

## Study on the influence mechanism of sintering hydroxyapatite (HA)

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As one of promising biomaterial, hydroxyapatite (HA) is potentially used as an implant component. Yet, to date, HA still encounter difficulties to be commercialise due to the easily deteriorate and often fluctuate mechanical performance which depends on the manufacturing process. Thus, this study aims to experiment the influence of HA composition and sintering parameter on the densification, morphological analysis and flexural strength in terms of green parts and sintered HA. The HA parts are fabricated through the powder injection moulding process with the pressure applied between 10 and 12 bar at 150 °C. The HA compositions are varied of 54 wt.%, 55 wt.% and 56 wt.% while the sintering parameter are set at 1,100 °C, 1,200 °C and 1,300 °C. The 56 wt.% of HA parts recorded the densification of 2.13 g/cm<sup>3</sup> and 2.95 g/cm<sup>3</sup> for both green parts and sintered parts at 1,300 °C. However, as the sintering temperature reduced to 1,200 °C, the densification reached the value of 2.9 g/cm<sup>3</sup> with the existence of porous structure to allow tissue growth. This finding suggested that the HA parts can be mass produce using powder injection moulding process at 1,200 °C, with a minimum existence of porosity to allow tissue growth in between the HA structure.

**Keywords:** powder injection moulding, flexural strength, densification

### Introduction

Hydroxyapatite (HA) shows a similar property as natural bone based on its chemical compound and structures [1, 2]. Due to this similarity, HA often used as a bone fillers which enhances growths of natural tissues as much as potential in connect of bone tissues firmly via the chemical bonding [3]. Even though, to date, there are extensive research performed involved the use of HA incorporated either with Titanium alloys or even Stainless steel (SS316L) materials, yet the optimum that meet the main purpose of implant materials are yet to come [4]. There are many factors which leaden the use of HA materials as implant materials including its deficient mechanical properties that is obvious [5]. Current development reported that coated implant using HA coated seems promising due to its excellent and progressive biocompatibility and osteoconductive behavior [6]. However, this technique has major limitation in terms of latest manufacturing technology that required depth knowledge and understanding of HA materials itself to be mass manufactured and commercialize. Based on this information, the standard and most common process are applied in this research involving the powder injection moulding

process [7].

Powder injection moulding (PIM) known as an efficient process especially when producing a small product components with complex and acquired high precision of the net shape [8, 9]. Gather potential in gaining trust among researchers and industrial, PIM process able to produce a green part as the densification, strength and defects can be easily determined [10, 11]. Those selected green parts will later undergo debinding and sintering process to strengthen the structures [4, 12]. Flexibility offer via this PIM process ensure the parameter to be adjusted based on needs and sensitivities [12, 13]. Although some investigation has move towards additive manufacturing (AM) in developing implant materials, yet difficulties often related with the melting and geometrical precisions [14, 15]. Controlling its porosity and sintered structured seems much more effective based on current availability and technology in today's market [16].

Also, studies reported that the occurrence of porosity structure within the HA components are crucial as its allowed tissues growth and filled the porous structure [4]. In fact, studies exhibited that sintering temperature plays the main domain in the fabrication of implant biomaterials as its can easily affects the overall thermal stability and mechanical performance [5]. Therefore, this study aims to investigate the HA materials fabricate by PIM process using different HA compositions and sintering parameter in order to identify the influence mechanism of inner HA structure.

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## Experimental

### Materials

Raw material of hydroxyapatite (HA) were collected from Sigma Aldrich Sdn. Bhd., Malaysia with the chemical composition of  $\text{Ca}_5(\text{PO}_4)_3\text{OH}$  in powder form with an average particle sizes of 5.34  $\mu\text{m}$ . The HA was supplied in spherical shape geometry which suitable for future manufacturing process using powder injection moulding. Also, low-density polyethylene (LDPE) used was collected from Cosmothene, The Polyolefin Company (Singapore) Pte. Ltd. These LDPE used were selected based on its ability as a binder and a backbone which hold the shapes of the samples before being debind during the end of the fabrication process. The palm stearin that supplied by Sime Darby Sdn. Bhd. acted as a lubricant during the powder injection moulding process.

