Determination of Critical Powder Loading of Titanium-Hydroxyapatite with Powder Space Holder for Powder Injection Molding Feedstocks

Mohd Yusuf Zakaria
Abu Bakar Sulong
Mohd Ikram Ramli
Department of Mechanicals and Materials, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia 43600 Bangi, Selangor, Malaysia

Muhammad Rafi Raza
Department of Mechanical Engineering
COMSATS Institute of Information Technology Sahiwal
Pakistan

ABSTRACT

Binder and powder formulation are crucial for powder injection molding (PIM) process that can be obtained based on critical powder volume percetange (CPVP) method. The binder is the main component for flowability of feedstock and proper composition can influence the feedstock whether can be injected, debinded and sintered without any defect. This study is focused on the determination of critical powder loading for titanium-hydroxyapatite (Ti-HA) with powder space holder for powder injection molding feedstock. The critical powder obtained at 82% of the powder with 90:10 ratios of the titanium and hydroxyapatite with 20% of a space holder. The optimal powder loading selected at 78%, which is 2~5% below to the critical powder loading value. Green part was successfully obtained without any physical defect using the optimal powder loading.

ISSN 1823- 5514, eISSN 2550-164X

Received for review: 2016-09-04
Accepted for publication: 2017-03-03
Published: 2017-07-15

Introduction

Titanium (Ti) is one of the most abundance element in existence. Titanium and its alloy have been widely used in various application include aerospace and medical application due to its superior properties [1]. Most used titanium alloy for implant material is Ti6Al4V which possess excellent strength and high corrosion resistance that similar to bone properties [2, 3]. However, some reports claimed that Ti6Al4V can be harmful to the implant where Al and V element can be cytotoxicity and adverse tissue reaction over a period of time [4]. To overcome this issue, titanium alloys is cooperated with bioceramics material such as hydroxyapatite to enhance the bioactivity of the implant [5]. Hydroxyapatite (HA) is biological active material that can promote bone growth for implant application as reported in various studies [6, 7]. Commonly, HA can be found in bones and teeth in the human body. Fabrication of Ti-HA composite has been very challenging due to the fact that both materials is different in nature. Various method has been proposed in order to produce Ti-HA composite for implant application as reported by Arifin et al. [8]. One of them is through powder injection molding process [9]. Powder injection molding (PIM) has become the main attraction in the manufacturing process which offer more complex shape, high tolerance at a low cost compare to other conventional manufacturing methods [10]. This advantages made PIM as the best candidate for processing titanium implant which often required complex shape and geometry. Moreover, the recent publication reported that PIM process successfully produced porous Ti-HA using space holder technique [11]. This indicates that PIM has a huge potential in manufacturing implant materials. Furthermore, selecting proper space holder materials is another key issue in producing highly porous structure especially for implant application. The main properties that space holder should possess are the space holder should not react with the binder, insoluble in debinding media, fully removable and able to withstand the PIM temperature during the process [12]. Producing a porous structure is crucial to promote cell growth for implant application [13]. Balancing the porosity and mechanical properties also challenging proses since both of them are greatly related [14]. Increasing porosity resulting poor mechanical properties for titanium implant [15].

In general, PIM consists of four main steps including feedstock preparation (mixing), injection, debinding and sintering [16]. This study is focused on the feedstock preparation step which is the determination of critical powder loading (CPVP) of Ti-HA with powder space holder. The optimum powder loading for the feedstock is important to obtain the best powder to binder ratio and provide the homogenous mixture to ensure the subsequence processes can be done without any defect [17]. Moreover, high powders volume leads to difficulty in injection process due to insufficient binder [18]. Critical solid loading of the powder can be determined by torque variation, density, melt flow, density and viscosity versus composition [19]. In this paper, critical and optimal powder loading of Ti6Al4V powder and hydroxyapatite powder together with NaCl space holder were determined using oil absorption method.

