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Evaluation of Sintered Hydroxyapatite (HA) via Powder Injection Molding

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ABSTRACT

Hydroxyapatite (HA), a ceramic phosphate with good biocompatibility, has been extensively used in the field of bone replacement, both in orthopedics and in dentistry. Desired molded part of HA is fabricated by using powder injection molding (PIM) method. Powder loading, rheological properties and sintering atmosphere can significantly affect the quality of molded HA. The effect of these factors on the microstructure and mechanical properties of powder injection molded HA were investigated. Different powder loading of HA (54, 55 and 56 vol%), were mixed with binder 40 wt.% of palm stearin and 60 wt.% polyethylene. The temperature injection were set at 150°C, 160°C and 170°C with the pressure injection of 12 bar. The green body were then sintered in the furnace at temperature of 1100°C, 1200°C and 1300°C for 4 hours. Analysis of variance (ANOVA) is used to determine the optimization of injection molding. Based on the analysis, it was found that 56 vol% powder loading, temperature injection at 150°C up to 170°C and 12 bar pressure injection are the optimum parameters for the process of injection molding. Results further demonstrate that the optimum condition involves the specified HA with temperature injection at 170°C and sintered at 1300°C provides the highest hardness value and flexural strength of 690 Hv and 17.75 MPa respectively.

Keywords: Powder injection molding; hydroxyapatite; sintering process; flexural strength

INTRODUCTION

Hydroxyapatite (HA) with the chemical formula $[Ca_{10}(PO_4)_6(OH)_2]$ is a calcium phosphate ceramics which is extensively used in the biomedical field (Canillas et al. 2017; Eliaz and Metoki 2017; Pokhrel 2018). Due to the excellent compatibility with living tissue, HA is considered as an important material for replacement of artificial human bones and dental bioceramic application. It is suitable for use as bioactive materials in dental and orthopedic treatments because HA has similar chemical features as bone and it can form a real bond with bone tissue (Kumar, Dehiya, and Sindhu 2018; Szcześ, Hołysz, and Chibowski 2017; Turon et al. 2018).

In order to produce a desirable application of HA products, the injection molding has been regarded as an attractive method among the near-net shape powder-based manufacturing (Rueschhoff, Trice, and Youngblood 2017). For years, powder injection molding (PIM) which is a combination of two processes of plastic injection molding and powder metallurgy, is used to produce metal, ceramic and carbide products. It offers the merits of higher efficiency, more excellent surface quality, and more precise and complex shape compared with the traditional molding techniques (Mannschatz, Höhn, and Moritz 2010) (Abajo, Jiménez-Morales, and Manuel Torralba 2015). PIM also avoids the density gradient that can cause defects and degradation of properties after sintering as is the case in producing ceramic (Shivashankar et al. 2013)(Sardarian, Mirzaee, and Habibolahzadeh 2017). In addition, sintering is also a cost-effective process to produce the molded ceramic product. Therefore, the powder injection molding (PIM) covers both the injection molding and sintering process and has the advantages of material flexibility, near-net shaping and shape complexity for HA.

Biocomposites with a polymer matrix as binder and ceramic powder fabricated via injection molding have been extensively documented in literature (Sa'ude, Ibrahim, and Saidin 2013; Sharmin 2015; Tülümen et al. 2019). Many have discussed the properties of hydroxyapatite after debinding and sintering in different temperatures. It has been mentioned that the maximum relative density and shrinkage occur at high temperature of 1250°C, but the maximum flexural strength occurs at 1200°C (Marçal 2016). The loss of strength at high temperatures was due to grain growth and decomposition of hydroxyapatite (HA) on α-tricalcium phosphate (α-TCP).

In the present study the major factors affecting powder injection molding and critical powder loading are initially identified. This represents an important step for providing the ideal feedstocks for subsequent debinding and sintering process. Similarly, the major parameters that may influence

the final HA products after sintering are also being investigated.

EXPERIMENTAL TECHNIQUE

MATERIAL PREPARATION

Hydroxyapatite powder, ($Ca_{10}(PO_4)_6(OH)_2$) used in this work has a particle size of 5 µm. The chemical was supplied by Sigma-Aldwas. The first step in the PIM process is to find out the optimal ratio of powder to binders so as to produce a homogeneous feedstock which can then be processed in the injection molding machine. The critical powder loading (CPVP) of the mixture is measured using the oil absorption technique based on ASTM D-281-31. The CPVP powder loading is set at 54, 55 and 56 vol%. HA material for the all three powder loading is mixed with a binder comprised of 60 wt.% of palm stearin and 40 wt.% polyethylene for 120 min using Brabender mixer running at 25 rpm. Palm stearin and wax-polymer of polyethylene have been chosen as they represent the common binder component in PIM (Gal et al. 2019). Table 1 described the characteristics of the binder system used in this research (Bonaventure Emeka et al. 2017)the powder materials were characterized. Two feedstock with solid loadings of 68% for stainless steel (17-4PH.

