Fabrication of Titanium-Matrix Composite with 40 wt% Hydroxyapatite by Powder Injection Molding

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Abstract In this work, the performance of composites feedstock HA/Ti for metal injection molding is investigated by rheological characterization with powder loading 65%. Titanium and Hydroxyapatite (HA) powder are mixed with a composite binder, which consists of Palm Stearin (PS) and Polyethylene (PE). The rheology properties are investigated by Shimadzu CFT-500D rheometer. Thermal debinding is utilized for removing the binder system under argon gas. The sintering process is performed under argon conditions at temperature 1200 °C for 2 h. The feedstock 60 wt%Ti and 40 wt%HA show *pseudopalstic* behaviour which is indicating suitable for MIM application. On the sintered part, Ca:P ratio of HA has changed based on the standard value of HA(1.67) as an indication decomposition of HA. Cracks have been observed on part of composite HA/Ti by SEM due to differences in thermal expansion of the two materials and not a good diffusion between HA and Ti. For further work, modification in the composition of mixture and sintering parameters are required to reach an optimal result.

Keywords PIM · Composite HA/Ti · Palm stearin

1 Introduction

Powder Injection Molding (PIM) is one part of powder metallurgy, which has advantages in fabricate small parts and have complex shapes in large numbers. PIM is usually comprised of several steps such as mixing, injection, debinding, and ending with sintering [1].

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Titanium alloys and Hydroxyapatite are well-known materials for application biomedical [2–6]. Titanium has well in specific strength, corrosion resistance and lower young's modulus close to cortical bone young's modulus (10–30 GPa). Beside some advantage that mentions previously, Titanium has poor biocompatibility properties. Hydroxyapatite (HA) has chemical and structure properties being similar to the human bone. HA has excellent on biocompatibility properties but has weakness in mechanical properties, additional of HA into Titanium Alloy is expected to enhance the biocompatibility properties of Titanium. Moreover, the combination of titanium and HA can be applied to load-bearing applications.

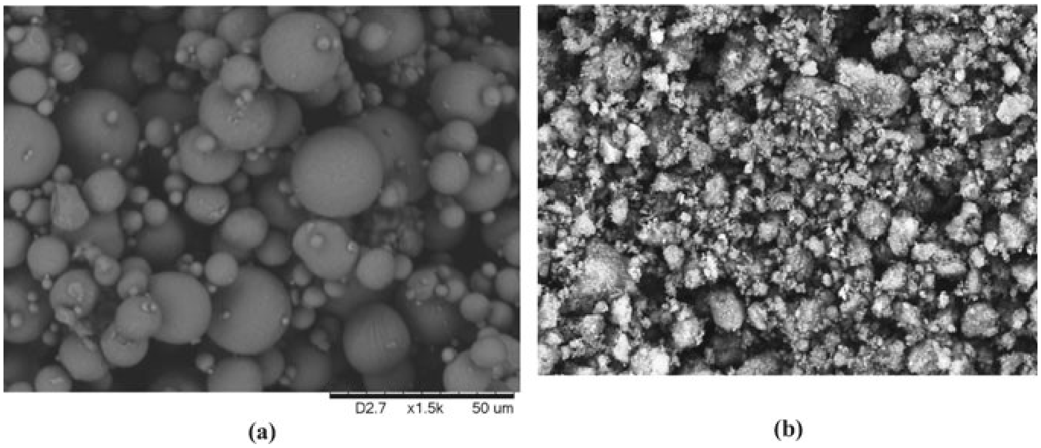
In these experiments, the binder system used comes from Natural Binder, namely palm stearin. It will be combined with Polyethylene who served as the backbone to keep the shape of the specimen. The use of palm stearin as a binder has been widely used by some previous researchers [7–9]. Palm stearin has the advantage of easily removed via solvent debinding in addition to its environmentally friendly [10].

Some author has performed to combine HA and titanium alloy using plasma spraying and powder metallurgy (PM) [8–12]. In term of Powder metallurgy (PM) technique. Fabrication HA/Ti composite tend to rare although PIM itself has many advantages compared to other PM technique. PIM has the advantage when producing small part with complex shapes in large amounts [11, 12].

This paper is the initial step in the development of HA/Ti composite using MIM. Characterization was performed on the powder and binder including feedstock characterization and some stage subsequently such as debinding and sintering.