Methodology

Materials

Titanium alloy powder use in this study is Ti4Al6V with the particle size of 19.61µm obtained from TLS Technik Germany. Hydroxyapatite was obtained from Sigma-Aldrich with the particle size of 5.34µm as shown in Figure 2. The powder space holder used in this study is sodium chloride (NaCl) due it's low cost and easy dissolution obtained from Sigma Aldrich [20]. The composition of titanium and hydroxyapatite is kept at 9:1 ratio with 20% of space holder. The materials properties can be concluded in Table 1.

Table 1: Materials properties

Material	**Density (g/cm^3)**	**Size (µm)**
Titanium alloy Ti6Al4V	4.43	19.61
Hydroxyapatite (HA)	3.13	5.34
Sodium Chloride (NaCl)	2.17	381.39

<u>Critical powder loading</u>

Critical powder loading is carried out to determine the optimum powder and binder ratio to make sure the material can be mixed homogeneously and injected without any problem. Critical powder loading is done based on the ASTM D-281-31 using Brabender mixer with roller rotors as seen in Figure 1. Critical powder volume percentage (CPVP) is obtained based on mixing torque where the maximum torque curves represent the critical powder loading that can be used for metal powders. This means that the particles are tightly packed and all the void are filled with the binder. The optimal powder loading is kept between 2-5% below than the critical loading. The CPVP value can be obtained based on the equation (1)

$$CPVP = 100x \frac{V_f}{V_f+V_o} (\%) \qquad (1)$$

Where V_f is the volume of the powder and V_o is the volume of oleic acid. Oleic acid is added in 1ml for every 3 minutes until the torque value stabilized.

Mixing and molding process

The powders and binders were mixes using Brabender machine at 150°C and at 30 rpm for 30 minutes. The binder system used in this study are polyethylene (PE) and palm stearin with the ratio of 40:60. The mixture then crushed into smaller pieces before injection molding process. The injection molding process is carried out using Xplore injection molding machine with injection parameter as shown in Table 2.

Figure 1: Brabender torque rheometer mixer

Table 2: Injection parameters

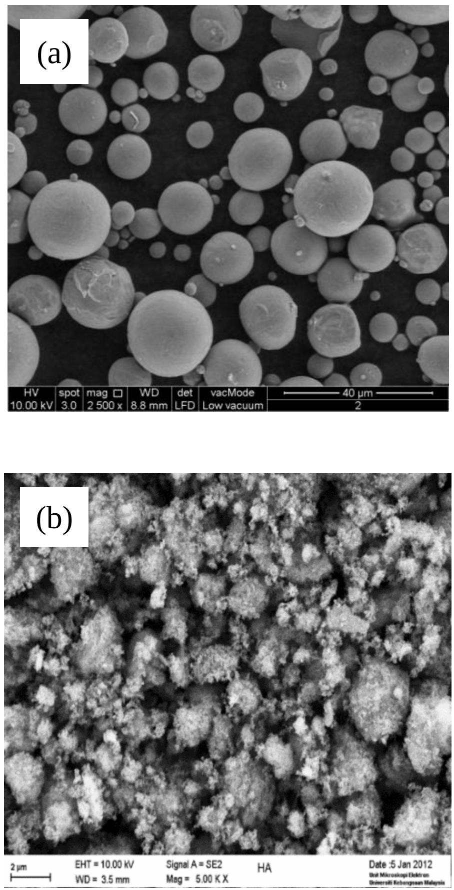
Parameter	Value
Temperature (°C)	150
Pressure (Bar)	10
Holding time (seconds)	60

Results and Discussion

Material Characterization

Scanning electron microscope reveals that titanium possess sphere shape with the particle size of ~20µm as seen in Figure 2(a). Differ from the titanium powder, the hydroxyapatite (HA) possesses irregular shape (needle-like) in agglomerates form as seen in Figure 2(b). The particle sizes are crucial in powder injection molding process due to fact that average particle size usually required less than 20µm [21]. Thus, these particle sizes were chosen in order to study the critical powder loading in PIM feedstock. Meanwhile, NaCl space holder possess box shape with the particle size of 381.39µm as seen in Figure 2(c). Bigger space holder size will provide bigger pore size which meets the requirement of pore size for implant material which is in the range of 100-400µm [22].

The energy dispersive analysis (EDX) spectrum shows the presence of Al, V and O peaks along the main two peaks for Ti and C as seen in Figure 3. There is slight contamination occurred where C and O element presence that might cause by oxidation and environment effect.



