The Effect of Zirconia Composition on HAp-Zirconia Feedstock Using Palm Stearin Binder System

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***Abstract*— The purpose of this study is to investigate the performance of feedstock containing HAp-ZrO_2 bioceramic powder with palm stearin (PS) based binder system. The feedstock was varied with three different weight percentage composition; 90-10, 80-20 and 70-30 of the HAp-ZrO_2 and the optimum powder loading of 60 vol % was remained for each composition. Different weight composition of the HAp-ZrO_2 resulted in different characteristics of the as-mixed powder similarly in their mixing behaviour. Therefore, the performance of HAp-ZrO_2 composite powder is studied through the particle size distribution, pycnometer density and X-ray diffraction (XRD). Then, the influence of ZrO_2 percentage content in the feedstock also is observed via the rheological study. The rheological response of MIM feedstock by means of a capillary rheometer is essential to be carried out in order to examine the viscosity and flow behaviour index of the feedstock. From the analysis, the increasing content of ZrO_2 by 30wt% in the feedstock is indeed affecting the mixing behaviour of the as-mixed powder as its XRD patterns showed the evident differences in the peak present. In term of rheological study, the 70-30wt% of HAp-ZrO_2 is deemed unfit for MIM processes based on the too high viscosity and too low of *n* value.**

***Keywords*— HAp-Zirconia, Rheological Behaviour, Palm Stearin Binder System**

I. INTRODUCTION

One of the well-known bioceramic material is hydroxyapatite (HAp), $Ca_{10}(PO_4)_6(OH)_2$. HAp has been intensely used as implant material such as bone replacement due to its resemblance in natural bone material with the composition of 70% in human body. Possessing the unique bioactivity characteristics such as good biocompatibility, osseoconductivity and bioaffinity with living tissues, HAp stimulates speedy bone growth besides provides strong interfacial fixation for orthopaedic and dental applications [2]. Yet, the major drawback of HAp is having the inferior mechanical properties such as high fragility, low strength and low fracture toughness. These disadvantages resulted in the limitation of usage in load-bearing orthopaedic implants such as spinal fusion bodies, pins plates and screws [20]. Therefore, the improvement on the mechanical properties of metal-ceramic is needed to be done by incorporating the metallic materials. Due to this, the reinforcement of zirconia (ZrO_2) in HAp matrix in the form of particles, platelets, fibers or nanoparticles had gathered much interest among the researchers [1].

According to previous research, ZrO_2 had been proven to have a good biocompatibility coupled with the tendency to boost the mechanical properties of HAp. By being biocompatible, ZrO_2 stimulates the proliferation of cell and differentiation in osteogenic pathways [27]. The study demonstrated in several studies suggested that the bone attachment on zirconia surface as well as the formation of a direct interface between bone and zirconia is often equivalent to or even superior than titania implants. The radiopaqueness of ZrO_2 makes the monitoring process of its function become easier as it can be seen clearly in radiographs [20]. Owing to the martensitic transformation of tetragonal↔monoclinic ZrO_2 (T↔M), zirconia-based materials display a remarkable toughness and improved strength compared to monolithic HAp itself. This was supported by the justification of their satisfactory biocompatibility via the medical implementation of ZrO_2 implants [3]. In ZrO_2 reinforced HAp composites (HAp- ZrO_2), it was forecasted to have the high possibility to incorporate exceptionally advantageous properties of both biomaterials which formerly being applied separately [21].

Using these findings, the effect of zirconia addition on HAp composite (HAp-ZrO_2) were investigated in order to study the dispersion of the nanometric reinforcement in the HAp matrix. Optimal dispersion of the reinforcement during the mixing of elemental powder has said to be very vital to attain a good homogeneity of the feedstock [20]. The homogenous feedstock is one of the compulsory criteria that is required to be achieved in order to ensure the success of injection moulding method. The metal injection moulding (MIM) process is described as a proficient process where the accurate products of complex shape can be produced.

