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Evaluation of Hydroxyapatite-Zirconia Composite using Palm Stearin Binder System

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Abstract*: The main objective of this paper is to analyse the ability of the feedstock HAp-ZrO$_2$, which has different compositions with the use of palm stearin (PS) based binder system. In this research, the feedstock was classified by the different weight percentage compositions of 90-10, 80-20 and 70-30 of the HAp-ZrO$_2$, with the same ratio of 60% from their optimum powder loading to palm stearin. Thus, the performance of HAp-ZrO$_2$ composite powder is studied through the Thermogravimetric Analysis (TGA), which shows that the palm stearin binder system had been completely removed in the presence of high temperature of 500°C with a heating rate of 10°C/min. Meanwhile, the analysis of Scanning Microscopy Electron (SEM) was used to identify their physical characterisation of the feedstock. The peak shown by the FTIR test proved that the palm stearin, hydroxyapatite and zirconia are present in each composition of the feedstock. Thus, based on these findings, this study have proven that the well mixing of synthesised HAp and zirconia, and the increasing amount of zirconia can affect the composite powder, especially in terms of time taken for completion of the feedstock process. The effect of zirconia content in the composition can be investigated through rheological test using Rosand RH2000 capillary rheometer. During the rheological test, feedstock containing the mixture and binder was carried out to determine its pseudoplastic behaviour and viscosity. The binder in the feedstock gives exceptional properties to ensure the success of the injection moulding process.

***Index Terms*: HAp-ZrO$_2$, feedstock, hydroxyapatite, injection moulding, rheology.**

I. INTRODUCTION

The use of Hydroxyapatite (HA), which comes from natural sources, has been commonly practiced. HA that comes from waste, such as that from animals, and/or are organic may raise concerns from the public on the process and method involved to get the HA [1]. Chemical processes using various reactants such as $Ca(OH)_2$ and H_3PO_4, or CaO and $CaHPO_4$ are able to produce synthetic HA [2]. However, these processes need to be discussed on its impact on biological processes and its high cost. Thus, the solution to this problem has been identified, such as using the microwave method in producing HA from eggshells [3].

Calcium acts as an element that frequently builds up bones and teeth tissues in our body. Bones contain calcium in the form of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). Hydroxyapatite is different from others that contain similar composition of the bones, and has the biocompatibility, which makes it an excellent substance for use [4]. Long periods of time need to be taken by the human body to enable the production of HA during recovery from a bone injury. Thus, the medical field has found that HA from other elements can be implemented to reduce the time taken and to rebuild the tissue more effectively.

Previous study has been done on the production of hydroxyapatite from various organic sources, such as the salmon fishbone, eggshells and clamshell [5]. These waste products are commonly used for their natural compositions of HA and calcium, in which these natural compositions serve a better purpose in the production of HA.

Clamshell, which most humans find having no use in our daily life, is increase in number. This could lead to serious problems, such as pollution. Hence, from the viewpoint of researchers such as scientists and engineers, it is a big loss to throw away tonnes of clamshell, as they may be beneficial in saving the environment. Nowadays, creating energy using biomass is a rather popular way of helping the environment. Analysing the properties or characteristics of this clamshell to convert it into something useful may become a successful solution to the current problem [6]. Clamshell acts as an economic resource because the use of synthetic HAp used in the biomedical field as bone and dental implant is very expensive. This product is cost saving because clamshell comes from waste and it can be collected from anywhere along the beach. Moreover, previous study found that eggshell and clamshell consume high energy to produce HAp using the high power of microwave synthesis method [4, 7].

Clamshell acts as the 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 beach. Thus, this research will identify the use of clamshell in the combination of hydroxyapatite-zirconia and also the injection moulding of HAp-ZrO$_2$ that will be injected in the injection moulding machine with the presence of palm stearin binder.

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II. EXPERIMENTAL PROCEDURE

A. Materials

The synthesised hydroxyapatite powder was prepared using the precipitation method. Commercial zirconia powder is obtained from Vistee Techology Services and the commercial 3-mol% yttria-stabilised zirconia (YSZ) from Inframat Advanced Materials, USA.