The binder system is important as it functions as the transportation agent for feedstock homogeneity and packing powder before being converted into desired shape prior to sintering phase. The quality of the feedstock is critical in obtaining defect-free products. Abnormalities will result in defects like distortion, cracks and voids in the final products. In addition, any small defects formed during the initial stages of PIM would worsen during subsequent processing steps. Thus, precautions are necessary to preserve feedstock homogeneity during processing.

INJECTION PROCESS

The injection process of HA was performed using an injection molding machine namely DSM Xplore Injection Molding. During the process, the injection temperature must be set higher than the binder melting point. This is to ensure that the feedstock can be filled into the cavity entirely. The mold temperature should also be close enough to the melting point of the binder to induce the filling process. Moreover, the mold should be heated to avoid transfer of a large gradient of heat from feedstock to the mold. The molded HA mixed with the binder is called green body. The density of the molded HA green body was measured to determine the optimal parameters to produce the most compact body.

THERMAL DEBINDING AND SINTERING PROCESS

After the injection molding process, the thermal debinding and subsequently sintering process were performed. The thermal debinding was performed to remove the binders while sintering at elevated temperatures to obtain the end shape. Thermal debinding was performed under Argon gas atmosphere. The green body were reflowed in the furnace using a temperature profile involving soaking temperature and peak temperature at 320°C for 3h (heating rate 3°C/min) and 500°C for 1h (heating rate 5°C/min), respectively. The slow heating rate was employed in the initial stage to remove the binder palm stearin completely and to avoid defect.

The debound molded HA were then sintered in high-vacuum furnace. Three different sintering temperature were set namely 1100°C, 1200°C and 1300°C for 2h in order to study the effect of the sintering on molded HA. This process is important in order to maintain the final shape of the sample.

MECHANICAL TESTING AND MICROSTRUCTURAL ANALYSIS

The mechanical properties of the sintered HA were analyzed by flexural strength using INSTRON 5567. Scanning electron microscopy (SEM) was used to observe the surface morphology. The mechanical testing for green body and sintered body were measured in order to analyze the mechanical properties of molded HA, before and after sintering.

RESULTS AND DISCUSSION

HA POWDER MORPHOLOGY

Figure 1(a)-(c) shows the morphological feedstocks of HA powder/binder with volumetric powder loading of 54, 55 and 56 vol%, respectively. Varying the powder loading results in variation of torque level which indicates differences in viscosity of the mixtures. Hence this has influenced its microstructural features. It was also observed that the powder was not distributed uniformly at mixture feedstock with powder loading of 54 vol% as a rough surface was observed on it. Big voids were also noticed at the HA powder morphology. These voids may cause cracking during debinding process later.

On the other hand, the mixture with powder loading of 55 vol% gave satisfactory properties for the green body although there were small porous formed in the feedstock. HA powder/binder mixture with 56 vol% powder loading proved to be the most homogenous feedstock because the

TABLE 1. Binder Characteristics (Ukwueze et al.)

Binder	Type	Composition	Melting Temperature	Density
Palm stearin	Primary	60%	63°C	0.891 g/cm^3
Polythelene	Secondary	40%	117.3°C	0.919 g/cm^3

powder are mixed very finely and distributed uniformly (Figure 1(c)). It has been recognized that failure to distribute powder uniformly on the feedstock can result in molding defects on the end product (Kong 2011).

DENSITY OF GREEN BODY

In order to investigate the effect of the injection process on the powder/binder mixture, the properties of green body of the molded HA is studied. The value of the green body density is performed using Archimedes' principle. Figure 2 represents the density value of the green body at 150°C injection temperature for the different powder loading.

In general, the density of the green part of HA increased as the powder loading increases. The density of the green part of 54, 55 and 56 vol% powder loading were 2.09, 2.11 and 2.13 g/cm3 respectively. Comparing all the three powder loadings, the feedstocks mixed at 56 vol%, produced the more compact green body.

FLEXURAL STRENGTH OF GREEN BODY

Figure 3 shows the flexural strengths of molded HA green body increase as the injection pressure is increased from 10 bar to 12 bar. The internal defects such as existent of voids at feedstock stage at 54 vol% powder loading would lead to the weak flexural strength of green body. Result also shows the most homogeneous feedstock of HA is at powder loading of 56 vol%. Both the feedstocks at injection pressure of 11 and 12 bar provide highest flexural strength of 11.95 and 11.90 MPa respectively.