2 Methodology

Figure 1a shows Ti6Al4V powder with an average size 20 µm which was kindly supplied by TLS Technik GmbH & Co. Hydroxyapatite powder with average size



(a) (b)

Fig. 1 Scanning electron micrograph of Ti6Al4V powder (**a**) and Hydroxyapatite (**b**)

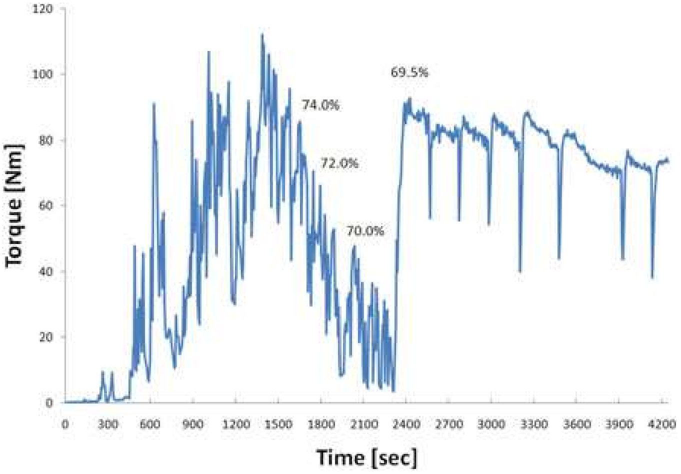


Fig. 2 Critical volume percentage of composite HA/Ti with 60 wt%Ti and 40 wt% HA

Table 1 Binder system

Binder	Type	Melting temperature (°C)	Density (g cm^3)
Palm Stearin (PS)	Primary, surfactant, lubricant	61	0.89
Polyethylene (PE)	Backbone	127	0.91

5 μm has been purchased by Sigma-Aldrich as shown on Fig. 2b. Ratio powder between titanium and hydroxyapatite is 60wt%Ti: 40wt%HA.

Binder systems were utilized in this work consist of 60 wt% palm stearin and 40 wt% Polyethylene as shown on Table 1. Brabender® was used to mix powders and binder at temperature mixing 150 °C and mixing speed 30 rpm. The mixing temperature was determined by the result of Differential Scanning Calorymetry (DSC) test for both binders. Mixing temperature should be higher than the melting point of the binder to make sure binder system easy to mix with powders. Melting temperature of palm stearin and polyethilene are 53.97 °C and 124.75 °C, respectively.

Powder loading value was determined by critical powder volume percentage (CPVP) test, According to German and bose [1] optimal powder loading value 2–5% less than the critical value. To obtain critical value, oleic acid was added into the composite powder HA/Ti mixture in 1 mL for every 5 min. The volume of oleic acid correlates with torque value can be defined as

$$CPVP = 100 \times \frac{V_f}{V_f + V_o}(\%) \tag{1}$$

Binder system on the part was removed using thermal debinding with two stages. Brown part was sintered using a tube furnace under argon condition at temperature 1200 °C for 2 h. The sintered part was characterized by scanning electron micrograph and EDX to investigate morphology and phase.

3 Results and Discussion

3.1 *Critical Solid Loading*

Critical solid loading is a situation of powder particles that are packed as tightly as possible without involving external pressure and the gap between particles has been filled by the binder. Parameters powder such as particle size distribution and particle shape tend to influence of critical solid loading of powders [1]. In the case of bimodal powder, the different sizes of powder, the maximum of packing density can be reached due to the space formed by large particles are filled by small particles. Moreover, the ratio both of powders tends to play an important role to determine their packing density [13].

Figure 2 shows maximum torque was reached on 69.5% when oleic acid is added at in 1 mL for every 5 min. Optimal powder loading according to German and Bose [1] is lower than 2–5% from critical solid loading. Powder loading 65% was chosen for investigation in terms of shear rate and viscosity.

3.2 *Rheology*

Homogeneity of feedstock can be evaluated using the rheological test. Commonly, the method to measure feedstock for metal injection molding is capillary rheometry. It can capable to characterize the flow behavior of shear rate in a wide range [14, 15].