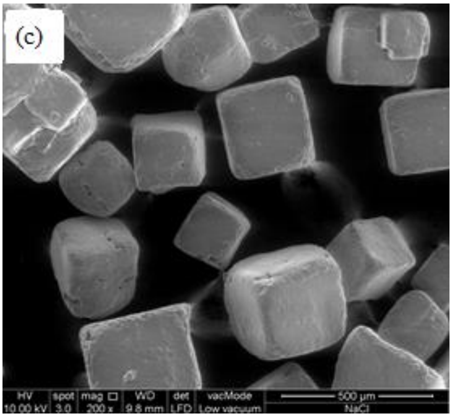


Figure 2: SEM image (a) Titanium alloy Ti6Al4V (b) Hydroxyapatite (c) NaCl

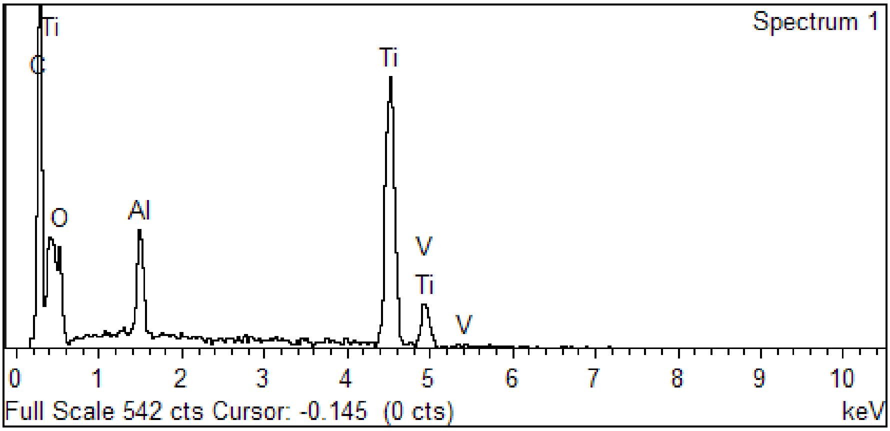


Figure 3: EDX spectrum for Ti6Al4V

Determination of powder loading

The optimal and critical powder loading can be determined based on torque rheometer as seen in Figure 4. Based on the figure 4, the maximum torque peak occurred at 82% of powder loading which indicates that the 82% is the critical powder volume percentage (CPVP). After the critical point, the torque value started lowering down to a steady state which reflected the homogenization of the mixture. The optimal powder loading is slightly lower than critical loading which is below 2~5% from critical loading. The optimum loading indicates that the ratio between powder volume and total volume (powder with binder volume) provided homogenous mixture due to the powder particles are tightly packed and further minimized the spaces between the particles by filling with the binder. This mixture indicated good injection conditions while the powder particle contact is sufficient enough to maintain the rigidity of the molded sample throughout the whole process [16]. Therefore, the optimum powder loading selected was 78% for further powder injection molding process. This optimum value showed good agreement with the optimal value reported by Ariffin et. al using the same material without space holder [23].

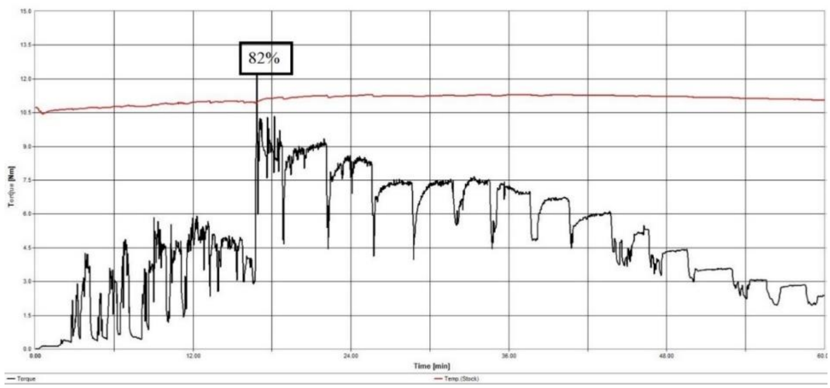


Figure 4: Critical powder loading for Ti-HA with powder space holder.

