Injection Moulding Of Hap-Zirconia Composite Using Palm Stearin Binder System

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***Abstract*—**The main objective of this paper is to analyze the ability of the feedstock HAp-ZrO_2 which has different composition with Palm Stearin (PS) based binder system. In this research, the feedstock was classified by different weight percentage composition which 90-10, 80-20 and 70-30 of the HAp-ZrO_2 with the same ratio 60% of their optimum powder loading to palm stearin. Thus, the performance of HAp-ZrO_2 composite powder is studied through the Thermogravimetric Analysis (TGA) which showing that palm stearin binder system completely being removed in the present of high temperature 500^{0}C with heating rate of 10°C/min.While the analysis of Scanning Microscopy Electron (SEM) to identify their physical characterization of feedstock. The effect of Zirconia content in the composition can be investigated through rheological test using Rosand RH2000 capillary rheometer. During the rheological test, the feedstock containing the mixture and the binder carried out pseudoplastic behavior and viscosity. The binder in the feedstock gives exceptional properties to ensure the success of injection molding process.

Keywords— Hydroxyapatite, composite, feedstock, injection molding, rheology.

I. INTRODUCTION

The use of HA which come from natural sources have been practices. HA comes from the waste such as animal and organic may raise the concern from people on the process and method involve to get the HA(Akindoyo, Beg et al. 2017). Chemical processes by using various reactants such as $Ca(OH)_2$ and H_3PO_4 or CaO and $CaHPO_4$ is able to produce synthetic HA. However this processes need to be discuss on impact on biologically processes and high cost. Thus, the solution to this problem have been identified such as microwave method in producing HA from eggshell.(Okada and Furuzono 2012).

Calcium act as element that frequently build up bones and teeth tissues in our body. Bones contain calcium which in the form of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). Hydroxyapatite is different from others that contain the similarity composition of bones and has the biocompatibility which make it excellent substance to being use. Long period of time need to be taken by human body to enable the production of HA by human to recovered during bone injury.

Thus, medical field found that HA from other elements can be implemented to reduce the time and to rebuild the tissue more excellent.

Previous study has been done on the production of hydroxyapatite from various organic sources such as the salmon fishbone and eggshell (Wu, Hsu et al. 2016). These waste product are commonly used for their natural composition of HA and calcium that act to a better way in producing of HA. Clamshell act as raw material in this research as they are made up of 95% $CaCO_3$. Clamshell can be obtained in the waste disposal and along the Thus this research will be identify to make use of the clamshell in the combination of Hydroxyapatite-Zirconia and also injection molding Hap-ZrO_2 that will be injected in the injection molding machine with the present of palm stearin binder.

The clamshell which most human find has no use to our daily life have increase. This could lead to serious problem like pollution. Hence, in the eyes of researcher such as scientist and engineers, it is a big loss to throw away tonnes of clamshell as they may contain many benefits and save the environment. Nowadays, as creating energy using biomass is quite popular way to save the environment. Analyzing, the properties or characteristics of this clamshell to convert into something useful may become success and solution to current problem. Clamshell act as economic resources as the synthetic Hap that used in biomedical field as the bone and dental implant is very expensive. This product can save the cost because clamshell is coming from waste and can be collected along the beach. Moreover, previous study found that eggshell and clamshell they consume high energy to produce Hap by using high power of microwave synthesis method.

II. METHODOLOGY

A. Preparation of Feedstock

The internal mixer HAAKE Rheomix was used to perform the mixing process which was conducted at 160 ^{0}C in the duration of 2 hour with rotational speed of 50 rpm. The PE was pour into the mixer as the blending temperature was achieved. When the PE was completely melted, the PS was added with the powder mixture of HAP-ZrO_2. There were different composition of HAp- ZrO_2 which show the toughness of ZrO_2 increase when its content up to 20% while 40% to 60% signifying poor mechanical behavior(Chen,2010). Table 1 and Table 2 shows that the comparison taken for the feedstock to be mix with different volume percent of binder which in Table 1 using 100%PS while Table 2 using 70%PS and 30%PE.

The Formulation of the Feedstock

Table 1

Formulation	Composition (wt%)		Powder Loading (vol%)	Binder Composition (vol%) PS
	HA	ZrO_2		
1	80	20	60	40
2	70	30		
3	60	40		
4	50	50		

Table 2

Formulation	Composition (wt%)		Powder Loading	Binder Composition (vol%)
	HA	ZrO_2		

			(vol%)		
1	80	20	60	40	
				PS	PE
				70	30

B. Rheological study of Feedstock

The rheological study of the feedstock was determined using a Rosand RH2000 capillary rheometer. The temperature was set at 65°C as it depends on the melting point of palm stearin binder system and the feedstock was put in the orifice until it charged into the rheometer barrel. This test was taking to ensure that the mixing powder of HAp-ZrO_2 will be success during the injection molding process (Ukwueze, B. E, 2016). Thus, different composition of palm stearin is used to analyze the pseudoplastic properties of feedstock.