### Fabrication process

The critical powder volume percentage (CPVP) of the HA used were determined at various powder loading including 54 wt.%, 55 wt.% and 56 wt.% based on ASTM D-281-31 [8]. Also, as for the binder, 60 wt.% of palm stearin and 40 wt.% of LDPE were later added onto the HA powder and mixed using the Brabender mixer, roller motor types at rotational speed of 30 rpm and operational temperature of 150 °C. The prepared feedstock was then undergo the rheological analysis using Shimadzu CFT-500D machine with the die diameter of 1 mm and 10 mm long based on ASTM D-3835 to ensure flowability of the feedstock and identify the injection parameter used. The prepared feedstock then injected using powder injection moulding, model DSM Xplore with the pressure applied between 10 and 12 bar at 150 °C of operating temperature. The injected compound is known as green part with the diameter of 5 mm and 20 mm height.

### Debinding and sintering process

The injected green part was debind by chemical debind and thermal debind in order to remove the LDPE and palm stearin used as a binder in the HA compound. The chemical debind was performed using heptane solution prepared in waterbath, model Memmert at 60 °C for 6 h used to remove the palm stearin. Later, the thermal debind process were prepared to remove the LDPE by using thermal debind furnace with the operating temperature of 500 °C for 60 min with the heating rate of 5 °C/min. The temperature of 500 °C remain for another 60 min before being cooled to room temperature at cooling rate of 5 °C/min. the prepared green part was then sintered using vacuum furnace, model KOREA VAC-TEC (VTC 500HTSF). Although, the sintering process acquired several stages, the first stages involved the heating rate of 5 °C/min till the temperature reach 900 °C for 1 h. Through the process,

only 56 wt.% of powder loading were selected and studies using different sintering parameter; 1,100 °C, 1,200 °C and 1,300 °C. The heating rate of 3 °C/min was consistent as the temperature reach it maximum and last for 5 hours before cooled down to room temperature with the cooling rate of 5 °C/min.

### Measurement and characterization

The densification and porosity of the HA compound was analysed using Archimedes principal, using Sartorius density machine, model BSA224S-CW, according to MPIF 42 and ASTM B962 for both green part and sintered part of the HA compound [4]. Micrographical characteristics was observed using scanning electron microscope (SEM), model Hitachi TM-1000. The flexural strength of the HA-compound was measured using a three-point bending test performed using 1 tonne Universal Testing Machine, model Instron 5567 with the crosshead speed of 0.1 mm/min [8]. The harden structure of HA compound was measured using Metallic Vickers Tester, model HVS10 based on ASTM D785 with the maximum load applied is 200g for 15 sec indentation time.

## Results and Discussion

### Flexural strength of green and sintered HA part

HA green part acquired certain level of strength as it may ease the handling process and able to be produce without any defected in which studies using HA/Ti6Al4V reported the average flexural strength of 7.6 MPa which slightly lower compared to these study as shown in Fig. 1(a) [1]. These demonstrate that there is an improvement in term of green part strength as the HA compound itself able to reach the minimum of 8.79 MPa for 54 wt.% of powder loading as seen in Fig. 1a. Although, it is clearly exhibited that the increase trend of flexural strength reflected the increment of the powder loading which in consistent with finding using 15 wt.% and 25 wt.% of HA- $\text{Al}_2\text{O}_3$  materials that obtained the maximum strength of 0.25 MPa and 1.01 MPa, respectively [17]. Also, results indicated that the optimum injection pressure is 11 bar with the maximum value of flexural strength of 11.79 MPa at 56 wt.%. Studies reported that suppling less pressure will result some defects including short sort occurrence. In contrast, studies reported that by supplying injection pressure at 13 MPa the maximum strength obtained only at average of 7.6 MPa [1]. These certainly listed in Fig. 1(a) as the pressure increase to 12 MPa, the flexural strength of the HA green part started to deteriorate to 11.78 MPa and remained stagnant. Studies using HA sintered part recorded the depletion of flexural toughness from 0.65  $\text{MPa}\cdot\text{m}^{1/2}$  to 0.4  $\text{MPa}\cdot\text{m}^{1/2}$ , as the pressure increase between 7.8 MPa to 62 MPa which explained the phenomenon occurrence in this study [18]. These supported results indicated in Fig. 1(b) in