In this study, the influence of varied percentage content of zirconia addition to HAp-ZrO_2 composition on the mixing behaviour and its effect on rheology are being investigated. The different mixing ratio of HAp-ZrO_2 results in different size of particles, their distributions and characteristics which directly influenced the viscosity [4]. Apart from the low activation energy, consistent flow index and low yielding stress, the low viscosity also is one of the fundamental criteria that is desired by the rheology properties [16]. Therefore, this study focused on the characterisation of the HAp-ZrO_2 composite powder and the rheological properties of feedstock using palm stearin binder system with different composition of powder mixture.

II. METHODOLOGY

A. *Preparation of Composite Powder*

The composite powders were prepared by mixing the hydroxyapatite (HAp) ($Ca_{10}(PO_4)_6(OH)_2$) with commercial 3% mol Yttria Stabilized Zirconia (ZrO_2) (supplied by Inframat Advanced Materials) at three different weight percentage composition as shown in Table 1. The addition of ZrO_2 powder to HAp powder was increased by 10wt% each in order to find the ideal composition of HAp- ZrO_2 composite.

Planetary Ball Mill, Pulverisette 6 was employed to carry out the mixing process of each composition of HAp and ZrO_2. To ensure the homogenous distribution of the mixture, the HAp and ZrO_2

powder were mixed in a stainless steel jar for 4 hours with rotational speed of 100 rpm. The Yttria Stabilized Zirconia (YZS) balls (supplied by Inframat Advanced Materials) were used as the grinding media with the ratio of 2:1 to the powder [6]. The composites were then proceed to the feedstocks were prepared.

Table 1: The composition of mixing ratio of HAp-ZrO_2

Formulation	Composition (wt%)	
	HAp	ZrO2
1	90	10
2	80	20
3	70	30

B. Characterisation of Composite Powder

The particles size of HAp-ZrO_2 and their distribution was determined by using a particle size analyser with a laser diffraction method (Mastersizer 2000, Malvern Instrument). The particle size measurement was significant due to the fact that the properties of distributed materials are firmly related with their molecule size and uniformity.

The theoretical or true density of the composite powder was performed through pycnometer density using Accupyc under the flow of helium gas.

Rigaku X-Ray Diffractometer (XRD) was employed to investigate the qualitative phase composition of the HAp-ZrO_2 composite. By operating at 40kv and 40mA with Cu-Kα radiation, the analysis was performed in the range of 2θ from 20° to 60° with 2 °/min of scan speed.

C. Preparation of Feedstock

The powder-binder mixture or generally known as feedstocks were prepared by mixing the powder loading of 60 vol % along with the binder system which contained palm stearin (PS) and polyethylene (PE) at 60 and 40 percentage of weight ratio respectively [5]. Each PS and PE used in this investigation were manufactured by Kempas Edible Sdn. Bhd. and Titan Polyethylene (M) Sdn. Bhd., correspondingly. The formulation for the feedstock was displayed in Table 2.

Table 2: Composition of Binder Systems

Composition (wt%)		Powder Loading (vol %)	Binder composition (wt%)	
HAp	ZrO2		Palm Stearin (PS)	Polyethylene (PE)
90	10			
80	20	60	60	40
70	30			

The internal mixer HAAKE Rheomix was used to perform the mixing process which was conducted at 160 °C in the duration of 2 hour with rotational speed of 50 rpm. At the point when the required blending temperature was achieved, the PE was addeded into the mixer. After being completely melted, the PS was added subsequently and followed by the powder mixture of HAp-ZrO_2 [7]. The uniformity of the feedstocks can be expected by perceiving the mixing torque value. When the torque attained a steady state value, the homogeneous mixing was presumed to have ensued [8]. Better mixing is said to be accomplished with the respect of the lower value of torque [9]. Once the mixing process was accomplished, a pallet knife was used to manually chop the feedstock. Then, followed by the cooling of the chopped feedstocks at the room temperature.

