

Physicochemical Characteristics of Magnesium Hydroxyapatite (MgHA) Derived via Wet Precipitation Method

C. M. Mardziah* and N. R. N. Masdek
Universiti Teknologi MARA, Shah Alam, Selangor,
MALAYSIA.

Koay Mei Hyie
Universiti Teknologi MARA, Permatang Pauh, Pulau
Pinang, MALAYSIA.

Iis Sopyan
International Islamic University of Malaysia, Gombak,
Kuala Lumpur, MALAYSIA.

*mardziahcm@yahoo.com

ABSTRACT

Hydroxyapatite (HA) has been known for so many decades as an implant material for medical applications due to its chemical composition that is very similar to the inorganic component of human bone. However, synthetic HA possesses relatively low mechanical strength characteristic, making it less suitable to be used in load bearing applications. Thus, the presence of metal ion like magnesium (Mg) is expected to improve the properties of synthetic HA as biomedical devices. The main objective of this research is to develop and characterize the magnesium hydroxyapatite (MgHA) nanopowders derived from the wet precipitation method. The amount of Mg, which acts as a metallic dopant in HA were varied at 0, 5 and 10% and calcined at 700 °C for imperative comparison. The resultant nanopowders were then characterized using thermogravimetric analysis (TGA), X-ray diffraction (XRD) and field-emission scanning electron microscopy (FESEM) to examine their physicochemical properties. Morphological evaluation by FESEM showed that the particle size of 10% MgHA powders was larger and spherical in shape but still highly agglomerated at calcination temperature of 700 °C. This result coincides with the data obtained from the XRD analysis, which revealed that the particle size of pure HA, 5 and 10% MgHA after

calcination was 87 nm, 98 nm and 116 nm, respectively. These results demonstrate that doping Mg into HA has caused an increase in the particle size, proving that Mg acts as a sintering additive during the calcination process.

Keywords: *Magnesium, Hydroxyapatite, Bio-Implant Material, Wet Precipitation Method, Physicochemical Properties*

Introduction

Bone grafting is widely used in orthopaedic practice to deal with problems associated with bone loss, bone defects and reconstruction. Many incidences of bone and joint related disorders such as osteoporosis, arthritis, chronic diseases and muscle deterioration can cause injury to orthopaedic tissues, resulting in bone and joint failures [1]. Plenty of research have been dedicated to the development and evaluation of a synthetic substitute because of the significant problems associated with the limitation of autogenous bone graft. Several materials have been tested and found to be unsuitable. The most promising materials to date are those based on calcium hydroxyapatite (HA).

HA has a wide range of applications both in bone graft applications and as a coatings for the improved integration of metallic joint replacements because of the chemical similarity to the mineral component of bone [2]-[4]. It is one of few materials that are classed as bioactive, meaning that it will support bone ingrowth when used in orthopaedic and dental applications. However, synthetic HA cannot be utilized in load bearing application due to its brittleness and lack of strength [2]. Another weakness include high degree of crystallinity which result in the undegradability of pure HA when it is embedded into the implant site [5]. These drawbacks are the reasons why pure HA is not ideal to be used as bone substitutes. In order to improve the main features of the bio-implants, i.e. the mechanical properties and implantation efficacy, HA ceramics can be doped with small amounts of ions that are found in natural bone mineral [6].

Magnesium is one of the metallic elements found in bones and teeth [7, 8]. Since calcium and magnesium share the properties of group 2A elements, it can substitute calcium in hydroxyapatite, and thus in bone easily. Magnesium is also known for its role in accelerating the cell osteoblastic activity and increasing the bone growth [7]. They are several synthesis methods that can be employed to produce HA but the most popular ones include sol-gel, wet precipitation and hydrothermal methods [5-6, 9].

In this present study, magnesium hydroxyapatite (MgHA) powders of various concentrations were developed via wet precipitation method. This technique is mostly preferred due to its simple process, cost effectiveness, and capability to produce highly crystalline fine powders. Not only that, this

synthesis route also only requires lower temperature and shorter duration of phase formation. This paper aims to investigate the effect of dopant concentrations (0, 5 and 10% Mg) on the phase behaviour of MgHA when calcined at 700°C. All results were analyzed and discussed in several sections for a better understanding.

Materials and Method

Synthesis of MgHA powders

In order to synthesize the MgHA powders, the calcium nitrate ($\text{Ca}[\text{NO}_3]_2$) was added into the distilled water inside a beaker, which was heated simultaneously on the external-controlled hot plate stirrer. Then, the ammonium di-hydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) was slowly inserted into the solution followed by an addition of magnesium nitrate ($\text{Mg}[\text{NO}_3]_2$). This mixed solution was stirred continuously at a constant speed and its temperature was maintained at 90°C for about 5 hours. The pasty mixtures was then aged overnight at room temperature to ensure that complete reaction has taken place. After that, the precipitates were dried in an oven at 100°C for 24 hours to remove any excess water. This resultant solid MgHA was then crushed into fine powders by using pastel and mortar. Finally, the amorphous fine white powders were subjected to a calcination process at 700°C in a conventional furnace with a heating rate of 20 °C/min to obtain high crystalline particles.