B. Instrumentation

The instrumentations and labwares used in this work are the internal mixer HAAKE Rheomix using capillary rheometer (Rosand RH2000), Planetary Ball Mill, Pulverisette 6, (SEM; S-4800, Hitachi), (Mastersizer 2000, Malvern Instrument), Rigaku X-RAY DIFFRACTION (XRD), furnace, and oven.

C. Preparation of Composite Powder HAp-ZrO_2

The composite powder of hydroxyapatite-zirconia was prepared by using three different weight percentage compositions, as shown in Table 1. The value of zirconia to the hydroxyapatite powder was increased by 10 wt% each in order to discover the ideal composition of hydroxyapatite-zirconia composite. The mixing process of the composite was carried out using the Planetary Ball Mill. In order to ensure homogenous distribution of the mixture, the hydroxyapatite and zirconia powders were incorporated in a grinding bowl of zirconium oxide for four hours with a rotational speed of 100 rpm.

Table 1: Composite powder of HAp/ Zirconia

Type	Composition (wt%)	
	Hydroxyapatite	Zirconia
1	90	10
2	80	20
3	70	30

D. Preparation of Composite Powder HAp-ZrO_2

The internal mixer HAAKE Rheomix was used to perform the mixing process, which was conducted at 160°C for two hours with a rotational speed of 50 rpm. The PE was poured into the mixer, as the blending temperature was achieved. When the PE has been completely melted, PS was added with the powder mixture of HAP-ZrO_2. There were different compositions of HAp-ZrO_2, which show the increased toughness of ZrO_2 when its content went up to 20%, while 40% to 60% signify poor mechanical behaviour [8]. Tables 2 and 3 show that comparisons were made on the feedstocks that are to be mixed with different volume percentage of binder, which in Table 2, 100% PS while Table 3 using 70%PS and 30%PE.

Table 2: Feedstock made from palm stearin

Formulation	Composition (wt%)		Powder Loading (vol%)	Binder Composition (vol%)
	HA	ZrO_2		PS
1	90	10		
2	80	20	60	40
3	70	30		

Table 3: Feedstock made from palm stearin and PE binder

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

III. RESULTS AND DISCUSSION

A. Particle Size Distribution & Density

The result of the particle size distribution of hydroxyapatite powder, zirconia powder and as-mixed HAp-ZrO_2 powder at different weight percentage compositions are shown in Table 4 and Figure 1.

Table 4: Particle size distribution

Powder Formulation	Particle Size (µm)			Particle Width Distribution	Specific Surface Area	Pycnometer Density
	D_{10}	D_{50}	D_{90}	S_w	(m^2/g)	(g/cm^3)
HAp	5.842	56.737	578.563	1.283	5.842	3.067
ZrO_2	0.221	26.381	107.581	0.953	7.06	6.10
90wt% HAp	3.008	21.123	55.43	2.023	0.731	3.3761
80wt% HAp	2.735	20.694	58.402	1.926	0.783	3.5078
70wt% HAp	2.531	17.535	52.068	1.949	0.865	3.1342

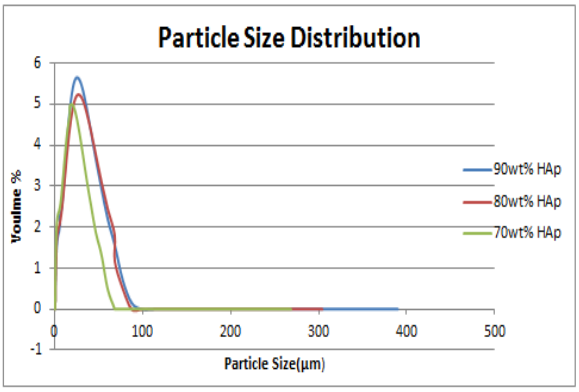

Figure 1: Particle Size Distribution of 90,80 and 70 wt% of HAp

The particle size of HAp, zirconia and as-mixed powder shows the increasing size of the as-mixed powder based on the percentage of the zirconia added. Based on the d_{50} of the HAp, zirconia, 90 wt% HAp, 80 wt% HAp and 70 wt% HAp, the values are shown at 56.737 µm, 26.381 µm, 21.123 µm, 20.694 µm, and 17.535 µm, respectively. The values of S_w of the elemental powder HAp and ZrO_2 are 1.283 and 0.953, respectively.