D. Rheological Test

The rheological behaviour of the feedstock was then identified by using a Rosand RH2000 capillary rheometer. This test was fundamental in order to determine the feedstock viscosity. The determination of viscosity is strongly correlated to the identification of pseudoplastic properties which can be an indication to the successful injection process. Amid the test, the feedstock was being ejected through a small cylindrical orifice which having a length, L of 16 mm and diameter, d of 1 mm (L/d = 16). The pelletized feedstock was then charged into the rheometer barrel and permit to preheat at 5°C/min of heating rate and at temperature of 210 °C.

III. RESULTS AND DISCUSSION

A. As-mixed Powder Characterization

Particle size distribution of composite powders at three different weight percentage were given in the Table 3. Apart from that, the width of particle size distribution, S_w calculated by using the Equation (1) also was shown in Table 3. Meanwhile, the graph for the particle size distribution for the elemental powder as well as the mixed powder were illustrated in Figure 1.

$$S_w = \frac{2.56}{log_{10}\left(\frac{D_{90}}{D_{10}}\right)} \quad (1)$$

Table 3: The particle size distribution of mixed powder

Powder	Particle Size (µm)			Particle Width Distribution	Specific Surface Area
	d_{10}	d_{50}	d_{90}	S_w	(m²/g)
90wt% HAp	8.507	34.096	95.537	2.437	0.323
80wt% HAp	7.036	38.059	114.892	2.111	0.36
70wt% HAp	2.881	18.679	69.635	1.851	0.747

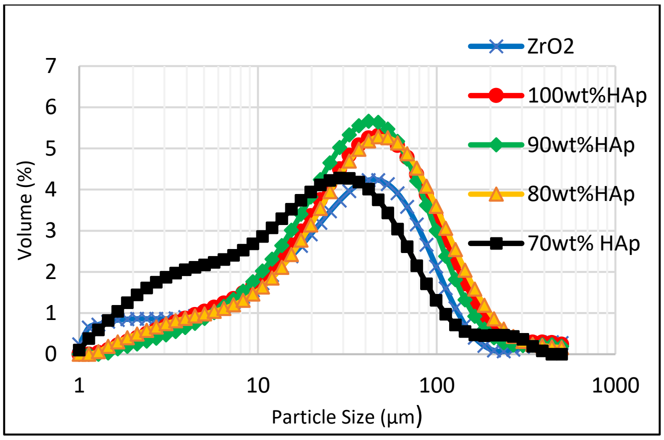

Figure 1: Particle Size Distribution

According to German and Bose [10], ideally, the value for S_w should be either less than 2 or greater than 7 presenting a very broad or a very narrow distribution respectively. From the Table 3, the value of S_w for mixed powder with 90wt% HAp, 80wt% HAp and 70wt% HAp were calculated to be 2.437, 2.111 and 1.851 correspondingly. All of these values obtained in this study indicate that the broad distribution of the powder which is believed to be beneficial for efficient particle packing. This is because the study conducted by German and Hens [11] showed that the powder with S_w value over 7 is being complicated to flow into mold. Moreover, by possessed the broad particle size distribution, the possibility of segregation of the mixture to ensue was very minimum and the viscosity also was being reduced [12]. Another investigation done by Subuki [2] also suggested that the benefit offers by broadness of the distribution was more ceramics could be packed in a given volume due to the small particles incline to fill up the available spaces between larger particles which lead to the possible high loads of the powder.

Generally, the surface area is affected by the particle size of the powder. Smaller particle size of powder is said to exhibit a high surface area. According to Ismail [13], high surface area of powder resulted in more powder packaging which then lead to the accuracy of the density reading. Basically, the density of as-mixed powder is essential in this study because it is employed in defining the mass required for preparation of feedstock for rheological test. Table 4 display the result of the pycnometer density for as-mixed powder. The rate of the density was said to be contributed by the composition of the powder [14]. Based on the results, the composition of 70wt% HAp and 30wt% ZrO_2 depicted a significant density decreasing.