Characterization of MgHA powders

Thermogravimetric analysis (TGA) [HITACHI, Japan] was performed on the MgHA powders by employing a 20°C/min heating rate to measure its weight loss along the temperatures from 20 - 1120°C. The MgHA powders were then analyzed using X-ray diffractometer (XRD) [Rigaku Ultima IV] to study any structural change that might occur due to the incorporation of Mg ion into the HA structure. The diffraction spectra were recorded in the range between 20° to 50° using monochromatic $\text{CuK}\alpha$ wavelength, 1.5406 Å, while the scan speed was set at 2 degree/min with step size of 0.01°. The identification of phase crystallographic was conducted by matching the samples with the standard data of HA (Card No. 9-432) and β -TCP (Card No. 009-0169) obtained from the International Centre for Diffraction Data (ICDD) reference files. On the other hand, the morphological analysis of samples containing various amount of Mg was carried out by using Field Emission Scanning Electron Microscope (FESEM) [SUPRA 40 VP (Carl Zeiss)] to attain direct information regarding the particle size of MgHA.

Results and Discussion

Thermogravimetric Analysis (TGA)

TGA was conducted to measure the changing in weight of the MgHA powders as a function of temperature. Figure 1 shows the graph of weight loss against temperature for 0, 5 and 10% MgHA powders. From this figure, it can be interpreted that bigger amount of weight loss occurred for 10% MgHA powders while only small amount of weight loss was observed for pure HA powders during the heating process.

The weight loss in this analysis could be categorized into three different stages. From the 10% MgHA line graph, it can be deduced that the first stage of weight loss (~15%) occurred at ~20°C to 200°C mostly due to the evaporation of adsorbed water. Then, in the second stage, between ~300°C to 400°C, it experienced about ~24% weight loss due to the dehydration and condensation of hydrogen phosphate (HPO_4^{2-}) group. It may also attributes to a further vaporization of H_2O from their lattice site.

Finally, the third stage of weight loss (~28%) took place at the temperature between ~620°C to 800°C. This weight loss occurred because of the decomposition of HPO_4^{2-} where Ca^{2+} ion is believed to have been replaced by Mg^{2+} ion in the HA phase. Additionally, the graph also implies that the insertion of Mg has increased the temperature of HA phase formation. There is virtually no weight loss that took place from ~820°C onwards, which inferred that the samples have become fully crystalline and HA did not transform into other phases.

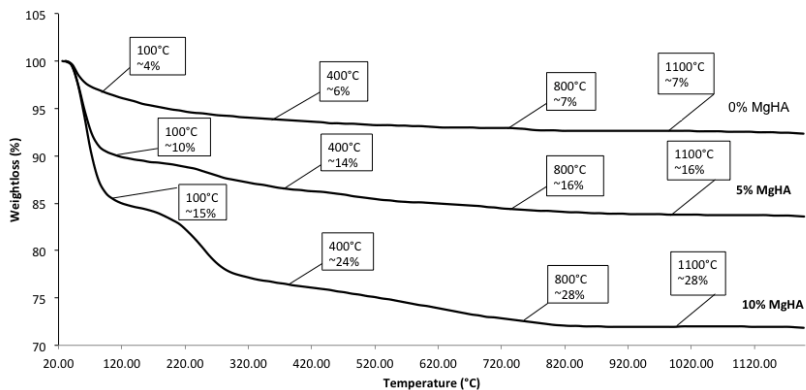


Figure 1: Thermogravimetric analysis of the as-synthesized 0, 5 and 10% MgHA powders

X-Ray Diffraction Analysis (XRD)

Figure 2 displays well-characterized peaks for pure HA, 5 and 10% MgHA powders at a calcination temperature of 700°C. XRD pattern of pure HA were broader and less intense, which implies that it possesses lowest crystallinity characteristic compared to 5 and 10% MgHA. It can be noted that the main HA peaks at around 31 – 34.5° 2 θ degree become sharper and higher in intensity as Mg concentration was increased. Nevertheless, the XRD analysis shows no presence of other secondary phases such as TCP and CaO for all three samples, proving that addition of Mg ion did not alter the phase structure of HA. This observation correlated with other study conducted by Kolmas et al. [8] who claimed that Mg²⁺ only has a minor influence on the crystal dimensions of HA, hence would not affect its phase stability.