Figure 3 shows the capillarity rheometry testing result for composites HA/Ti at temperatures 160, 180, 200, and 220 °C. Composite HA/Ti feedstock at every temperature testing tends to in pseudoplastic condition which is viscosity decrease with shear rate. It was indicating no separation between powder and binder. Figure 3 also shows viscosity tends to decrease with increasing temperature due to expansion thermal of binder and disentanglement of the molecular chain [16]. At the highest

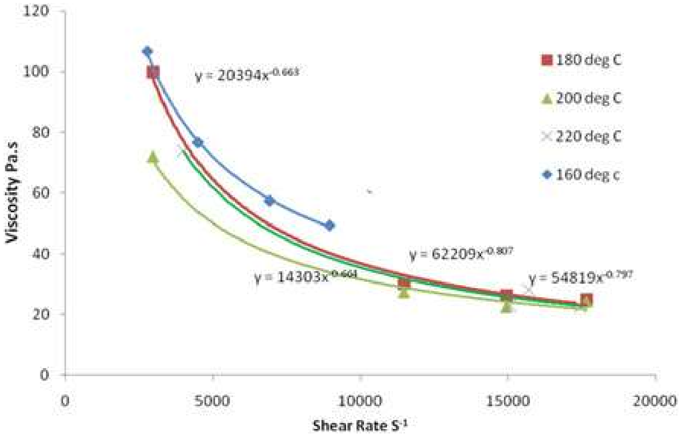


Fig. 3 Correlation of viscosity and shear rate at temperature 160, 180, 200 and 220 °C

Table 2 Flow behavior index, n

Temperature (°C)	Flow behaviour index (n)
160	0.337
180	0.197
200	0.336
220	0.203

temperature (220 °C) there was no decrease in viscosity. It was believed due to the saturated condition of the binder.

This phenomenon can be expressed with the power law equation (Eq. 2) and flow behavior index n where η is the viscosity and K is the constant.

$$\eta = K\gamma^{n-1} \tag{2}$$

Pseudopalstic behavior can be identified if flow behavior index n is less than 1. Table 2 shows all of the values of n less than 1. Feedstock at temperature 160 °C has the highest value of 0.337 that indicating has better rheological stability and greater pseudoelasticity.

The sensitivity of feedstock also can be measured based on activation energy, E, using the Arrhenius equation. Feedstock with low energy activation tends to be more suitable for application MIM due to produce fewer defects. Arrhenius equation can be defined as;

$$\eta = \eta_0 \exp\left(\frac{E}{RT}\right) \tag{3}$$

where η_o is viscosity, R is gas constant and T is the temperature in Kelvin. Based on a calculation using Arhenius equation, the lowest energy activation was 23.29 kJ/mol at temperature 160 °C and the highest value was 38.89 kJ/mol at temperature 180 °C. As shown in Fig. 4, feedstock under temperature 160 °C tends to have a lower gradient value.

3.3 Injection Process

The injection process was performed using an injection molding machine (DSM Xplore Injection Molding) as shown of Fig. 5a. The injection process was performed successfully under powder loading 65 vol% at 100, 150 °C, and 5 bar for mold temperature, melt temperature, and injection pressure, respectively. Figure 5b presents an injected part composite HA/Ti. Determination of the injection molding process parameter is based on the highest melting point temperature of the binder. In addition, rheological results are also used as a factor in determining the temperature of the injection.