Table 4: The density measured of HAp-ZrO_2 composite powder

Powder	Pycnometer density(g/cm3)
90wt% HAp	3.3761
80wt% HAp	3.5078
70wt% HAp	3.1342

The XRD pattern for the elemental powder of ZrO_2 and HAp in comparison with the composite powders with different composition were shown in the Figure 2. This analysis was carried out in order to ensure all the elemental powders were distributed homogenously during the mixing process. Based on the result, both 90wt% and 80wt% HAp as-mixed powder showed the same pattern of peaks whereby the present peaks correspond to the HAp as well as the ZrO_2 existence. However, the diffractograms for 70wt% HAp as-mixed powder showed the obvious differences in XRD pattern when the ZrO_2 content was increased by 30wt%. Eventhough there was no new peak was existed indicating no new bonds were being formed, the decomposition of HAp were observed in the composites. This result was believed to be caused by the existence of the non-stable ZrO_2 phase due to its non-uniformity dispersion in HAp matrix [23]. The finding were supported by Chen [22] where the poor properties of composites due to presence of high porosities and poor phase distribution were observed when ZrO_2 content was higher than 30 wt%. In addition, the previous study also reported that the non-uniform ZrO_2 phase distribution in mechanical mixing of HAp and ZrO_2 powders was caused by the segregation of ZrO_2 particles [3][24].

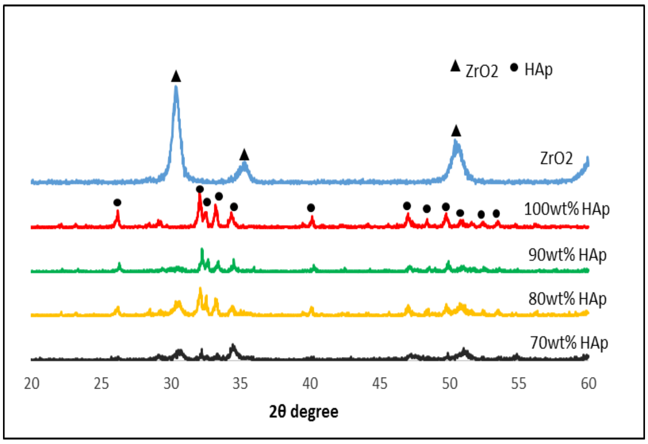

Figure 2: XRD

B. Rheological Study

The correlation of feedstocks viscosity and shear rate for three different weight composition of HAp-ZrO_2 powder was illustrated in Figure 3. It was evidently shows that the viscosity decreases as the shear rate increases (shear thinning). The result obtained for all the feedstock clearly exhibit the pseudo plastic behaviour. The suitable pseudo plastic behaviour for injection moulding is accomplished if viscosity value is less than 1000 Pa.s and the range of shear rate is between 100 and 10000 (1/s) [15]. This pseudo plastic behaviour helps in facilitate the moulding filling, minimising jetting and aid to preserve the shape of the moulded part. The correlation of ZrO_2 content and viscosity also was being observed. It can be examined that the viscosity was decreased from the 10wt% ZrO_2 to the addition of 20wt% ZrO_2. However, when the ZrO_2 was added by 30wt%, the viscosity was significantly increased. In term of feasibility of injection moulding processes, both viscosity of the feedstock with 90wt% and 80wt% HAp were considered viable. On the other hand, the feedstock containing 70wt% HAp was found to be not suitable as the MIM feedstock. This is mainly due to its resulting viscosity which is higher than 1000 Pa.s. This exceeding viscosity is reported to be due inhomogeneity of the feedstock. In addition, the agglomerates lead to initial difficulty of mixing viscosity as well as the mixing torque [25]. This is corresponding to the XRD result of 70-30wt% HAp- ZrO_2 which contradict to the homogenous mixing of elemental powder.