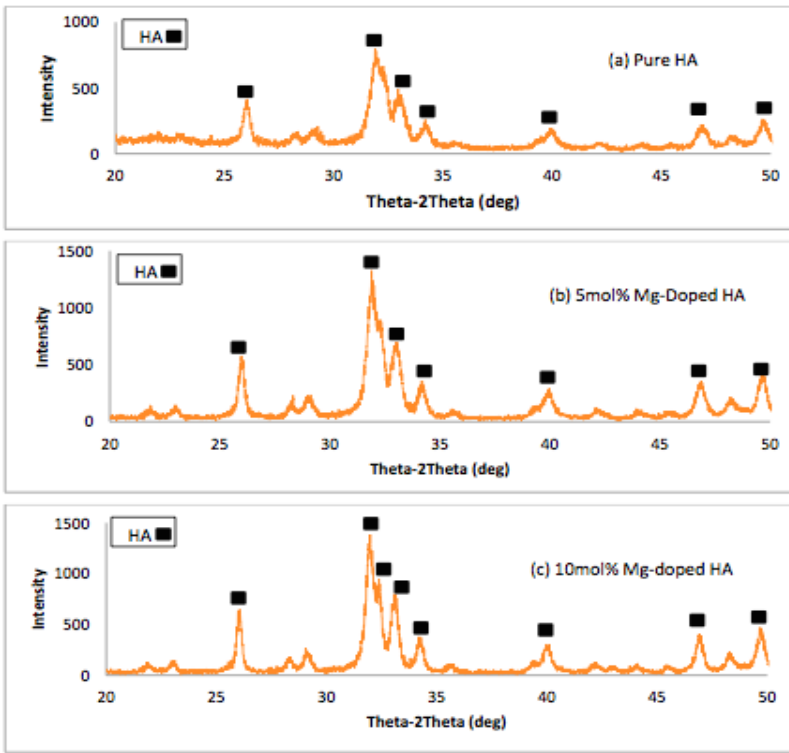


Figure 2: XRD pattern for (a) pure HA, (b) 5 and (c) 10% MgHA powders at 700°C calcination temperature

Using the data obtained from XRD, the size of a single particle of MgHA can be determined. The calculation is based on Scherrer's equation as stated below:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where, λ is the Cu K_{α} radiation wavelength = 1.5406, β is the full width at half-maximum of the isolated HA peak, θ is the diffraction angle, while K is a generally equated as 0.94.

Table 1: Particle size of 0, 5 and 10% MgHA powders calcined at 700°C

Sample	Particle size (nm)
0% MgHA (Pure HA)	87
5% MgHA	98
10% MgHA	116

Table 1 shows the calculated particle size of pure HA, 5 and 10% MgHA calcined at 700°C using the Scherrer's equation. From the table, it can be elucidated that the particle grows bigger as the concentration of Mg in HA increases. The particle size of 10% MgHA sample was found to be the largest compared to the other two samples (pure HA and 5% MgHA) indicating that Mg acts as a sintering additive, which in consequently promotes the growth of the HA particle. The particles were calculated as 87 nm, 98 nm and 116 nm for 0, 5 and 10% MgHA, respectively. This finding however, is not consistent with other published paper, which reported that Mg ion had an inhibitory effect on the particle growth of HA [10]. The discrepancy in result for the present study could be due to the different natures of how the MgHA powders were prepared. Those factors include different processing condition, Mg concentration, and type of reagents used as well as temperature employed for the thermal treatment.

Morphology Evaluation by Field Emission Scanning Electron Microscope (FESEM)

Figure 3 presents the FESEM images for 0, 5 and 10% MgHA powders calcined at 700°C. These images revealed that the powders for all samples were spherical in shape, slightly elongated and tightly agglomerated. The particles were also observed to significantly increase in size when the

amount of Mg was increased, which coincides with the result calculated from Scherrer's equation. Due to its increase in size, the agglomerated powders also became less dense-packed as more Mg ion was added.