The performance and the characterization of the feedstock were then analyzed using 3 analysis chosen which is rheological analysis, Scanning Electron Microscopy (SEM) and Thermogravimetric Analyzer (TGA). All of them is been used for different purpose of analysis.

III. RESULTS AND DISCUSSION

A. Analysis of Rheological Behavior

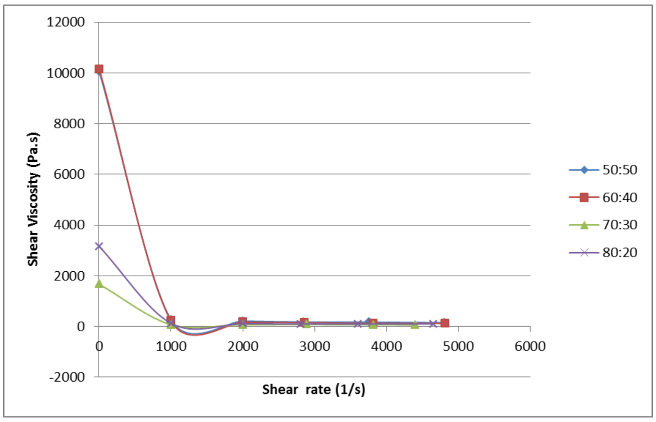


Figure 1 : Shear Viscosity versus shear rate of feedstock at temperature 65°C

Figure 1 indicates that shear viscosity decreasing with shear rate showing the pseudoplastic behavior which can be satisfied using n-value.

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

Where η is the feedstock viscosity, K is the flow consistency constant and y is the shear rate in the pseudoplastic flow region, the n value is below 1. The feedstock which their n value is less than 1 known as pseudoplastic behavior wherby n=1 is callled Newtonion. The lower n-value represent that the faster viscosity of the feedstock change with the shear rate. The flow behaviour of index value for the composition 80-20 is 0.36, 70-30 is 0.64 ,60-40 is 0.11 and 50-50 is 0.14. The n-value shows all type of composition having pseudoplastic behavior but the smallest value of n showing by composition of 60-40 and the highest stated by 70:30.Thus, all the sample was proved to follow the pseudoplastic behaviour. However in increasing ZrO_2 with up to 30wt% showed increase in *n* value but the *n* value was suddenly decreased when the ZrO_2 increased by 40wt% contain high viscosity. In addition the result shows non of the sample suitable for injection moulding process as it gives more than 1000Pa.s of shear viscosity while the shear rate were in the range of 10^2 to 10^5 s^{-1} which help to maintain the shape of molded part. The flow of activation energy,Ea showing that temperature act as important role that will give an impact to the feedstock viscosity. Temperature below 70°C was identified as suitable for succes of injection moulding with HAp feedstock to get a better moulded specimen (Liu *et al*., 2002).

On the other hand, with an increase in temperature the viscosity of feedstock. Heat was present during the time cause the large expansion of the binder. Large number of shear sensitivity is important in producing complex and instrinsic specimens that will be given further product for injection moulding. The feedstock should be in pseudplastic condition eventhough there is argument which dilatant condition that being considered as injectable (B. German,1997). The particle size of HAp,zirconia and the as-mixed powder shows the increasing size of the percentage of the zirconia added. Based on the d_{50} of the HAp, zirconia, 80wt% HAp and 70wt% Hap. the value shows 56.737 µm, 26.381 µm , 20.694 µm and 17.535µm respectively. The particles size showing decreasing trend indicates that increase of specific area of sample. Thus, it will increase the reactivity of sample towards shear viscosity.

B. Thermogravimetric Analysis (TGA)

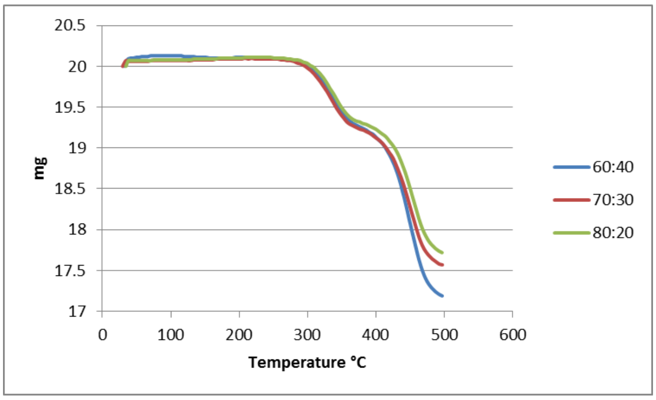


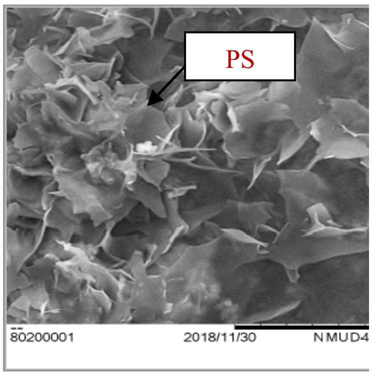
Figure 2: TGA Curve for Feedstock of 60% Vol% HAp after undergoes rheology test.