Meanwhile, for S_w values of 90 wt%, 80 wt% and 70 wt% of the Hap, they were calculated at 2.023 µm, 1.926 µm and 1.949 µm, respectively. Study by Omar, et al. [9] stated that the ideal value of the S_w must be either less than two or greater than seven because these values present a very broad or narrow distribution, respectively. Based on the calculated value, it represents a broad distribution of the powder that is beneficial for efficient particle packing, which complicates the flow into the mould.

B. Feedstock Evaluation

Figure 2 shows the feedstock evaluation of HAp/zirconia made from 100% palm stearin binder.

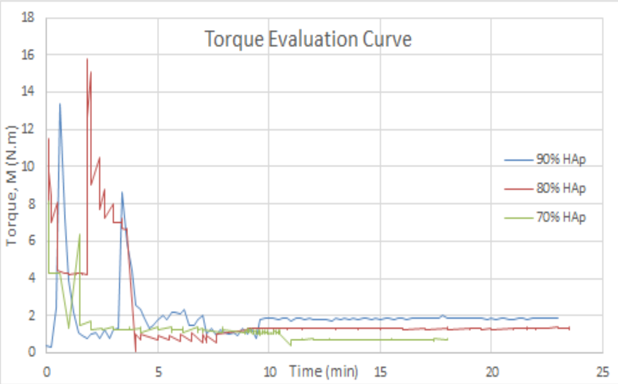

Figure 2: Torque Evaluation Curve

Based on Figure 2, the powder of 90% HAp shows that the torque value started to become stable at 10 min, while for 80% HAp and 70% HAp, they were at 7 min and 11 min, respectively. The torque value shows that at the beginning of the process, the torque value of 90% HAp is the highest, followed by the torque value of 80% HAp and 70% HAp. Next, the high peak showed by the 80% HAp may come from the cleanliness error at the internal machine, which resulted in the different peaks when compared with the other composite powder.

C. Fourier-transform Infrared Spectroscopy (FTIR)

The graph of FTIR spectrum for pure palm stearin is shown in Figure 3. The feedstock is created after the composite powder of 70%, 80% and 90% HAp is mixed with the palm stearin in the internal mixer. The process was run at 70°C for two hours. By conducting the FTIR test, the binding of the palm stearin with all three composite powders can be determined. Based on the FTIR spectrum of the three composite powders, it agrees that the palm stearin is bound to the powder. The chain of the fatty acid can be observed in the three composite powders at 2917 cm^{-1} to 2850 cm^{-1} (C-H stretching of $–CH_3$ and $–CH_2$ groups). Next, peaks at 1740 cm^{-1} (C=O stretching of ester group), 1176 cm^{-1} (C-O stretching of ester) are present, as there are ester linkages in the palm stearin.

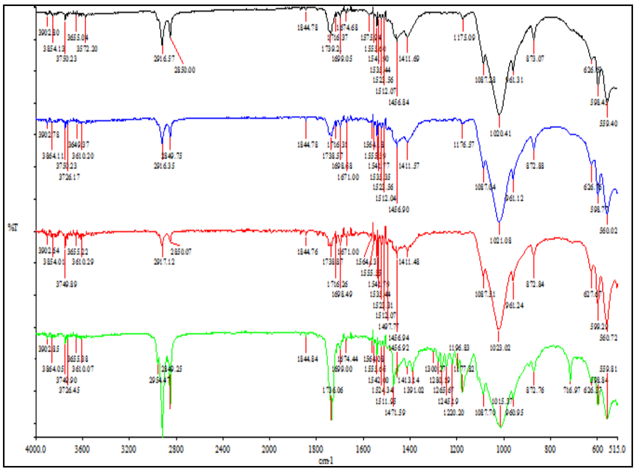

Figure 3: FTIR Spectra: (a) Palm stearin; (b) Feedstock of 90% HAp; (c) Feedstock of 80% HAp; and (d) Feedstock of 70% HAp

