. The peaks of the pure HA sample corresponded to the peaks of the synthetic HA and no significant peaks were observed for other compounds. The sample with 60 wt% HA and 40 wt% zirconia exhibited a peak

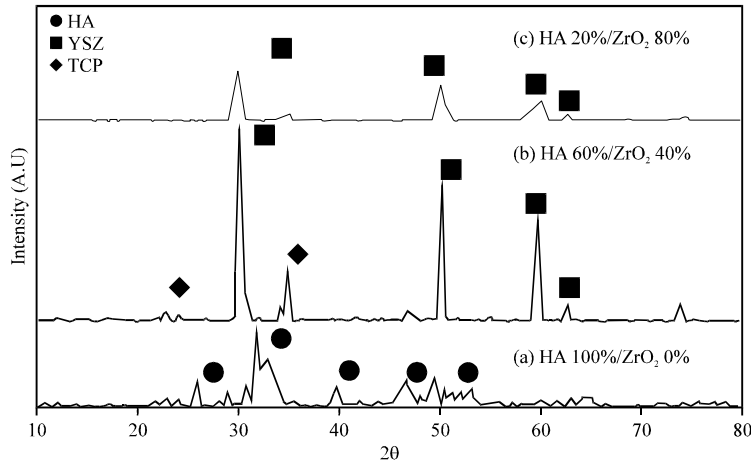


Fig. 1(a-c): XRD patterns of HA-zirconia composites sintered at 1300°C, (a) HA 100%/ZrO₂ 0%, (b) HA 60%/ZrO₂ 40% and (c) HA 20%/ZrO₂ 80%

Table 1: Average grain sizes of the samples

Sample	Average grain size (μm)
100% HA/0% ZrO ₂	4.7
60% HA/40% ZrO ₂	1.5
20% HA/80% ZrO ₂	0.2

for YSZ and tricalcium silicate, whereas the sample with 20 wt% HA and 80 wt% zirconia only exhibited a peak for YSZ. The pure HA underwent slight decomposition despite being sintered at 1300°C. However, the addition of zirconia increased the tendency of the pure HA to decompose into tricalcium phosphate (Leong *et al.*, 2013). These findings were consistent with the findings of Evis *et al.* (2008) and Yang *et al.* (2010), who found that hydroxyapatite decomposed into tricalcium phosphate when sintered at temperatures above 1200°C with the addition of zirconia powder. The HA decomposition into tricalcium phosphate was unfavorable because the latter had a higher biodegradation rate than the former, thus increasing the possibility of implant failure (Nandi *et al.*, 2010). Water vapor was also released during the decomposition process, thus increasing the porosity of the sample (Evis, 2007).

Scanning electron microscopy: Morphology of the samples sintered at 1300°C as viewed from a 10 K magnification is illustrated in Fig. 2. Table 1 shows the average grain sizes of the samples. The sample with 100% HA exhibited an irregular structure and a large grain size (4.7 μm) without porosity (Fig. 2a). No other compounds were detected on the sample; this result was consistent with the XRD results. The sample with 60% HA/40% ZrO₂ (Fig. 2b) exhibited high porosity. This change in microstructure could decrease the microhardness and compression strength of the sample. Figure 2c shows a structure dominated by zirconia grain that exhibited a fine grain size (0.2 μm).

Density: The sintered samples had relative densities ranging from 83-94%, thus indicating that the samples were not fully densified (Fig. 3). Consistent with the FESEM micrograph, the sample with pure HA had the highest density and reached the maximum level when sintered at 1300°C. The density of pure HA sintered at 1200°C was also high. The addition of 20-40 wt% zirconia