TGA analysis was conducted as it can carried out the rate of thermal decomposition of organic binders when use high value of temperature. Nitrogen gas at room temperature was flow to 500°C with heating rate of 10°C/min. The temperature should be increase 500°C slowly as it will defect the sample (Luo et al., 2009). Based on analysis, the binder are completely removed above the decomposition temperature of binder but there were PE in the second stage of decomposition. This may due to contamination during the early stage of mixing whereby the are not being cleaned up during sutable material such as polypropylene. The wide range is important for the fast debinding process. According to graph, the decomposition of PS start from 318°C and end at the temperature of 500°C. It shows that the particle at 318°C was strengthly bonded The curve was used to design the thermal debinding cycle.

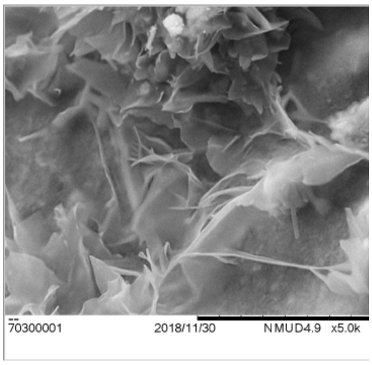
C. Scanning Electron Microscopy Analysis (SEM)

Before Debinding

a

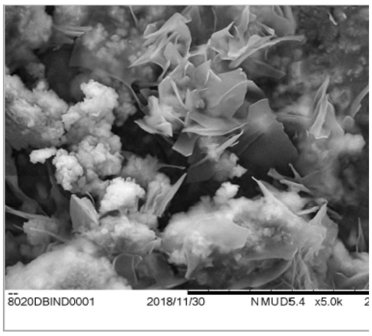


b



After Debinding

c



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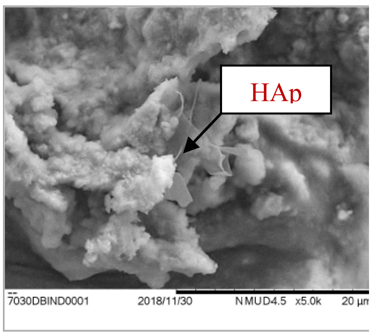

Figure 3 : Scanning electron micrograph before and after debinding

Scanning electron microscopy (SEM) analyses is used to determine the physical characterization through the morphology of Hap-ZrO_2 and also the porosity on the surface. SEM type used was (SEM; S-4800, Hitachi). The sample was in solid form obtain from the extruded sample and powder form which has undergoes debinding process. Debinding process was being conducted by emerged the extruded sample into liquid hexane at temperature 60°C for at least 5hour. The sample being coated with gold first to ensure stabilization of the sample before undergoes analysis for one minute. Figure 3 illustrate that sample (a,b,c and d) undergoes SEM micrograph of the feedstock after the rheological test. It shows the HAp-ZrO_2 were surrounded binders that containing flakes of HA agglomerate during the mixing process. The form of agglomerated due to the presence of water molecule that cannot be removed during drying stage (N. Zainuddin, 2016). While Figure 3 (e,f,g and h) indicates that the structure of binder after debinding process take place. It shows that palm stearin binder system disappeared and HAp-ZrO_2 was clearly observed in the spherical shape.

IV. Conclusion

From the result obtain, increase ZrO_2 content of the feedstock will affect the mixing behavior of the powder. Rheological properties showing that all the composition 80-20,70-30 and 60-40 are not suitable for injection moulding process. The n-value shows all type of composition having pseudoplastic behavior which the lowest *n* value give faster viscosity of the feedstock change with the shear rate. The feedstock with 70wt% HAp gives the highest value of n compared to other composition of feedstock and hence, it would be the best candidate for MIM feedstocks and state the lowest viscosity among others. The particle size of HAp,zirconia and the as-mixed powder shows the increasing size based on the percentage of the zirconia added. The particles size showing decreasing trend indicates that increase of specific area of sample. Thus, it will increase the reactivity of sample towards shear viscosity. It is proven that the ZrO_2 is compatible to be coupled up with HAp to boost the performance of HAp which is being widely applied especially in biomedical industry. However, several recommendations are needed to be taken into consideration in order to enhance the compatibility of the HAp-ZrO_2 by minimize the inhomogeneity of the feedstock prepared for the MIM process due to its stability of the process and prolong the time of the mixing process of the both elemental HAp and ZrO_2 powder. Thus, it will assure the elemental powder of HAp and ZrO_2 to be well distributed throughout the process.

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