D. Rheological Analysis

Figure 4 shows the rheological study of feedstock prepared with 100%PS, while Figure 5 represents 70%PS and 30%PE. From Figure 4, it indicates that the shear viscosity decreases with shear rate. The results from all the compositions of HAp-ZrO_2 from 80-20 to 50-50 were not in the range of pseudoplastic behaviour, where the shear viscosity value is more than 1000 Pa.s and the shear rate value is not between 100 and 10000 (1/s) [10]. On the other hand, the addition of ZrO_2 was observed on whether it will affect the viscosity of the sample or not. Figure 4 shows that the viscosity decreases with the addition of 30 wt% ZrO_2, but increases with the addition of 20 wt% ZrO_2. Meanwhile, Figure 5 shows that the viscosity is much lower than when PE is being added, compared to the 100%PS.

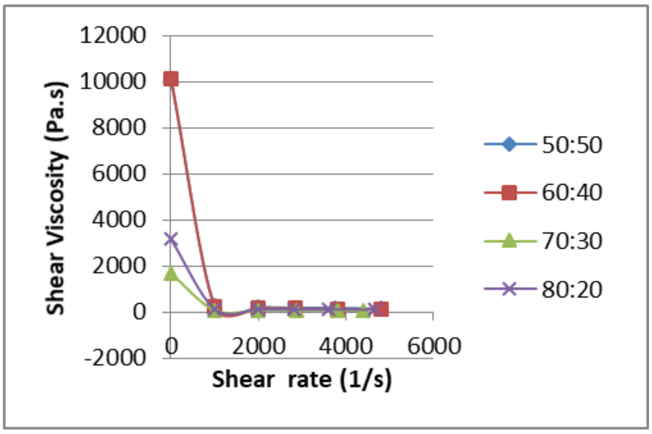

Figure 4: Rheological study of feedstock made from 100% palm stearin

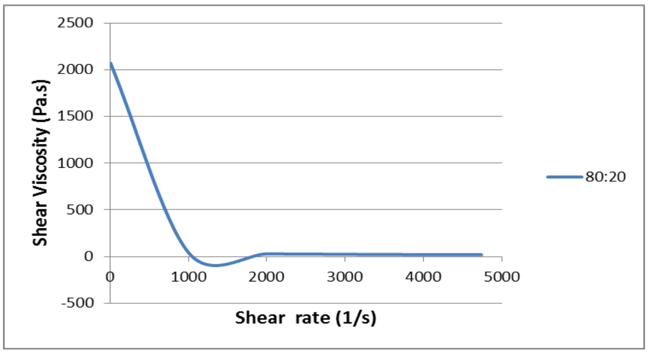

Figure 5: Rheological study of feedstock made with palm stearin and polyethylene binder

The rheological properties show that all of the compositions: 80-20, 70-30 and 60-40 are not suitable for the injection moulding process. The n-value shows that all types of composition have a pseudoplastic behaviour, where the lower the *n* value is, the faster the viscosity of the feedstock will change with shear rate. Feedstock with 70 wt% HAp gives the highest value of n, compared to other compositions of the feedstock; hence, it would be the best candidate for MIM feedstocks and in the best state, as it has the lowest viscosity among others. The particle sizes of the HAp, zirconia and as-mixed powder show the increase in size based on the percentage of the zirconia added. The particle sizes show a decreasing trend that indicates the increase of a specific area of the sample. Thus, it will increase the reactivity of the sample towards shear viscosity [11]. It is proven that the ZrO_2 is compatible to be coupled up with HAp to boost the performance of HAp, as it is being widely applied, especially in the biomedical industry [12,13]. However, several recommendations need to be taken into consideration in order to enhance the compatibility of the HAp-ZrO_2. This can be done by minimising the inhomogeneity of the feedstock prepared for the MIM process due to the stability of the process and prolonged duration of the mixing process of both elemental HAp and ZrO_2 powder [14]. Hence, this will ensure that the elemental powders of HAp and ZrO_2 are well distributed throughout the process. Figure 6 shows the SEM image of the HAp-ZrO_2 specimen made of PS/PE binder system. It shows the bonding and interaction between the HAp-ZrO_2 powder and PS/PE binder component. The irregular shape of the powder helps the binder to attach itself among the powder particles more easily.