Mixing and Injection Molding Result

Dough like feedstock was successfully obtained from the mixing process and the scanning electron microscope (SEM) image of the feedstock is shown in Figure 5. From the figure, the binder and powder are randomly dispersed resulting a homogeneous mixture of the feedstock. Meanwhile, Figure 6 shows the injected green part of the Ti-HA with powder space holder. The green part was successfully produced without any physical defect as seen in Figure 6. This result shows that the binder content is adequate to facilitate the powder to flow into the mold during the injection process, indicating the optimum powder loading used in this study is suitable for the powder injection molding process for Ti-HA with powder space holder.

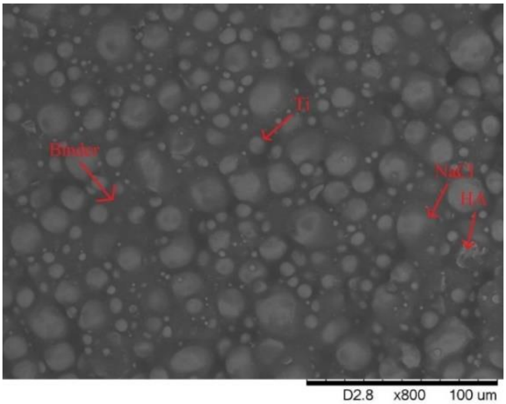


Figure 5: SEM image for the feedstock

Figure 6: Injected sample

Conclusion

Critical powder volume percentage (CPVP) was successfully determined at 82% of powder loading using oil absorption with torque rheology method based on the ASTM D-281-31. The optimum powder loading value is kept below 2~5% from the critical powder loading for powder injection molding process. For this study, the optimal powder loading is selected at 78% of powder volume for further process in powder injection molding Ti-HA with powder space holder. Green part was successfully injected without defect using the optimal powder loading.

Acknowledgement

This work was supported by the Ministry of Higher Education Malaysia (MOHE) under grant number TRGS/2/2014/UKM/02/4/1 and MyBrain15 Programme

References

[1] N. Jha, D.P. Mondal, J. Dutta Majumdar, A. Badkul, A.K. Jha, A.K. Khare, Highly porous open cell Ti-foam using NaCl as temporary space holder through powder metallurgy route, Materials & Design, 47 (2013) 810-819.

[2] G. Miranda, A. Araújo, F. Bartolomeu, M. Buciumeanu, O. Carvalho, J.C.M. Souza, F.S. Silva, B. Henriques, Design of Ti6Al4V-HA composites produced by hot pressing for biomedical applications, Mater. Des., 108 (2016) 488-493.

[3] D. Bovand, M. Yousefpour, S. Rasouli, S. Bagherifard, N. Bovand, A. Tamayol, Characterization of Ti-HA composite fabricated by mechanical alloying, Materials & Design, 65 (2015) 447-453.

[4] A.M. Omran, K.D. Woo, D.S. Kang, G.T. Abdel-Gaber, H. Fouad, H.S. Abdo, K.A. Khalil, Fabrication and evaluation of porous Ti–HA bio-nanomaterial by leaching process, Arabian Journal of Chemistry, 8 (2015) 372-379.

[5] L. Zhang, Z.Y. He, Y.Q. Zhang, Y.H. Jiang, R. Zhou, Rapidly sintering of interconnected porous Ti-HA biocomposite with high strength and enhanced bioactivity, Mater. Sci. Eng. C, 67 (2016) 104-114.

[6] M.R. Mansur, J. Wang, C.C. Berndt, Microstructure, composition and hardness of laser-assisted hydroxyapatite and Ti-6Al-4V composite coatings, Surface and Coatings Technology, 232 (2013) 482-488.

[7] K.A. Khor, Y.W. Gu, D. Pan, P. Cheang, Microstructure and mechanical properties of plasma sprayed HA/YSZ/Ti–6Al–4V composite coatings, Biomaterials, 25 (2004) 4009-4017.

