

# The Effect Of Microwave Drying On The Sinterability Of Hydroxyapatite

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**Abstract** –In the present work, hydroxyapatite (HA) powder was synthesized via wet chemical method with the assist of rapid drying by microwave heating. The use of microwave drying accelerates the manufacturing of HA powder as only 15 minutes were required to dry the HA powder (MHA) while at least 16 hours of drying time were required for the conventional oven drying (OHA). XRD analysis indicated that the use of microwave drying in the synthesis process did not alter the phase stability of HA as all the peaks corresponded to the stoichiometric HA. MHA was found to exhibit a high specific surface area (SSA) of  $\sim 111.07 \text{ m}^2/\text{g}$  and has a needle-like morphology with an average length and width of 66.7 nm and 23.6 nm. Besides, MHA was found to possess overall better sinterability and mechanical properties than OHA. The findings showed that pure HA can be synthesized by incorporating microwave drying into the wet chemical method.

**Keywords:** Microwave drying; Hydroxyapatite; Sinterability; Wet chemical method

## 1. Introduction

Hydroxyapatite (HA) is one of the calcium phosphate based bioceramic material which makes up the majority of the inorganic components of human hard tissues (Irma et al., 2006). HA has the chemical formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$  (Liu et al., 1997) and it is a suitable material to be used for hard tissue replacement because its composition match closely with some of the properties of human bones and teeth (Hench, 1998). Furthermore, HA is a bioactive material, having excellent biocompatibility which denotes that it does not exhibit any rejection by the human body (Suchanek and Yoshimura, 1998). Hence, great demand has been placed on the synthesis of HA where a variety of HA synthesising methods were established such as wet chemical precipitation (Loo et al., 2008; Sung et al., 2004), mechanochemical (Mochales et al., 2004; Nasiri-Tabrizi et al., 2009), sol-gel (Han et al., 2004; Rajabi-Zamani et al., 2008) and microwave synthesis (Liu et al., 2005).

Amongst all the synthesising methods, the wet chemical precipitation method is more worthy due to its simplicity and cost-effective (Kong et al., 2007; Verwilghen et al., 2007). Furthermore, earlier work showed that powder synthesised through the wet chemical precipitation method is homogenous, with good crystallinity, physiologically stable, morphologically similar to hard tissue and has high relative density (Kothapalli et al., 2004; Donadel et al., 2005; Tolouei et al., 2012) However, wet chemical method is usually accompanied with long drying hour for the precipitate to dry thoroughly. This is very time consuming as the use of conventional oven drying could take up to 16 hours of drying time. Therefore, a rapid drying process could ideally enhance the manufacturing speed of HA. Microwave drying has been identified as one of the alternative in accelerating the drying process of HA precipitate as this drying method offers several advantages including shorter processing times, volumetric dissipation of heat throughout the product and provides reduction of energy requirements in synthesizing (Atong et al., 2006). Unlike conventional drying method, the energy is transmitted directly to the bulk of wet material almost instantaneously in microwave drying; instead of heat transferring from the surface to the interior of the product which is ten to twenty times slower (Berteli et al., 2009).

Therefore, the primary objective of this research is to study the sinterability of HA powders prepared through microwave drying. The sintering behavior of HA powders produced via conventional oven drying was also studied for comparison purposes.