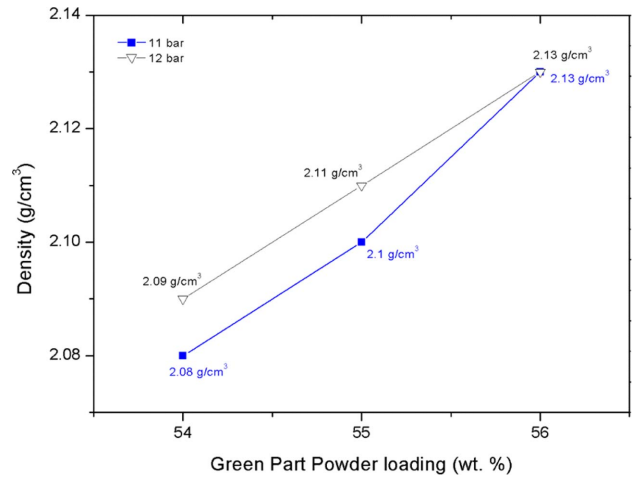
which the flexural strength of sintered HA was improved from 7.3 MPa to 17.75 MPa as the sintering temperature increase from 1,100 °C to 1,300 °C, respectively. These are corresponded to morphological analysis and densification discussed on following subtopics in which the sintered HA harden and results in excellent flexural strength due to the occurrence of grain growth and minimum existence of porosity [19].

**Densitication of HA compound**

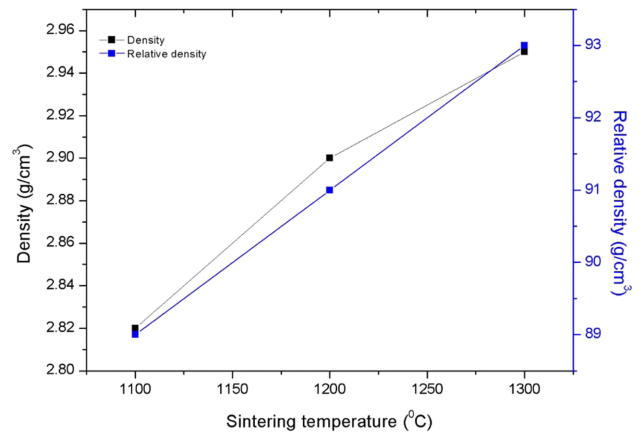
Densitication of the HA compound were details in Fig. 2 in which as the temperature maintained 150 °C the prolonged densitication acquired the same value of 2.13 g/cm<sup>3</sup> even though the pressure applied were different. These clearly exhibited that the pressure and powder loading examine do have a prominent effect, consistent with studies reported using the HA powders in which the density of the compound are dramatically increase before shows a plateau sign [20]. Although, the temperature did not gave any significant different on HA green part, yet, the powder loading clearly indicated that increase in powder loading will drastically increase the densitication of the HA compound. As the powder loading increase, theoretically it will cause more compact structure and allow agglomerations occurrance. Also, the densitication remain constant as the powder loading increase shows that the abilities of tissues growths to dissolve within these porous HA structures especially after being sintered.

The HA green parts were then sintered and analysed as shown in Fig. 3 which the density of sintered parts increase as the sintering temperature increase. Although, the densitication of the overall sintered part increase at the minimum amount of 2.82 g/cm<sup>3</sup>, its clearly demonstrate that the HA parts are now solidified hence, results in strengthen its overall structure. Also, as the sintering temperature rise to 1,300 °C, the maximum densitication recorded at 2.95 g/cm<sup>3</sup>. Studies using