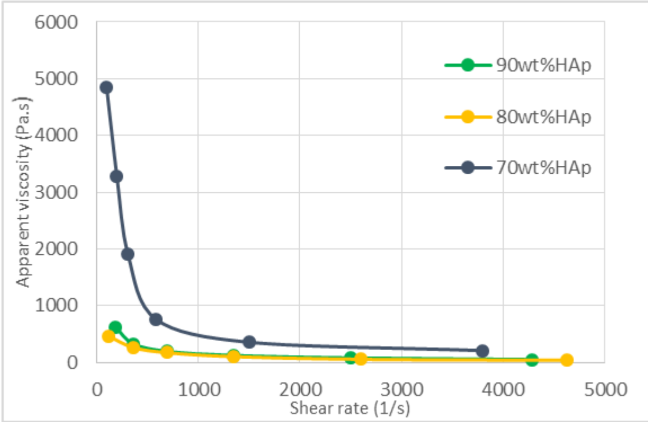

Figure 3:

The temperature of 210^{O}C was selected to perform the rheology test as the feedstocks shows a good fluidity where the greater heat input was required due to high viscosity of the HAp-ZrO_2 powder. At the temperature below 200^{O}C, the feedstocks was observed to be too viscous to flow which then cause the feedstock to remain in the rheometer barrel.

Generally, the pseudo plastic behaviour corresponding to the breakage of particle agglomerates with the release of the fluid binder [10]. This behaviour also can be defined by the following equation:

$$\tau = K\gamma^n \tag{2}$$

Where τ is denotes as shear stress, γ indicates the shear rate, *n* the flow behaviour index and K signifies a constant.

Meanwhile, the relationship between the data of shear stress to shear rate for pseudo plastic behaviour and dilatants fluids which identified as the power-law equation can be portrayed via ln (2). The exponent *n* of the power-law index represent the shear sensitivity whereby the smaller value of *n* implies higher shear sensitivity and exhibit more pseudo plastic properties. On the other hand, dilatants material is retained for n>1. According to Wenjea [19], dilatant material is described as the separation of metal powder and binder under the influence of high shear rate. The shear sensitivity, n can be obtained by plotting the graph based on the Equation (3) below:

$$log_{10}\,\tau = \,log_{10}\,k \,+ n\,log_{10}\,\gamma \tag{3}$$

Apart from that, equation (4) shows the essential properties of rheology in term of viscosity (η):

$$\eta = \frac{\tau}{\gamma} \quad (4)$$

By correlating the apparent viscosity η and power-law index n, the value of n also can be attained from the logarithm form by calculating the slope of the curve $|n-1|$ as performed in Figure 4. Their relationship can be referred to the following equation:

$$\eta = \frac{\tau}{\gamma} = K\frac{\gamma^n}{\gamma} = k\gamma^{n-1} \quad (5)$$

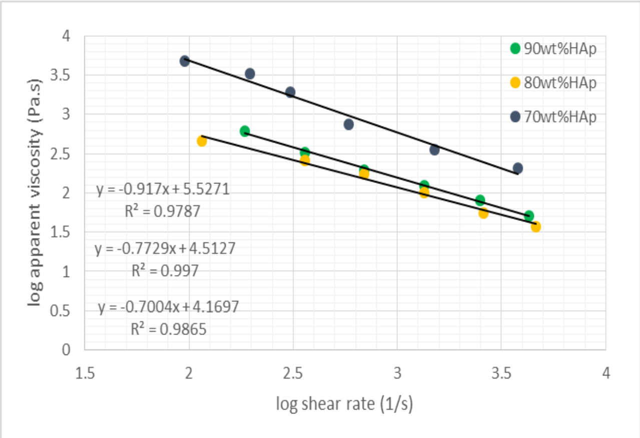

Figure 4: The Log Viscosity Against Log Shear Rate at 210^{O}C of HAp-ZrO_2

Based on the result tabulated in Table 5, the shear sensitivity of all the feedstock shows the value less than 1. All the feedstock ranging from 90wt% to 70wt% HAp were calculated to be 0.227, 0.300 and 0.083 which proven to obey the pseudo plastic behaviour. The obtained results describes in increasing of ZrO_2 content up to 20wt% shows an increase in n value. Meanwhile the n value drastically decreases when the content of ZrO_2 is increased by 30wt% proportionally equivalent to its high viscosity. Moreover, this n value for this feedstock was deemed too low for the injection molding. The excessively low of n value may contribute to the slip flow phenomenon which then lead to the moulding defects [26]. For successful injection molding, it is advisable to use the feedstock with high value of n which in the range of 0.5 to 0.7. The high value of n signify that the viscosity decrease slowly with increasing shear rate [17]. However, the n value as low as 0.1 also has been reported in the previous studies [18].