The relationship between the flexural strength of the green body and the three factors, namely the injection pressure, injection temperature and powder loading has been studied using regression analysis. It is concluded that 56 vol% powder loading with injection temperature of 150°C up to 170°C and 12 bar pressure injection represent the ideal parameters for achieving the highest flexural strength.

DENSITY OF SINTERED PART

Figure 4 shows the density of HA sintering part at the sintering temperature of 1100°C, 1200°C and 1300°C. The sintered part density increases with increasing sintering temperature. The density are recorded at 2.82, 2.90 and 2.95 g/cm3 for 1100°C, 1200°C and 1300°C sintering temperature, respectively. It is believed that the bonds between the particles in the sintered body tend to increase with increase in sintering temperature. This leads to the closure of more porous openings as sintering temperature increases. Thus density of the sintered body tends to increase with increasing sintering temperature.

POROSITY PERCENTAGE OF SINTERED PART

Percentage of porosity of sintered part have been determined for the three sintering temperature. Results on the percentage of porosity are as shown in Table 2. The percentage porosity of the sintered body increases with decreasing sintering temperature. This is because, when the particle size increases the many pores between the particles will disappear and will lead to reduced porosity.

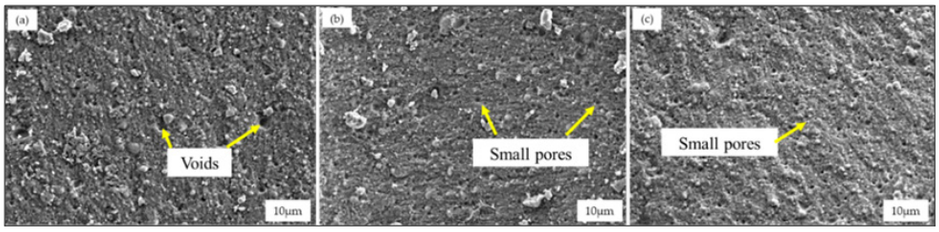

FIGURE 1. HA powder morphology mixed with binder at volumetric powder loading of (a)54 vol%, (b)55 vol% and (c)56 vol%

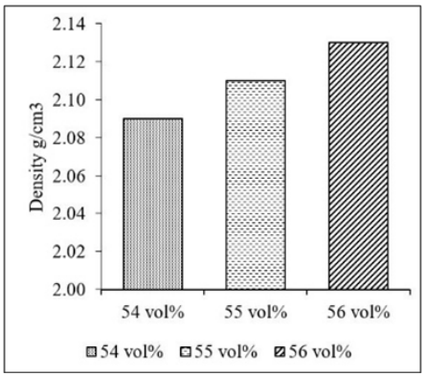

FIGURE 2. Density of green body molded HA against powder loading at 150°C injection temperature

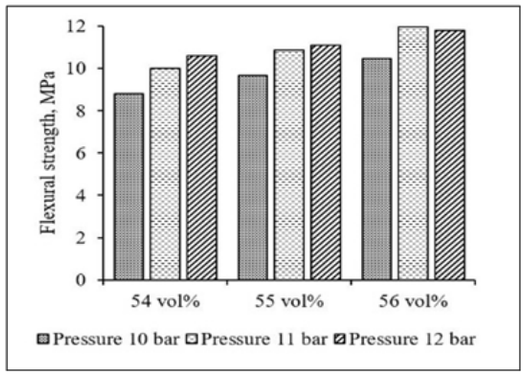

FIGURE 3. Flexural strength of green body against injection pressure of 10, 11 and 12 bar for different volumetric powder loading

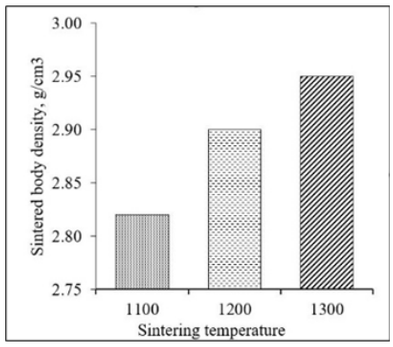

FIGURE 4. Density of sintered body at 1100°C, 1200°C and 1300°C sintering temperature

