

## Development of Triphasic Calcium Phosphate–Carbon Nanotubes(HA/TCP-CNT) Composite: A Preliminary Study

Gunawan<sup>1,2,a</sup>, I. Sopyan<sup>1,b</sup>, S. Nurfaezah<sup>1</sup> and M. 'Ammar<sup>1</sup>

<sup>1</sup>Department of Manufacturing and Materials Engineering, Faculty of Engineering, International Islamic University Malaysia, P.O. Box 10, Kuala Lumpur 50728, Malaysia

<sup>2</sup>Mechanical Engineering Department, Faculty of Engineering, Sriwijaya University, Indonesia

<sup>a</sup>gunsyauqi@yahoo.co.id, <sup>b</sup>sopyan@iium.edu.my

**Keywords:** Hydroxyapatite,  $\alpha$ -TCP,  $\beta$ -TCP, Carbon Nanotubes, Hydrothermal method

**Abstract.** Triphasic calcium phosphate, composed of a more stable phase hydroxyapatite (HA) and highly soluble tricalcium phosphates ( $\alpha$ - and  $\beta$ -TCP) has been synthesized through hydrothermal method. In the present work, an *in-situ* method to disperse 1wt% multiwall carbon nanotubes (MWCNTs) within HA/TCP powder has been used in order to develop HA/TCP-CNTs composite. XRD results confirmed the formation of HA,  $\alpha$ -TCP and  $\beta$ -TCP in both as-prepared powder and composite samples. The graphite peaks appeared in the composite samples as well. FTIR analysis of sintered compacted powder showed the formation of weak bands of  $\text{PO}_4^{3-}$  as the temperature was increased. The sintered compacts were mechanically tested by Vickers microhardness indentation method. HA/TCP-CNTs composite was found to have a significant Vickers Hardness of 1.98 GPa after 1100°C sintering. The morphology analysis showed that *in-situ* deposition technique provides homogeneous dispersion of CNTs in the calcium phosphate matrix.

### Introduction

Hydroxyapatite (HA,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ), is a synthetic biomaterial similar to calcium phosphate present as the inorganic components of teeth and bones. It has been used and applied widely in the medical field, especially as the dental and bone transplant materials due to its excellent biocompatibility and bioactivity properties [1]. Triphasic calcium phosphates (HA/TCP) composed of nonresorbable hydroxyapatite (HA) and resorbable tricalcium phosphate ( $\alpha$ - and  $\beta$ -TCP). HA/TCP is believed to enhance the osteoconductivity and osteogenesis of the bones [2].  $\alpha$ -TCP is a high-temperature phase and crystallizes at a temperature of 1120°C whereas  $\beta$ -TCP is unstable at room temperature. However lately, HA/TCP has been successfully produced at temperature as low as 800°C by researchers [3, 4].

HA is a typical highly bioactive ceramic; however it has poor mechanical property such as brittleness and low tensile strength, which has impeded its use in clinical applications, particularly under conditions that require load-bearing application [5]. Thus, use of secondary component materials is needed to improve the properties of HA.

Recently, many researchers have attempted to manufacture composites of HA reinforced with CNTs in expectation of enhanced mechanical properties. Moreover, HA-CNTs composite has the potential to strengthen and to toughen HA without offsetting its bioactivity, thus opening up a wide range of possible clinical uses for these materials [6]. One of the major and recurring problems encountered in developing HA reinforced CNTs composites are the ability to create a homogeneous dispersion of CNTs. It is important to ensure uniform properties throughout the composite. Several physicochemical blending methods have been developed to disperse CNT powder throughout the HA matrix, such as ball milling [7], mixing in solvent [8], and *in situ* formation of CNTs in HA matrix. Li et al. [9] demonstrated the preparation of HA-CNT nanocomposites by *in-situ* deposition techniques. The results showed that the *in-situ* technique is effective in dispersing the nanotubes within HA powder, which simultaneously protects the nanotubes from damage.

In the present investigation hydroxyapatite nanopowder has been synthesized by hydrothermal method and a bulk HA/TCP body reinforced with CNTs has been developed for biomedical

application. Moreover, the properties of HA/TCP and HA/TCP-CNTs for both green (un-sintered) and dense materials have been evaluated using XRD and FTIR. Mechanical and microscopic analysis of the properties has also been conducted.

### Experimental Procedures

The pure HA powder was prepared through hydrothermal method. Calcium oxide, CaO (R&M chemicals, UK), and ammonium di-hydrogen phosphate,  $(\text{NH}_4)_2\text{HPO}_4$  (R&M chemicals, UK) was hydrothermally reacted at 86-92°C under stirring condition on hot plate for 60 minutes. The produced HA/TCP powder was then oven-dried and left at 90°C overnight. The following day, HA powder was crushed and calcined at 900°C. The powder of pure HA/TCP was mixed with commercial 1 wt% multi walled carbon nanotubes (MWCNTs). Each solution of HA and CNTs was sonicated for approximately 30min and followed by the heating 90°C in hot plate, and 1 wt% of additive ethyl alcohol (System) was added to this suspension.