Table 5: Shear sensitivity (n) of HAp-ZrO_2 feedstock

Formulation	Shear sensitivity (n)
90wt%HAp	0.227
80wt%HAp	0.300
70wt%HAp	0.083

IV. CONCLUSION

From the analysis, the increasing content of ZrO_2 in the feedstock is indeed affecting the mixing behaviour of the as-mixed powder. With the increasing up to 20wt% of ZrO_2 content, the XRD pattern shows the homogenous mixing of the both HAp and ZrO_2 powder. However, the XRD pattern for 70-30wt% HAp-ZrO_2 displays the significant differences in the peak present. Due to this, the rheological properties are also being affected due to inhomogeneous mixing behaviour. The high viscosity and too low of n value made the feedstock with 30 wt% ZrO_2 content deemed unfit for MIM processes. On the other hand, both 90-10wt% and 80-20wt% of HAp-ZrO_2 feedstock exhibit a pseudo plastic properties which favourable for MIM processes. The viscosity of both feedstock also proven to be sensitive with shear rate as the n value obtained was below than 0.3. In this case, the feedstock with 80wt% HAp shows the best properties as it possessed the highest value of n compared to other feedstock composition. Apart from that, it also possess the lowest viscosity for easier flowability.

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References

[1] Rapacz-Kmita, A.; Slosaczyk, A. & Paszkiewicz, Z. (2006). Mechanical Properties of HAPZrO2 Composites, *J. Eur. Ceram. Soc., Vol.*26, pp. 1481-1488
[2] Subuki, I. et. al., (2014). Rheological Properties of Hydroxyapatite Synthesized Clamshell mix with Palm Stearin Binder System. Advanced Materials Research. ISSN: 1662-8985, Vol. 911, pp 366-370. doi:10.4028/www.scientific.net/AMR.911.366
[3] Rapacz-Kmita, A.; Slosaczyk, A. & Paszkiewicz, Z. (2006). Mechanical Properties of HAPZrO2 Composites, J. Eur. Ceram. Soc., Vol.26, pp. 1481-1488
[4] Sharma, D., et. al., (2015). Essential parameters responsible for rheological assessment of concentrated dispersion:-a comprehensive review. Journal of Ceramic Processing Research. Vol. 16, No. 6, pp. 690~704 (2015)
[5] Arifin, A., Sulong, A. B., Muhamad, N., Syarif, J., & Ramli, M. I. (2014). HA/Ti6Al4V Powder with Palm Stearin Binder System - Feedstock Characterization. Applied Mechanics and Materials, 564, 372-375. doi:10.4028/www.scientific.net/AMM.564.372
[6] Wu, S. L., Liu, X. M., Chu, P K., Chung, C. Y., Chu C. L., & Yeung, K. W. K. (2008). Phase Transformation behaviour of porous NiTi alloys fabricated by capsule-free hoot isostatic pressing. Journal of Alloys and Compounds, 449(1-2),139-143.
[7] Arifin, A., Sulong, A. B., Muhamad, N., Syarif, J., & Ramli, M. I. (2015). Powder injection molding of HA/Ti6Al4V composite using palm stearin as based binder for implant material. Materials & Design (1980-2015), 65, 1028-1034. doi:10.1016/j.matdes.2014.10.039
[8] Nordin, N. A., Rabzi, I., Wahab, N. a., Jumahat, A., & Ismail, M. H. (2014). Viscosity Analysis of Copper Powder Mixed with Palm Stearin Based Binder. Applied Mechanics and Materials, 660, 259-264. doi:10.4028/www.scientific.net/AMM.660.259
[9] Supati, R., Loh,N. H., Khor, K.A., & Tor, S. B. (2000). Mixing and characterisation of feedstock for powder injection molding. Materials Letters, 46, 109-114.
[10] German. R.M. and Bose, A. (1997). Injection Molding Of Metals and Ceramic, Metal Powder Industries Federation, Princeton, New Jersey.
[11] German, R. M., & Hens, K. (1992). Identification of the Effect of Key Powder Characteristic in PIM. In *Proc. of Powder Injection Molding Symposium*, MPIF, Priceton, NJ (pp. 1-16).
[12] Subuki, I. (2010). Injection Moulding of 316L Stainless Steel Powder Using Palm Stearin Based Binder System. Universiti Teknologi Mara.
[13] Ismail,M. H. (2012). *Porous NiTi Alloy By Metal Injection Molding (MIM) using Partly Water Soluble Binder System*. University of Sheffield.
[14] Balázsi, C., Gergely, G., Sahin, F. C., & Göller, G. (2011). Spark plasma sintered hydroxyapatite - Zirconia composites: Structural and mechanical properties. In ICCM International Conferences on Composite Materials.
[15] Arifin, A., Sulong, A. B., Muhamad, N., Syarif, J., & Ramli, M. I. (2014). HA/Ti6Al4V Powder with Palm Stearin Binder System - Feedstock Characterization. Applied Mechanics and Materials, 564, 372-375. doi:10.4028/www.scientific.net/AMM.564.372
[16] Ukwueze, B. E., Sulong, A. B., Muhamad, N. & Sajuri, Z. (2016). Rheological Investigation of Powder Injection Molding Materials using Polyethylene with Palm Stearin Binder System. Advanced Processes and Systems in Manufacturing An International Conference 2016. Pp 17-18.
[17] Harun, M. R., Muhamad, N, Sulong, A. B, Mohamad Nor, N. H. & Ibrahim, M. H. I (2011). Rheological Investigation of ZK60 Magnesium Alloy Feedstock for Metal. Applied Mechanics and Materials. Vols. 44-47, pp 4126-4130
[18] German, R. M. (1990). *Powder Injection Moulding*
[19] Wenjea J. T. (2000). İnfluence of Surfactant on the Behaviors of Injection- Molded Alumina Suspension. Material Science & Engineering A289 116-112.