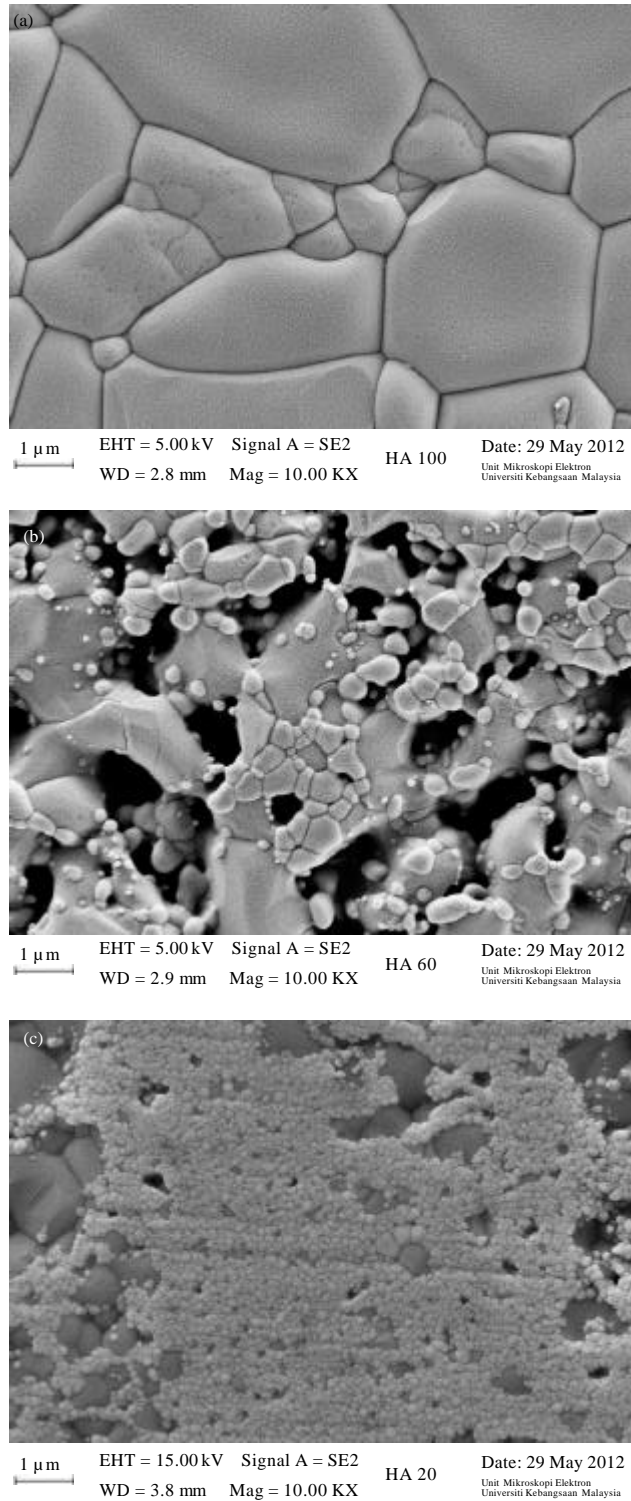


Fig. 2(a-c): The FESEM micrographs showing grain structure of the samples, (a) HA 100%/ZrO₂ 0%, (b) HA 60%/ZrO₂ 40% and (c) HA 20%/ZrO₂ 80%

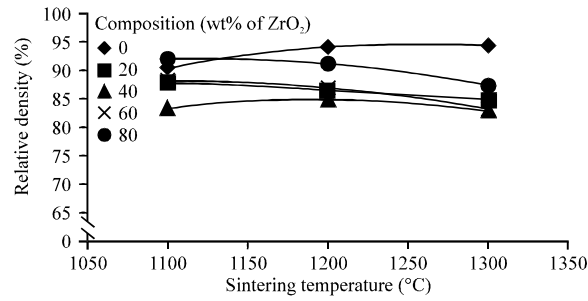


Fig. 3: Relative density of the samples sintered at various temperatures

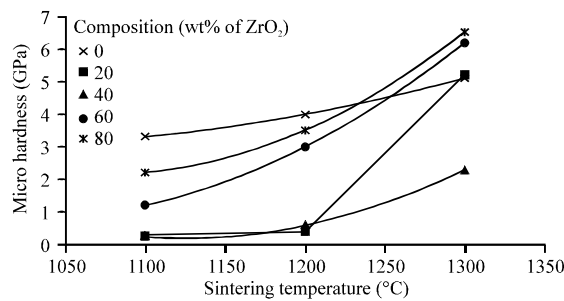


Fig. 4: Microhardness of the samples with varying ZrO₂ addition

reduced the density of the sample, specifically when sintered at 1300°C. Such a decrease was caused by the HA decomposition induced by the addition of zirconia. The HA decomposition enhanced the porosity and decreased the density of the sample; this result was consistent with the results of Towler and Gibson (2001). Therefore, the addition of zirconia increased the porosity and not the density of the sample.

Hardness: Figure 4 shows that the increase in sintering temperatures increased the microhardness of the samples. Samples with 60 and 80 wt% zirconia exhibited the highest hardness at 6.2 and 6.5 GPa, respectively. The hardness of samples with 20 and 40 wt% zirconia were very low when sintered at 1100 and 1200°C, respectively. However, the hardness of these samples sharply increased when sintered at 1300°C, thus indicating that increasing the sintering temperature above 1200°C is required to produce samples with high microhardness. The increase in microhardness could be attributed to the mechanical strength of zirconia and to the fine grain structure of the sample with 80 wt% zirconia.

Compressive strength: Compressive strength measures the capacity of the sample to withstand loads. The sample with 20 wt% zirconia exhibited the highest compressive strength (1.68 GPa) when sintered at 1300°C (Fig. 5). The compression strength of the sample with 20 wt% zirconia was higher than the compression strength of the pure HA sample. However, samples with more than 20 wt% zirconia exhibited strengths that were lower than those of pure HA samples. Such a decrease could be attributed to the exchange of Ca⁺² and ZrO²⁺ ions between HA and zirconia which decomposed HA and increased the porosity of the sample (Evis, 2007). Such a phenomenon was previously discussed by Evis (2007), who suggested that the diffusion of large ZrO²⁺ ions into the

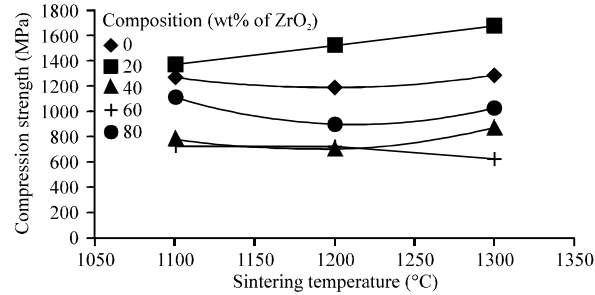


Fig. 5: Compressive strengths of the sintered samples

HA network could promote strain, thus increasing the decomposition tendency. Further study of this aspect is required to enable the production of HA-zirconia composite with satisfactory mechanical properties and low decomposition tendency.

CONCLUSION

HA-zirconia composites were prepared by wet precipitation and mechanical mixing. The HA-zirconia composite with 20 wt% zirconia exhibited satisfactory mechanical strength with a microhardness and compression strength of 5.2 and 1.68 GPa, respectively. The XRD analysis showed that the addition of zirconia into the sample induced HA decomposition to other type of calcium phosphate such as tricalcium phosphate. These findings were verified by the FESEM micrographs which indicated that HA decomposition increased the porosity of the samples.

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