HA/TCP-CNTs powder (approximately 0.8 g) was compacted under uniaxial load of 2.5 MPa in a 13 mm evacuable steel pellet die and held for 2 minutes under the load before releasing the pressure and ejecting the compact. The green compacts were then subjected to cold isostatic press (CIP) of 250 MPa. Afterwards all the compacted samples were sintered at 900 and 1100°C. The heating and cooling rates were set to 5°C/min. The porosity was measured considering the theoretical density of HA, and the following formula was applied Eq. (1):

$$P(\%) = 100\% - \frac{\rho_c \times 100\%}{\rho_t} \quad (1)$$

where,  $P(\%)$  is the porosity calculated in percentage,  $\rho_c$  is the calculated density and  $\rho_t$  is the theoretical density of HA (3.16 g/cm<sup>3</sup>).

### Results and Discussion

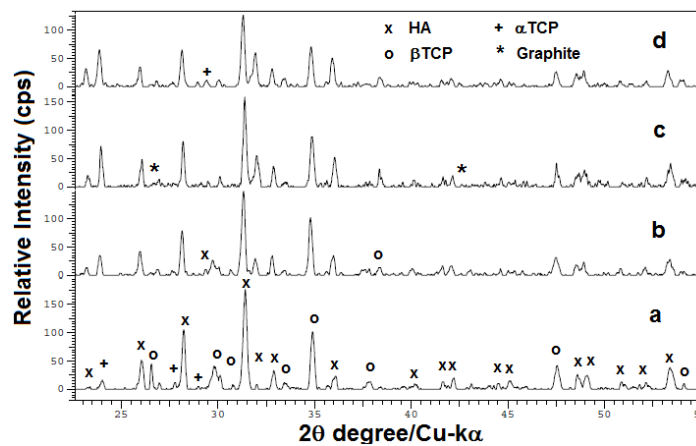


Fig. 1 XRD patterns of: a) HA/TCP Powder calcined at 900°C b) HA/TCP dense sintered at 900°C c) HA/TCP-CNTs sintered at 900°C d) HA/TCP-CNTs sintered at 1100°C

The figure 1.a shows peaks of dense HA attributed to HA (JCPDS 09-432) as the main phase,  $\beta$ -TCP (JCPDS 09-169) and  $\alpha$ -TCP (JCPDS 09-348) as the secondary and third phase respectively. No peaks corresponding to  $\text{CaCO}_3$  or CaO were found, suggesting that the conversion was complete. The diffraction peak of  $\beta$ -TCP (122) at  $2\theta$  of 26.3°, (300) at  $2\theta$  of 29.8° and (0210) at  $2\theta$  of 31.0° became smaller after sintering, on the other hand peak of HA (111) at  $2\theta$  of 23.1° and (112) at  $2\theta$  of 32.1° as well as peak of  $\alpha$ -TCP (132) at  $2\theta$  of 24.1° became narrower after sintering. It is indicated that conversion of  $\beta$ -TCP to HA and  $\alpha$ -TCP occurred at lower cooling rate [10]. Fig. 1(c, d) shows HA/TCP-CNTs composite patterns, the peaks at 26.6° and 43.1° are assigned to graphite crystallographic (0 0 2) and (1 0 0) plane of CNTs [11].

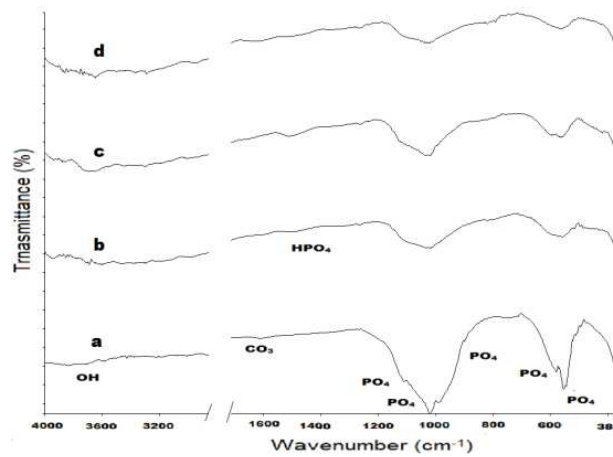


Fig. 2 FTIR spectra of: a) HA/TCP Powder calcined at 900°C b) HA/TCP dense sintered at 900°C c) HA/TCP-CNTs sintered at 900°C d) HA/TCP-CNTs sintered at 1100°C