[8] A. Arifin, A.B. Sulong, N. Muhamad, J. Syarif, M.I. Ramli, Material processing of hydroxyapatite and titanium alloy (HA/Ti) composite as implant materials using powder metallurgy: A review, Materials & Design, 55 (2014) 165-175.

[9] E.S. Thian, N.H. Loh, K.A. Khor, S.B. Tor, Microstructures and mechanical properties of powder injection molded Ti-6Al-4V/HA powder, Biomaterials, 23 (2002) 2927-2938.

[10] W. Fang, X. He, R. Zhang, S. Yang, X. Qu, The effects of filling patterns on the powder–binder separation in powder injection molding, Powder Technology, 256 (2014) 367-376.

[11] M.R. Raza, A.B. Sulong, N. Muhamad, M.N. Akhtar, J. Rajabi, Effects of binder system and processing parameters on formability of porous Ti/HA composite through powder injection molding, Materials & Design, 87 (2015) 386-392.

[12] N. Tuncer, M. Bram, A. Laptev, T. Beck, A. Moser, H.P. Buchkremer, Study of metal injection molding of highly porous titanium by physical modeling and direct experiments, Journal of Materials Processing Technology, 214 (2014) 1352-1360.

[13] S.W. Kim, H.-D. Jung, M.-H. Kang, H.-E. Kim, Y.-H. Koh, Y. Estrin, Fabrication of porous titanium scaffold with controlled porous structure and net-shape using magnesium as spacer, Materials Science and Engineering: C, 33 (2013) 2808-2815.

[14] F. Li, J. Li, G. Xu, G. Liu, H. Kou, L. Zhou, Fabrication, pore structure and compressive behavior of anisotropic porous titanium for human trabecular bone implant applications, Journal of the Mechanical Behavior of Biomedical Materials, 46 (2015) 104-114.

[15] S. Muñoz, J. Pavón, J.A. Rodríguez-Ortiz, A. Civantos, J.P. Allain, Y. Torres, On the influence of space holder in the development of porous titanium implants: Mechanical, computational and biological evaluation, Materials Characterization, 108 (2015) 68-78.

[16] D. Checot-Moinard, C. Rigollet, P. Lourdin, Powder injection moulding PIM of feedstock based on hydrosoluble binder and submicronic powder to manufacture parts having micro-details, Powder Technology, 208 (2011) 472-479.

[17] K.H. Kate, R.K. Enneti, V.P. Onbattuvelli, S.V. Atre, Feedstock properties and injection molding simulations of bimodal mixtures of nanoscale and microscale aluminum nitride, Ceramics International, 39 (2013) 6887-6897.

[18] X. Kong, T. Barriere, J.C. Gelin, Determination of critical and optimal powder loadings for 316L fine stainless steel feedstocks for micro-powder injection molding, Journal of Materials Processing Technology, 212 (2012) 2173-2182.

[19] J. Hidalgo, A. Jiménez-Morales, J.M. Torralba, Torque rheology of zircon feedstocks for powder injection moulding, Journal of the European Ceramic Society, 32 (2012) 4063-4072.

[20] Y. Torres, J. Pavón, P. Trueba, J. Cobos, J.A. Rodriguez-Ortiz, Design, Fabrication and Characterization of Titanium with Graded Porosity by using Space-holder Technique, Procedia Materials Science, 4 (2014) 115-119.

[21] M. Aslam, F. Ahmad, P.S.M.B.M. Yusoff, K. Altaf, M.A. Omar, R. M.German, Powder injection molding of biocompatible stainless steel biodevices, Powder Technology, 295 (2016) 84-95.

[22] B. Chang, W. Song, T. Han, J. Yan, F. Li, L. Zhao, H. Kou, Y. Zhang, Influence of pore size of porous titanium fabricated by vacuum diffusion bonding of titanium meshes on cell penetration and bone ingrowth, Acta Biomaterialia, 33 (2016) 311-321.

[23] A. Arifin, A.B. Sulong, N. Muhamad, J. Syarif, M.I. Ramli, Powder injection molding of HA/Ti6Al4V composite using palm stearin as based binder for implant material, Materials & Design, 65 (2015) 1028-1034.