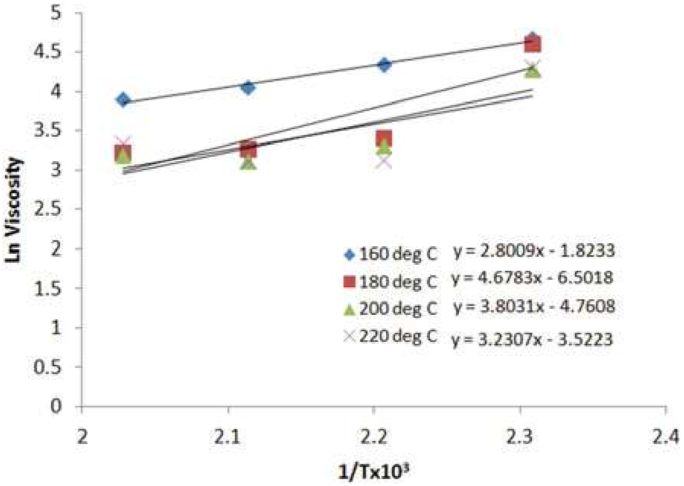


Fig. 4 Temperature vs dependence of viscosity

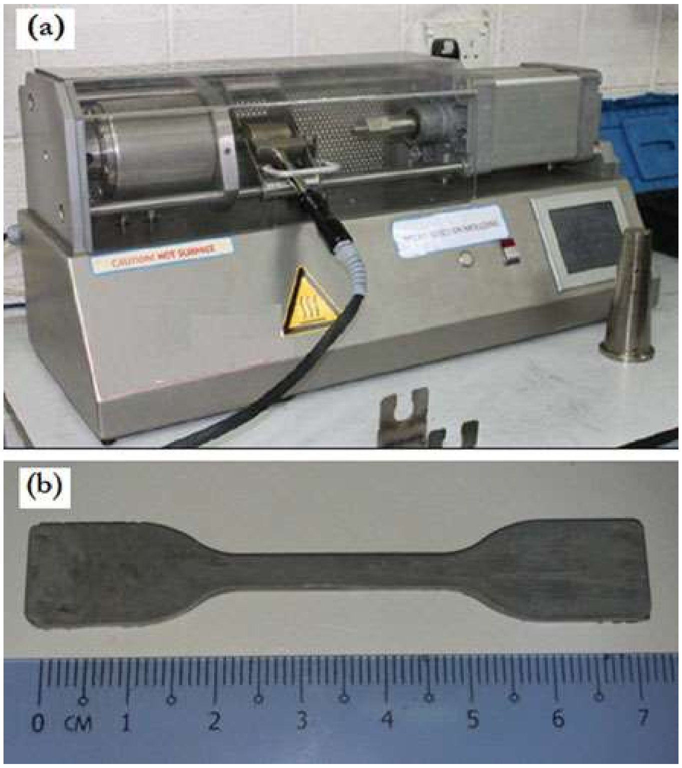


Fig. 5 DSM Xplore Injection Molding (**a**) Injected part composite HA/Ti (**b**)

3.4 Debinding Process

The main objective of debinding process is removing the binder in a short time without defect on the part [17]. 60 wt% palm stearin and 40 wt% Polyethylene were removed through thermal debinding under argon flow.

Debinding process was performed successfully using thermal debinding with two stages was utilized to remove binder with debinding temperature 320 and 500 °C. In the first stages, low heating rate 3 °C/min was used to remove palm stearin, which has lower molecular weight components. A low heating rate in the early stage was required to avoid defects on debound part. At the next stage higher heating rate was used (5 °C/min).

3.5 Sintering Process

SEM result shows the structure of composite Titanium alloy and HA which Titanium alloys particles as reinforced and the matrix is HA. Titanium alloys particles uniformly distributed on the surface of the sintered part. Moreover, on the surface of sintered part has been observed cracks. The initial crack was started from titanium particles as shown on the Fig. 6. It was believed as a result of the difference of thermal expansion titanium and hydroxyapatite. Moreover, between titanium and HA particles, there is no good diffusion bonding due to the secondary phase resulted by Titanium and HA interaction. The presence of a secondary phase on the surface of the titanium particles prevents the occurrence of diffusion.

Energy Dispersive X-Ray Analysis (EDX) is an x-ray technique used to identify the elemental composition of materials. In this work, EDX was conducted on the surface composite HA/Ti to identify elements particularly on the surface of titanium particles. EDX results for composite HA/Ti are shown on Fig. 7.

Figure 7 shows on the sintered part have occurred secondary phase of hydroxyapatite, on the vicinity of titanium particle as shown on the pink box, the composition ratio of Ca/P is 2.36. On the surface of titanium particle EDX analysis also was conducted to identify the composition of elements. EDX result revealed that the composition ratio of Ca/P is 0.58. Ca/P ratio phase standard for HA is 1.67 however on elevated temperature HA tend to decompose become secondary phases such as TTCP, TCP, and some amorphous phase [18–20]. Another author also reported occurred some phases such as $Ca_2Ti_2O_5$, TiO_2, and $CaTiO_3$ as a result of interaction Ti and HA at elevated temperature [21, 22].