[20] Bondioli, F. et al. (2007). Synthesis and Sinterability of Hydroxyapatite-coated Zirconia Nanopowders. NSTI-Nanotech 2007, ISBN 1420063766 Vol. 4

[21] Moon, B. K., Kamada, K., Enomoto, N., Hojo, J., & Lee, S. W. (2007). Effect of Calcination on Mechanical Properties of Hydroxyapatite / Zirconia Composite Sintered by Spark Plasma Sintering. Materials Science Forum, 561-565, 613-616. doi:10.4028/www.scientific.net/MSF.561-565.613

[22] Chen, Y.; Dong, Z. & Miao, X. (2008). The Effect of Yttria-Stabilized Zirconia on the Properties of the Fluorine–Substituted Hydroxyapatite Ceramics Prepared by Pressureless Sintering, Journal of Biomimetics, Biomaterials and Tissue Engineering, Vol.1 pp. 57-68.

[23] Vasconcelos, C. (2012). New Challenges in the Sintering of HA/ZrO2 Composites, Sintering of Ceramics -New Emerging Techniques, Dr. Arunachalam Lakshmanan (Ed.), ISBN: 978-953-51-0017-1, InTech

[24] Kim, H. W., H.-E. Kim, V. Salih and J. C. Knowles. (2005). Hydroxyapatite and titania sol gel composite coatings on titanium for hard tissue implants; mechanical and in vitro biological performance, J. Biomed. Mater. Res., Part B, 2005, 72, 1–8.

[25] German R. M (1994). Homogeneity Effects on Feedstock Viscosity in Powder Injection Molding. Communications of the American Ceramic Society Vol 77, No 1.

[26] Asmawi, R. (2016). Characterisation of stainless steel 316dstock for metal injection molding mim using waste polystytrene and palm kernel oil binder system. International engineering research and innovation symposium (IRIS)

[27] Afzal, A. (2014). Implantable zirconia bioceramics for bone repair and replacement: A chronological review. Mater. Express, Vol. 4, No. 1, 2014