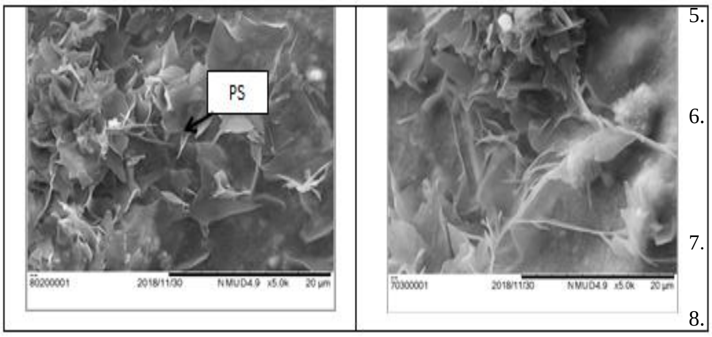

Figure 6: SEM image of 80 wt% HAp- ZrO_2 moulded specimen

Figure 7 shows the SEM image of HAp-ZrO_2 after being immersed in heptane. It shows that all of the palm stearin binders were removed, leaving the insoluble PE either in the contact region or as whiskers holding the particles together, as shown in Figure 7. It is clearly seen that there is a network of porous PE ligaments with sufficient brown strength for handling purpose.

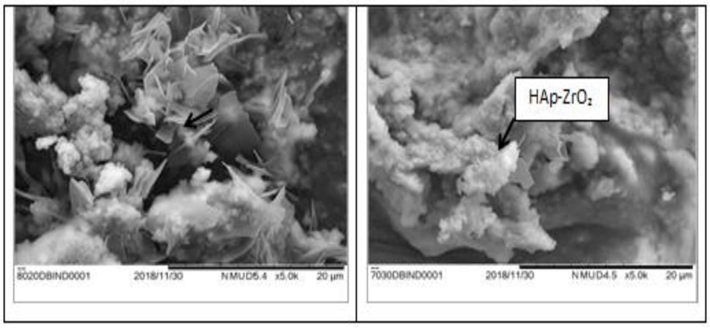

Figure 7: SEM image 80 wt% HAp-ZrO_2 after debinding

IV. CONCLUSION

Increase in the ZrO_2 content of the feedstock will affect the mixing behaviour of the powder. The feedstock made from a 100% PS binder was not suitable for the injection moulding purpose. Addition of PE as a backbone binder will bond HAp-ZrO_2 powder and shows stability of feedstock that cen be injection moulding and have contact region with the powder and PS binder. Furthermore, the insoluble binder of PE held the specimen before the sintering process took place.

V. ACKNOWLEDGEMENT

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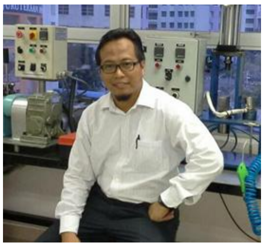
REFERENCES

1. J. O. Akindoyo, M. D. H. Beg, S. Ghazali, E. O. Akindoyo, N. Jeyaratnam, Synthesis of Hydroxyapatite through Ultrasound and Calcination Techniques." IOP Conference Series: Materials Science and Engineering 203: 012003, 2017.
2. M. Mucalo, *Hydroxyapatite (HAp) for Biomedical Applications*. Woodhead Publishing: xvii-xix. 2015.
3. M. Okada, T. Furuzono, "Hydroxylapatite nanoparticles: fabrication methods and medical applications." Sci Technol Adv Mater 13(6): 064103, 2012.
4. Evis, "Reactions in hydroxylapatite–zirconia composites" Ceramics International 33(6), 2007, pp. 987-991.
5. S-C. Wu, H-C. Hsu, S-K, Hsu, Y-C. Chang, W-F. Ho, "synthesis of hydroxyapatite from eggshell powders through ball milling and heat treatment, "Journal of Asian Ceramic Societies", Vol 4, Issues 1, 2016, pp. 85-90.
6. M. Z. A. Khiri, K. A. Matori, N. Zainuddin, C. A. C. Abdullah, Z. N. Alassan, N. F. Baharuddin, M. H. M. Zaid, "The usability of ark clam shell (Anadara granosa) as calcium precursor to produce hydroxyapatite nanoparticle via wet chemical precipitate, SpringerPlus 5:1206, 2016, pp 2-15.
7. I. Subuki, N. H. M. Ali, M.H. Ismail, "Rheological properties of Hydroxyapatite synthesized clamshell mix with palm Stearin binder system, Advanced Material Research, 2014, pp. 366-370.
8. C-Y. Chiu, H-C. Hsu, W-H. Tuan, "Effect of zirconia addition on the microstructural evolution of porous hydroxyapatite", Ceramic International, Vol 33 (5), 2007, pp 715-718.