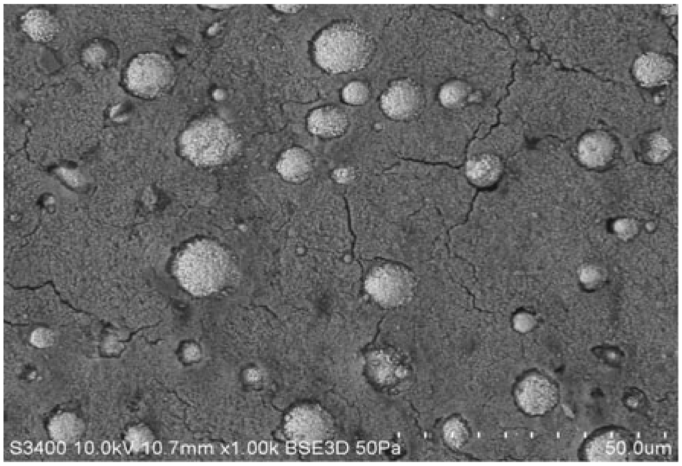
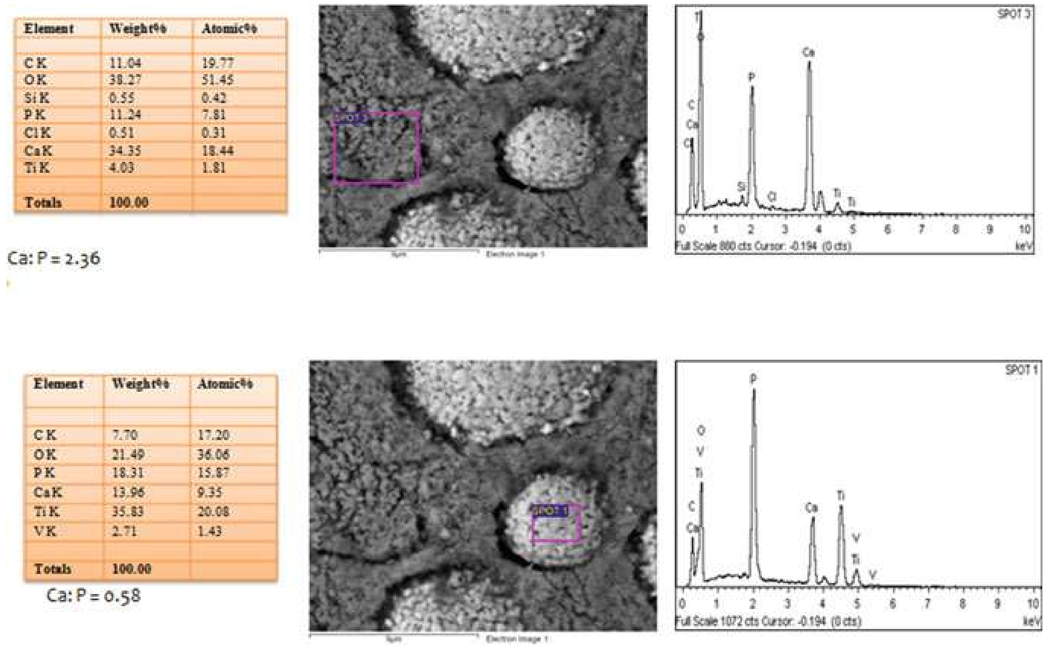


Fig. 6 Sintered part of composite HA/Ti with sintering temperature 1200 °C, heating rate 7 °C/min, and holding time 2 h



Element	Weight%	Atomic%
C K	11.04	19.77
O K	38.27	51.45
Si K	0.55	0.42
P K	11.24	7.81
Cl K	0.51	0.31
Ca K	34.35	18.44
Ti K	4.03	1.81
Totals	100.00	

Ca: P = 2.36

Element	Weight%	Atomic%
C K	7.70	17.20
O K	21.49	36.06
P K	18.31	15.87
Ca K	13.96	9.35
Ti K	35.83	20.08
V K	2.71	1.43
Totals	100.00	

Ca: P = 0.58

Fig. 7 EDX result of composites HA/Ti

4 Conclusion

Composite HA/Ti with binder system palm stearin and hydroxyapatite has shown pseudoplastic behavior. Dilatants behavior on feedstock was not observed as an indication of homogeneity of feedstock. Removal of binder using thermal debinding with two stages has been performed successfully without defect on debound part. Crack on the surface of sintered part has been observed due to differences in thermal expansion and both Ti and HA were not diffuse well. A new phase on the sintered part has been observed as a result of the decomposition of HA and a result of interaction HA and Ti. To achieve the optimal result on the sintered part modification in powders composition and parameter on the sintering process is required.

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