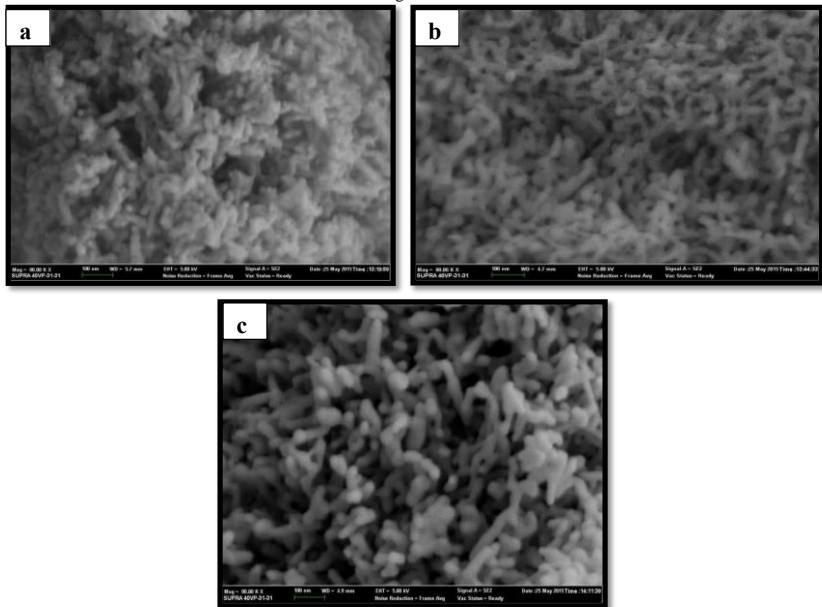


Figure 3: FESEM images for (a) 0 (b) 5 and (c) 10% MgHA powders calcined at 700°C

Conclusion

Mg-doped HA powders have been successfully developed by using wet-chemical precipitation method. After calcination at 700°C, XRD analysis confirmed that all powders containing 0, 5 and 10% of Mg were highly crystalline and similar to the apatitic structure of HA with no detection of any secondary phase. The Mg ion was found to have an influence on the particle growth of HA by acting as a sintering additive. This has caused the coarsening of the powders particle during calcination process as the Mg concentration was increased, which was also validated from the FESEM evaluation. The result calculated using the Scherrer's equation showing that the average sizes of the particles were about 86-116 nm. This physicochemical study on MgHA could provide valuable information for future in-depth studies, in an effort to develop a new alternative biomaterial with superior properties for various biomedical applications.

Acknowledgement

The authors would like to thank Institute of Research Management & Innovation (IRMI) UiTM and Ministry of Higher Education Malaysia for financial supports. The research was funded by Research Acculturation Grant Scheme (RAGS) under Grant No. 600-RMI/RAGS 5/3 (37/2015).

References

1. D. Arcos, A.R. Boccaccini, M. Bohner, A. Diez-Perez, M. Epple, et al., "The relevance of biomaterials to the prevention and treatment of osteoporosis," *Acta Biomaterialia* 10, 1793-1805 (2014).
2. D. Bellucci, L. Desogus, S. Montinaro, R. Orru, G. Cao and V. Cannillo, "Innovative hydroxyapatite/bioactive glass composites processed by spark plasma sintering for bone tissue repair," *Journal of the European Ceramic Society* 37, 1723-1733 (2017).
3. T. Furuzono, D. Walsh, K. Sato, K. Sonoda, and J. Tanaka, "Effect of reaction temperature on the morphology and size of hydroxyapatite nanoparticles in an emulsion system," *Journal of Materials Science Letters* 20 (2), 111-114 (2001).
4. F. Heidari, M. Razavi, M. Ghaedi, M. Forooghi, M. Tahriri and L. Tayebi," *Journal of Alloys and Compounds* 693, 1150-1156 (2017).
5. C.M. Mardziah, I. Sopyan and S. Ramesh, "Strontium-doped hydroxyapatite nanopowder via sol-gel method: Effect on strontium concentration on phase behavior," *Trends Biomater. Artif. Organs* 23 (2), 105-113 (2009).
6. A. Zanotto, M. Saladino, D. Martino, and E. Caponetti, "Influence of temperature on calcium hydroxyapatite nanopowders," *Advances in Nanoparticles* 1, 21-28 (2012).
7. Z.S. Tao, W.S. Zhou, X.W. He, W. Liu, B.L. Bai, et al., "A comparative study of zinc, magnesium, strontium-incorporated hydroxyapatite-coated titanium implants for osseointegration of osteopenic rats," *Materials Science and Engineering C* 62, 226-232 (2016).
8. J. Kolmas, A. Jaklewicz, A. Zima, M. Bucko, Z. Paszkewicz, et al., "Incorporation of carbonate and magnesium ions into synthetic hydroxyapatite: The effect on physicochemical properties," *Journal of Molecular Structure* 987, 40-50 (2012).
9. A.S.F. Alqap and I. Sopyan, "Low temperature hydrothermal synthesis of calcium phosphate ceramics: Effect of excess Ca precursor on phase behavior," *Indian Journal of Chemistry* 48A, 1492-1500 (2009).
10. A. Farzadi, F. Bakhshi, M. Solati-Hashjin, M. Asadi-Eydivand and N.A. Abu Osman, "Magnesium incorporated hydroxyapatite: Synthesis and structural properties characterization," *Ceramics International* 40, 6021-6029 (2014).