9. M. A. Omar, I. Subuki, N. Abdullah, "Development of metal injection moulding process for medical applications" Advanced Materials Research, Vol 428, 2012, pp. 38-42.
10. A. Arifin, A. B. Sulong, N. Muhamad, J. Syarif, and M. I. Ramli, "Powder injection molding of HA/Ti6Al4V composite using palm stearin as based binder for implant material. Materials & Design 65, 2015, pp. 1028-1034.
11. J. Song, Y. Liu, Y. Zhang, L. Jiao "Mechanical properties of hydroxyapatite ceramics sintered from powders with different morphologies" Materials Science and Engineering: A 528(16), 2011, pp. 5421-5427.2011
12. M. Foudzi, N. Muhamad, A. B. Sulong, H. Zakaria, Yttria stabilized zirconia formed by micro ceramic injection molding: Rheological properties and debinding effects on the sintered part. Ceramics International, 39(3), 2013, pp. 2665–2674.
13. M. I. Jamaludin, N. A. A. Kasim, N. H. M. Nor, M. H. Ismail, "Development of porous Ti-6Al-4V mix with palm stearin binder by metal injection moulding," American Journal of Applied Science, 12 (10), 2015, pp 742-751.
14. M. Mbarki, P. Sharrock, M. Fiallo, H. Elfeki, "Hydroxyapatite bioceramic with large porosity." Mater Sci Eng C Mater Biol Appl 76, 2017, pp. 985-990.

AUTHORS PROFILE

Istikamah Subuki received the Chemical Engineering degree and the PhD degree in Mechanical Engineering from the Universiti Teknologi MARA (UiTM) Shah Alam, Malaysia in 2004 and 2010 respectively. From 2007 to 2010, she was the researcher of the Advanced Materials Research Center (AMREC), SIRIM Berhad. She is currently a Senior Lecturer in the Faculty of Chemical Engineering, UiTM Shah Alam. Her current research interests are in advanced materials of synthesize hydroxyapatite powder, injection moulding process, develop new binder system for injection moulding process, plasma spray coating of hydroxyapatite, metal and ceramic composite and polymer composite foam.



Assoc. Prof. Dr Muhammad Hussain Ismail obtained his PhD degree from the University of Sheffield, UK in 2012 at the Department of Materials Science and Engineering. The title of his PhD dissertation is Processing of Porous NiTi by Metal Injection Moulding (MIM) using Partly Water Soluble Binder System. He obtained both B. Eng. (Hons) and MSc in Mechanical and Materials Engineering from the National University of Malaysia in Bangi. He joined the Faculty of Mechanical Engineering UiTM as a lecturer in 2001 and has been appointed as a Deputy Dean for Research and Industrial Linkages since Nov 2017. Dr. MH Ismail has been lecturing several subjects from Diploma, Degree and Masters Degree such as Automotive Technology, Metallurgy, Strength of Materials, Statics, Materials Science and Management of Innovation, which lead to his areas of interest in Materials Processing, particularly in Powder Metallurgy, biomedical implants and ceramic materials. He is the founder and the Head for EK5 Research Interest Group (RIG), namely Industrial Metallurgy Research Group (IMReG) since Nov 2016. At the National level, he is a Secretary of Malaysian Powder Metallurgy and Particulate Materials Association (MPM^{2}A). He has supervised more than 100 undergraduate students and more than 30 postgraduate students at PhD and MSc levels which lead to publication more than 100 research articles in several indexed and non-indexed publications, nationally & internationally.