## 2. Methods and Materials

The hydroxyapatite (HA) powder in the current work was produced according to the wet chemical method with the use of precipitation from aqueous medium through titration process by reacting calcium ion with phosphate ion in accordance to the molar ratio of  $\text{Ca/P} = 1.67$ . The starting precursors chosen were commercially available calcium hydroxide  $\text{Ca(OH)}_2$  (98% purity, RNM) and orthophosphoric acid  $\text{H}_3\text{PO}_4$  (85% purity, Merck). The prepared  $\text{H}_3\text{PO}_4$  solution was then added dropwise into the stirring suspension of  $\text{Ca(OH)}_2$  in distilled water. Throughout the titration process, the pH of the mixture was monitored and kept above 10.5 by the addition of  $\text{NH}_3$  solution. After the titration process, stirring was continued for another 6 hours. The obtained precipitate was allowed to settle down overnight and then filtered, washed and rinsed three times by using distilled water. The precipitate was subsequently dried for 16 hours in an oven at about  $60^\circ\text{C}$ . The dried filtered cake was crushed and sieved to obtain a well-defined, highly crystalline HA powder, hereafter is known as OHA. On the other hand, the synthesis process of the HA powder via microwave drying is similar to the synthesis of HA stated earlier except that the oven drying for 16 hours was replaced by microwave drying of 15 minutes. The filtered precipitate was rinsed three times by using distilled water and then subjected to microwave irradiation in a domestic microwave oven (Sharp, R-898M, 900 W power) for 15 minutes until the precipitate was completely dried. The microwave dried filtered cake was crushed and sieved to obtain a well-defined, highly crystalline HA powder, hereafter named MHA. The synthesis flow sheet for both methods is shown in Figure 1.

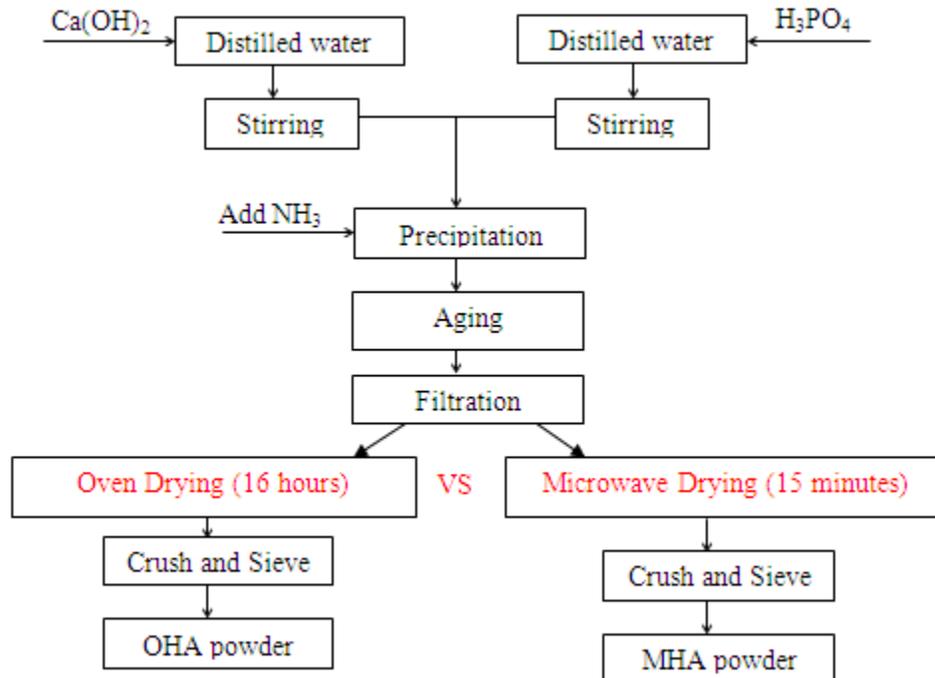


Fig. 1. HA synthesis flow sheet for both drying methods

The as prepared HA powder was uniaxially compacted at about 1.3 MPa to 2.5 MPa into discs (20 mm dia.  $\times$  5 mm thickness) followed by cold isostatically pressed (CIP) at 200 MPa. The CIP pellets were sintered via conventional pressureless sintering at temperatures ranging from  $1050^\circ\text{C}$  to  $1350^\circ\text{C}$ , for 2

hours with a heating rate of 2°C/min, and then furnace cooled at 2°C/min. All the samples were polished to 1µm finish prior to testing.