TABLE 2. The percentage of porosity

Sintering Temperature (°C)	Apparent Porosity (%)
1100	19.3
1200	4.0
1300	2.0

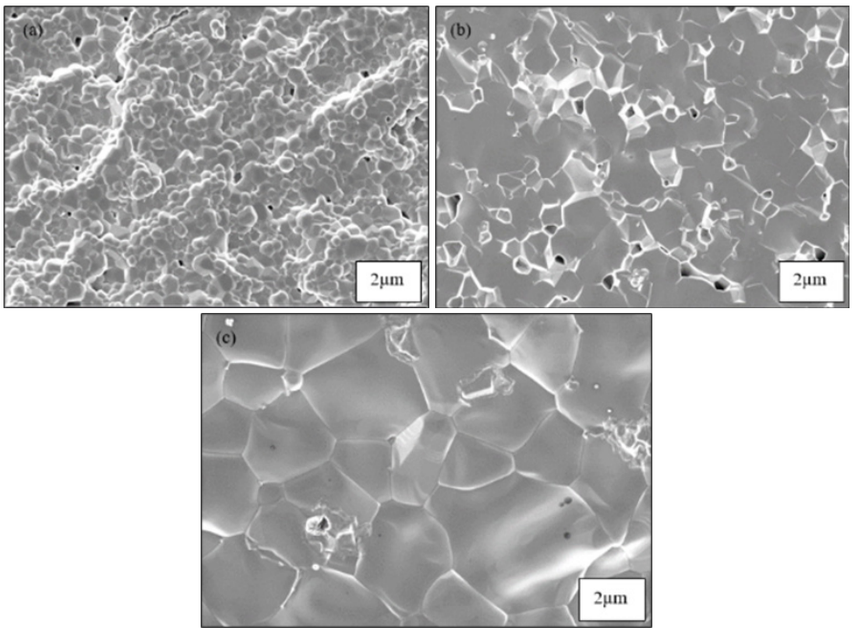

FIGURE 5. Morphological microstructures on sintered part for (a) 1100°C, (b) 1200°C, and (c) 1300°C sintering temperature

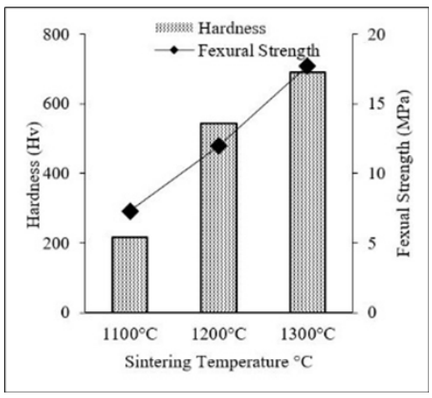

FIGURE 6. Hardness and flexual strength of sintered part for sintering temperature of 1100°C, 1200°C dan 1300°C

MICROSTRUCTURE OF SINTERED PART

Figure 5(a), (b) and (c) shows the morphological microstructures at high magnification on the sintered part for sintering temperature of 1100°C, 1200°C and 1300°C., respectively. As explained above, rising temperatures have led to reduced percentage of the resulting porosity. Porosity is reduced because the greater necking have closed the pores formed between the particles.

HARDNESS AND FLEXURAL STRENGTH

The effect of sintering temperature on the hardness and flexural strength of the sintered body are as shown in Figure 6. The hardness of sintered part increase from 217 Hv to 690 Hv when the sintering temperature is icreased from 1100°C to 1300°C. Flexural strength was evaluated using three-point bending test method. The same trend as that for hardness are observed. The flexural strengths recorded for sintering temperature of 1100°C, 1200°C and 1300°Care 7.3, 11.96 and 17.75 MPa, respectively.

CONCLUSION

Morphological characterization of HA powdered material and the critical powder loading represent the first important steps in providing an ideal feedstock for powder injection mold. The major parameters affecting powder injection molding are identified. Mixing of HA powder with 60 wt.% of palm stearin and 40 wt.% polyethylene binders showed 56 vol% HA powder loading produced the most homogenous feedstock because the powder are mixed very finely and distributed uniformly. This characteristic can be revealed from the microstructure morphology of the feedstock. In addition, it can be seen that the feedstock produced more compact green body with highest flexural strength at injection pressure of 11 or 12 bar. The relationship between the flexural strength and the three factors, namely the injection pressure, injection temperature and powder loading is studied using regression analysis. It is concluded that 56 vol% powder loading with injection temperature of 150°C up to 170°C and 12 bar pressure injection represent the ideal parameters for achieving the highest flexural strength. After debinding treatments and sintering process, the parameters affecting the final products of powder injection mold are also determined. The density of HA sintering part increases as the sintering temperature increases from 1100°C to 1300°C. The percentage porosity of the sintered body also increases with decreasing sintering temperature. The hardness and flexural strengths of sintered part both increase with increasing sintering temperature. Sintering at the highest temperature of 1300°C provide the highest hardnes and flexural strength.

ACKNOWLEDGMENTS

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DECLARATION OF COMPETING INTEREST

None.

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