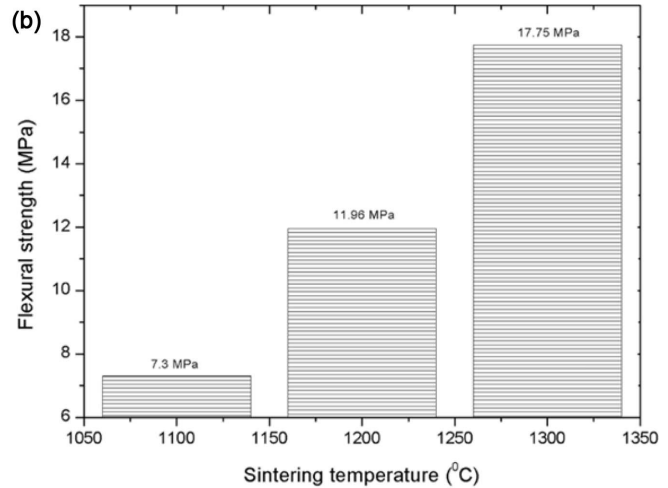
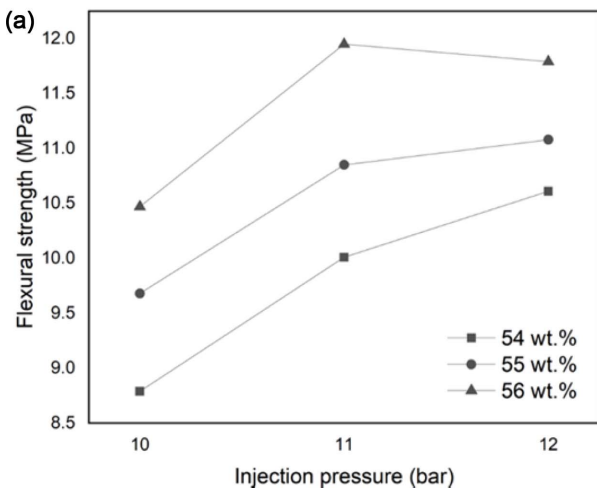
ceramic materials reported that the sintering temperature of 1,300 °C, seems an acceptable temperature which



**Fig. 2.** Densitication of HA green parts at different powder loading.



**Fig. 3.** Densitication of HA green parts at different sintering temperature.



**Fig. 1.** Flexural strength of (a) HA green part at different injection pressure and powder loading of 54 wt.%, 55 wt.% and 56 wt.% and (b) sintered HA part at 1,100 °C, 1,200 °C and 1,300 °C.

reveals a pure material [21]. These phenomena indicated that any higher temperature will only worsen its properties. Moreover, the study also posted that as the sintering temperature increase to 1,300 °C, the structure of materials tends to encounter a grain growth which reflected its densification. However, the results obtained in this study slightly contrast with other study using HA-sodium alginate materials in which the sintering temperature between 1,000 °C and 1,100 °C. The study reported that the acquired densification values remain in average of 1.82 g/cm<sup>3</sup>. These are due to the fact that as the sintering temperature increase, the sodium alginate started to dwindle hence the densification of produce HA-sodium alginate is unstable [17, 22]. Meanwhile, studies using SS316L-HA composites reported that insufficient sintering temperature and sintering time will lead to excessive porosity occurrence which lower the end-produced materials [8]. Noted that the type of solvent used during the densification measurement has insignificant effects toward the relative density, Fig. 3 lists the maximum density of 2.95 g/cm<sup>3</sup> at sintering temperature of 1,300 °C. Fig. 3 recorded that the relative density stabilized at approximate 99% during the sintering temperature of 1,100 °C and 1,300 °C. Yet, at sintering temperature of 1,200 °C the relative density seems slightly lower at 96% which clearly suggested the existence of excessive porosity or agglomeration which invisible to physical view as reported by others research [8, 20].

### Hardness, porosity and morphological evolution of sintered part

Fig. 4 clearly indicated that the hardness of sintered HA parts is increase as the sintering temperature increase which in accordance with studies using HA-sodium alginate [22]. Studies suggested that the HA particles are closely packed hence, form a dense structure at higher sintering temperature [23]. For instance, undoped HA usually reported with an average of 3 GPa (~305 Hv), while doped HA materials usually will further harden and able to reach ~4 GPa [23, 24]. Yet, this study as shown in Fig. 4, able to attain 700 Hv (~7 GPa) for pure sintered HA parts due to the fact that the occurrence of packed and grain arrangement onto