The specific surface area of the powder was also measured by the Brunauer-Emmett-Teller (BET) method. The morphology of the as synthesized oven dried (OHA) and microwave dried (MHA) powder was analysed using TEM (JEOL, JEM-2100F, Japan) operated at an accelerating voltage of 120 kV. The particle size of the powder was measured from TEM micrographs. Phase stability of the synthesized powders and sintered samples were done by using X-ray diffraction (XRD) (Panalytical Empyrean) operated at 35 kV and 15 mA with Cu-Kα as the radiation source. The X-ray scan speed and step scan were 0.5°/min. and 0.02°, respectively. The peaks obtained were compared to standard reference JCPDS-ICCD (Joint Committee of Powder Diffraction Standard – International Center for Diffraction Data) files for HA (PDF No. 74-566 for Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> or PDF No. 9-432 for Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>(OH)).

The density of samples in the as-polished condition will be determined in accordance with the water immersion technique which also known as Archimedes principle, using distilled water as immersion medium. The relative density was obtained by taking the theoretical density of HA as 3.156 gcm<sup>-3</sup>. Hardness and fracture toughness tests were conducted by using Vickers hardness tester. Forces of 50 g to 200 g were applied perpendicularly on the surface of samples for a dwell time of 10 seconds by consuming a pyramidal diamond indenter. The indentation was used to estimate the fracture toughness of sintered samples by measuring the cracks generated at the four corners of the indentation via equation derived by Niihara (1985).

### 3. Results and Discussions

#### 3. 1. XRD Analysis for Powder

It is very important to make sure that the microwave drying does not alter the phase stability of HA powder. Hence, XRD analysis of both OHA and MHA powder was carried out. XRD analysis of OHA and MHA powders produced only peaks which corresponded to the standard JCPDS card no: 74-566 for stoichiometric HA as shown in Figure 2. No secondary phases were detected in the XRD diagram. This finding proved that microwave drying significantly shortens the synthesis duration without altering the phase stability of HA.

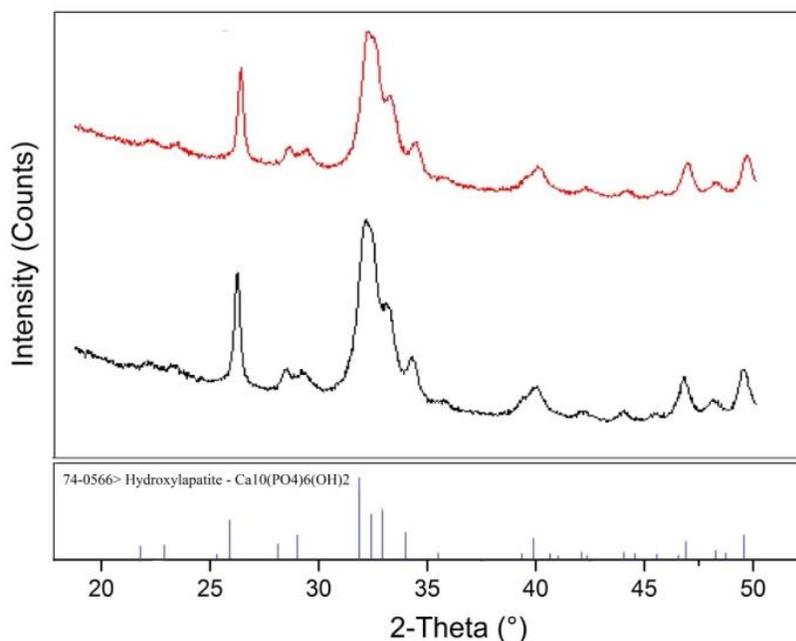


Fig. 2. XRD patterns of HA powders: (a) OHA; (b) MHA

### 3. 2. Specific Surface Area (SSA)

The specific surface area for OHA and MHA powder is 97.1126 m<sup>2</sup>/g and 111.0783 m<sup>2</sup>/g, respectively. Therefore, it can be concluded that microwave drying could produce HA powder with higher SSA. The higher SSA of MHA could be beneficial as some authors claimed that the high surface area of powders induced higher driving force in enhancing densification processing kinetic and sintering activity (Lin et al., 2007).