The characteristic peak observed in Fig. 2 show the FTIR spectra for both the HA/TCP powder and HA/TCP-CNTs dense materials. The spectra show vibration characteristic of apatite phase. The characteristic phosphate (mode  $\nu_4$ ) vibrations of HA are spotted at 556 and 580  $\text{cm}^{-1}$  and other mode  $\nu_1$ , and mode  $\nu_3$  of  $\text{PO}_4^{3-}$  peaks at 991, 1020 and 1112  $\text{cm}^{-1}$  respectively. The bands at 3400-3600  $\text{cm}^{-1}$  could be attributed to the presence of hydroxyl group (OH). Furthermore the bands at 1380-1550  $\text{cm}^{-1}$  correspond to  $\text{CO}_3^{2-}$  groups while 1465 to  $\text{HPO}_4^{2-}$  [1]. The intensity of the peaks decreases on an increase in the sintering temperature for both dense HA/TCP and HA/TCP-CNTs composite. Moreover  $\text{PO}_4^{3-}$  peaks spotted at 580  $\text{cm}^{-1}$ , 991  $\text{cm}^{-1}$  and 112  $\text{cm}^{-1}$  became obliterate for the sintered samples. The low intensity hydroxyl group at 3.455  $\text{cm}^{-1}$  indicates the presence of HA/TCP [12].

Table 1. Result of shrinkage, porosity and hardness value

SAMPLE	Sinter temperature ( $^{\circ}\text{C}$ )	Linear shrinkage (%)	Volume shrinkage (%)	Porosity (%)	Hardness (Hv)
HA/TCP	900	10.24	24.36	40.6	0.4
	1100	11.43	23.1	19.1	1.35
HA/TCP-CNTs	900	9.4	26.9	27.1	0.8
	1100	17.01	39.84	17.3	1.98

Table 1 indicates that with an increase in the sintering temperature from 900 to 1100°C, there is an increase in linear and volume shrinkage percentages of compacted materials. However linear shrinkage at sintering temperatures of 1100°C for HA/TCP-CNTs composite materials are quite higher than HA/TCP material. From porosity and Vickers Hardness measurement of both the samples it is depicted that with an increase in sintering temperature there is an apparent decrease in porosity and an increase in the hardness number. HA/TCP-CNTs composite, sintered at 1100°C was found to have higher Vickers Hardness viz; 1.98 GPa. Theoretically, sintering results in a remarkable shrinkage of materials due to their glass flow once the transition temperature is reached, which is then followed by consolidation of the powders with a considerable reduction in the porosity of materials. As porosity has an effect on the mechanical properties of the materials, a less porous sample will result in a higher mechanical strength due to an increase in the density.

Fig. 3 shows the morphology of both HA/TCP dense and HA/TCP-CNTs composite sintered at 900°C. The HA/TCP-CNTs composite sample appears to have a homogeneous dispersion of CNTs in the matrix, suggesting that dispersion of CNTs has been successful through *in-situ* method. Furthermore the individual HA/TCP have globular shape with HA/TCP already melted and diffused together.

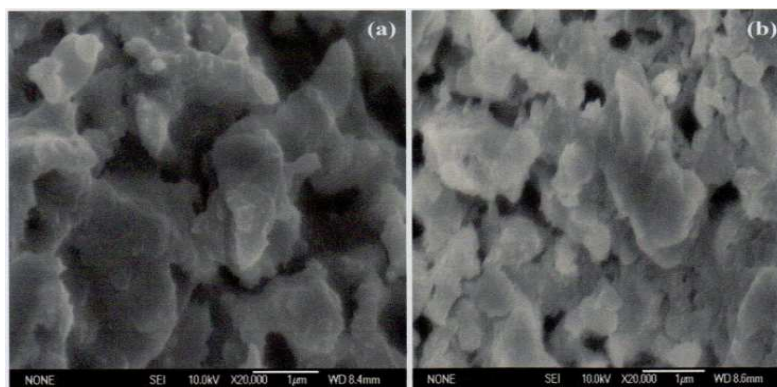


Fig. 3 FESEM micrograph of samples sintered at 900°C: a) HA/TCP b) HA/TCP-CNTs composite

### Summary

HA/TCP powders have been successfully synthesized using hydrothermal method. The properties of HA/TCP and HA/TCP-CNTs for both powder and dense materials were analysed using XRD and FTIR, followed by mechanical as well as microscopic analyses. The morphology analysis shows that *in-situ* deposition technique using ethyl alcohol as the additive provides homogeneous dispersion of CNTs in the calcium phosphate matrix.

### Acknowledgement

The authors would like to thank the financial support provided by Ministry of Higher Education (MOHE) under the FRGS programme (Project No. FRGS11-025-0173).

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