the HA microstructure. Also, as seen in Fig. 4, the increment in HA hardness are contradict with the porosity eventuate in the HA structures. This result is constants with others findings that reported the porosity reduction as the sintering temperature increase hence harden the structural materials [25]. It can be noted that the maximum porosity of 20% value recorded at 1,100 °C meanwhile, the porosity value decreases till 2.5% as the temperature increase to 1,300 °C. These evidences clearly indicated by Fig. 5 in which the porosity occurrence decreased as the sintering temperature increase from 1,100 °C to 1,300 °C. Fig. 5(a) demonstrate that the existence of porosity is obvious with no sign of grain growth. Meanwhile, as the temperature increase to 1,200 °C, it seems that a slight porosity emerges within the sintered HA materials as indicated in Fig. 5(b). Also, Fig. 5(c) provided clear evidence that the grain growth appears to minimize the porosity occurrence hence result in very little porosity. These morphological images correlated well with the measured density which showed almost full of densification at temperature of 1,300 °C. Although the fully dense HA parts are not attained in this present work, yet, the obtained data has a great potential for clinical implant application as supported by others finding [11]. Also, studies of ceramic materials, silicon carbides (SiC) porosity reported that the reduction of porosity percentage as the

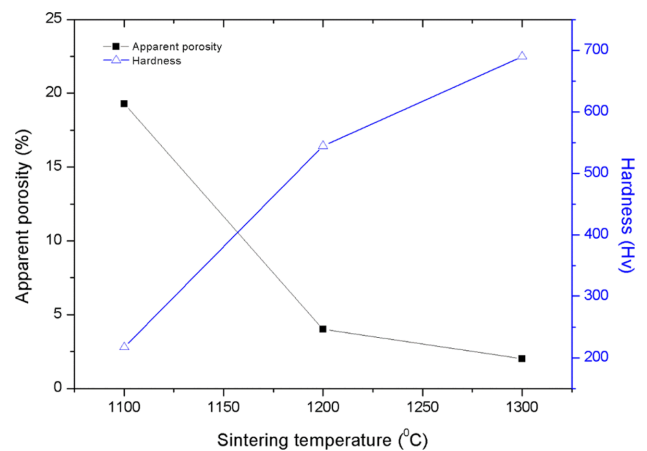


Fig. 4. Hardness and porosity at different sintering temperature.

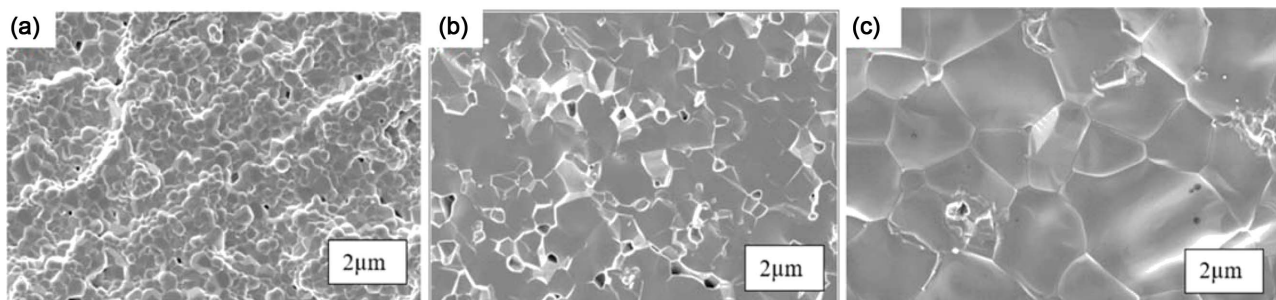


Fig. 5. Morphological images of the sintered HA part at sintering temperature of (a) 1,100 °C, (b) 1,200 °C, (c) 1,300 °C.

temperature increase was subjected to the necking behavior [26].

### Conclusion

Sintered parts of HA potential in behaviour as implants materials as the flexural strength can reached up till 17.75 MPa meanwhile the hardness recorded at 700 Hv that prove as the HA parts being sintered the mechanical performance improved and strengthen due to minimum occurrence of porosity. Also, the critical powder loading of 56 wt.% able to obtain the dense with minimum porous structure compared to 54 wt.% and 55 wt.%. This research also clearly highlights that as the sintered HA parts able to possess a smooth and compact structure at 1,300 °C compared to 1,100 °C and 1,200 °C of sintering temperature. These findings allow a benchmarks of HA compound acquired in order to form a proper strength and micrograph structure of implant materials. In order to allow enough tissues growth the optimum 56 wt.% and sintering temperature of 1,200 °C seems the appropriate parameter to be consider of.

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### Conflict of interest

No potential conflict of interest was reported by the authors.

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