### 3. 3. Transmission Electron Microscopy (TEM)

The morphological analysis of the OHA and MHA powder was determined via transmission electron microscopy (TEM). Based on the analysis of TEM micrographs as shown in Figure 3.2, the morphology of both OHA and MHA resembled a needle-like structure. It is evident that microwave irradiation did not change the morphology of the HA particle. The needle like structure of the synthesized HA is similar to the natural bio-crystals found in the human hard tissue (Ferraz et al., 2004; Nejati et al., 2009) which could be potential candidates in biomedical application. Furthermore, it is postulated that the presence of particles with a needle like morphology in bulk materials are capable of enhancing the fracture toughness of the ceramic material (Fujishiro et al., 1993). This further highlights the advantages of HA particles with needle like structures.

Besides, the TEM micrograph of MHA (Figure 3b) shows average length of 66.74 nm and width of 23.57 nm, and for OHA (Figure 3a) the respective dimensions were 75 nm and 26.2 nm. The results revealed that the size of the particle was smaller under microwave drying (MHA) when compared to oven dried samples (OHA). Refer to the figure below for a sample.

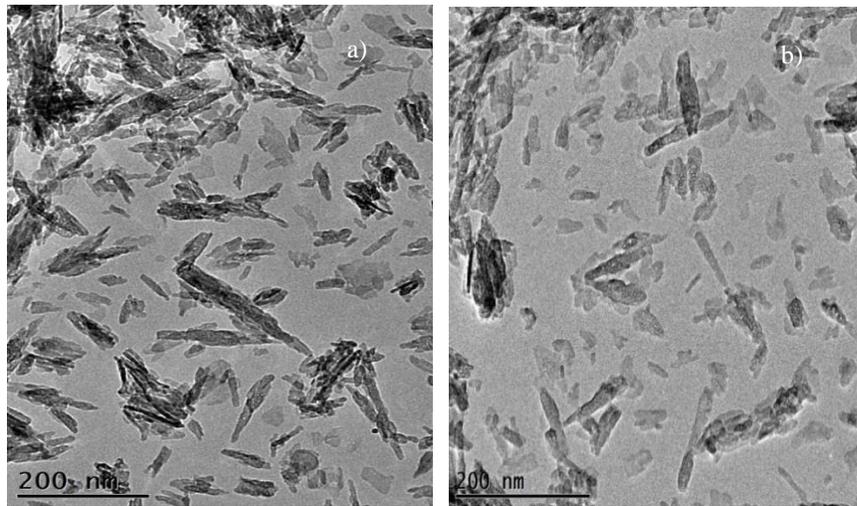


Fig. 3. The TEM micrographs of as-synthesized HA powder: (a) OHA; (b) MHA

### 3. 4. Phase Stability of HA Sintered Samples

The sintering of OHA and MHA at high temperature of 1350°C revealed the presence of only HA phase as shown in Figure 4. The formation of secondary phases such as tricalcium phosphate (TCP), tetracalcium phosphate (TTCP) and calcium oxide (CaO) was not detected throughout the sintering regime for both OHA and MHA samples. It can be concluded that microwave drying method did not alter the phase stability of HA samples even at high temperature of 1350°C.

### 3. 5. Relative Density

The effects of sintering temperature on the sintered densities of the OHA and MHA are shown in Figure 5. In general, the relative density increases with increasing temperature regardless of the drying methods and then decrease sharply beyond 1300°C. Both OHA and MHA samples attained the maximum relative density of ~98.43 at 1300°C.

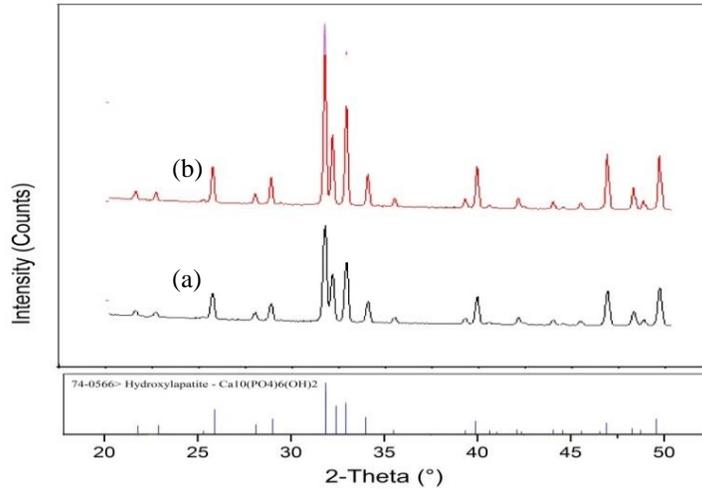


Fig. 4. XRD patterns of HA samples sintered at 1350°C: (a) OHA; (b) MHA

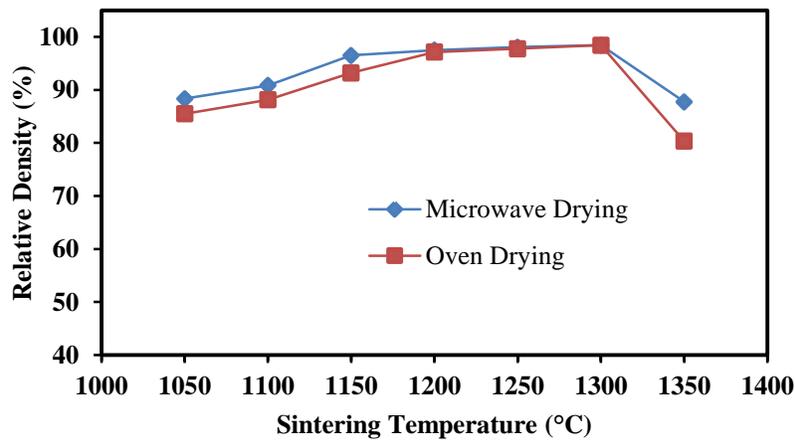


Fig. 5. The effect of sintering temperature on the relative density of sintered HA

### 3. 6. Vickers Hardness and Fracture Toughness

The effect of sintering temperature on the Vickers hardness of OHA and MHA is shown in Figure 6. Both OHA and MHA possessed a very similar trend to each other. An increasing trend on the hardness was observed when sintering temperature was increased. A steep increase in the hardness was observed between 1100°C to 1150°C. The highest hardness value of 4.55 GPa was obtained from MHA sintered at 1150°C while OHA could only attained highest hardness value of 4.33 GPa at a higher sintering temperature of 1300°C.

The effects of sintering temperatures on the fracture toughness of OHA and MHA is shown in Figure 7. The highest fracture toughness value (1.1 MPam<sup>1/2</sup>) was recorded from MHA when sintered at 1200°C. HA produced by conventional oven drying could only attained the maximum fracture toughness of 1.01 MPam<sup>1/2</sup> at the same temperature. The results revealed that HA produced by microwave drying demonstrated better mechanical properties than oven dried HA powder.

## 4. Conclusions

The present work reports on the sintering behaviour of HA powder produced by wet chemical methods with two different drying methods. It was found that microwave drying significant accelerate the synthesis of HA by 15 hours. Besides, based on the BET and TEM analysis, HA powder synthesized via microwave drying tend to produce powders with high specific surface area and also consisted of less

agglomerate with smaller particle sizes. It was shown that both OHA and MHA sintered samples exhibit XRD signatures that correspond to stoichiometric HA at 1350°C. This result shows that both OHA and MHA have high thermal stability.

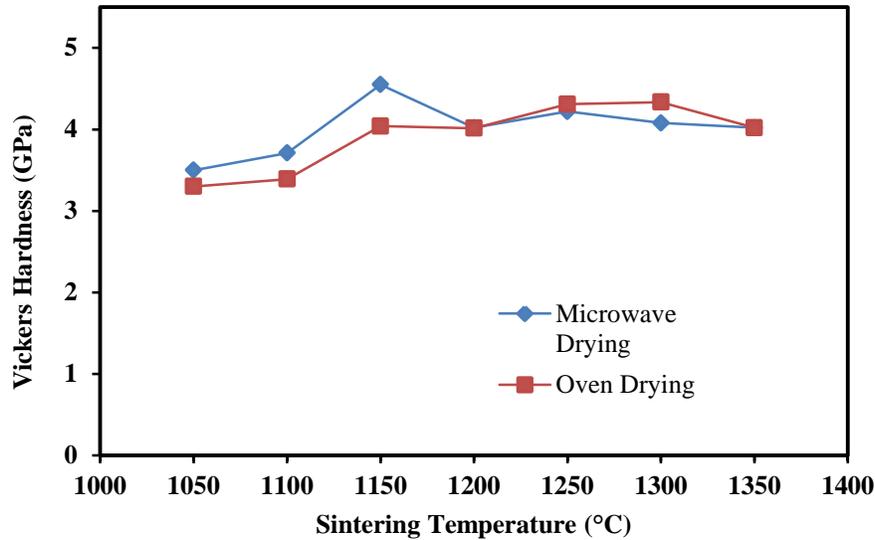


Fig. 6. The effect of sintering temperature on the hardness of sintered HA

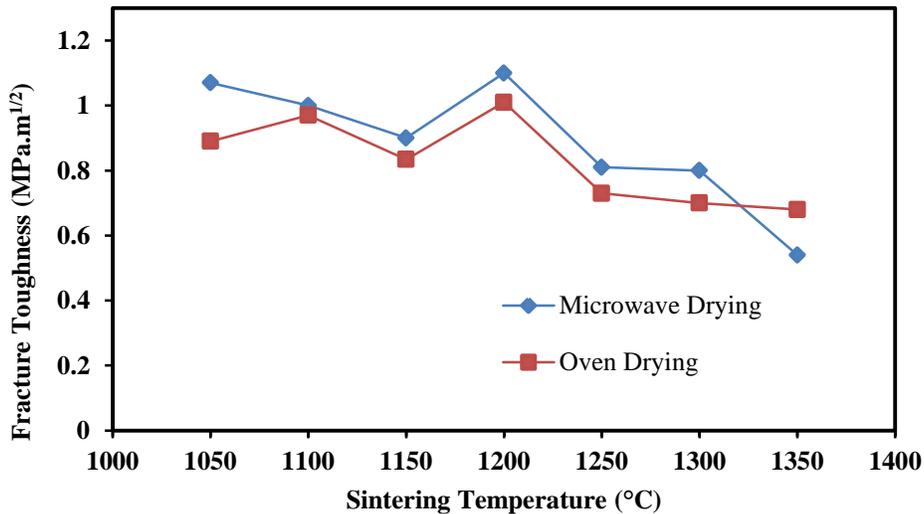


Fig. 7. The effect of sintering temperature on the fracture toughness of sintered HA

In terms of densification behaviour, MHA has a higher densification rate at low temperatures (1050°C - 1150°C). However, at higher temperature (1200 °C and above), the relative density of both MHA and OHA are very similar. In terms of mechanical properties, the MHA shows better Vickers hardness and fracture toughness than OHA. The highest hardness of 4.55 GPa was obtained from MHA sintered at 1150°C while OHA could only attained maximum hardness value of 4.33 GPa at a higher sintering temperature of 1300°C. The highest fracture toughness value (1.1 MPam<sup>1/2</sup>) was recorded from MHA when sintered at 1200°C. HA produced by conventional oven drying could only attained the maximum fracture toughness of 1.01 MPam<sup>1/2</sup> at the same temperature.

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