Flow Behaviour Characterization of Hydroxyapatite for Powder Injection Moulding (PIM)

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ABSTRACT

The selection and formulation of binder systems play an important role in powder injection moulding (PIM). The rheological properties of feedstock need to be controlled due to preventing any formation of defects during injection, debinding and sintering. For this study, the Hydroxyapatite (HA) feedstock was prepared by mixing with 40 vol% Palm Stearin (PS) and 60 vol% Polyethelyne (PE) binder system. Three feedstocks (F1, F2 and F3) at different powder loadings of 54, 55 and 56 vol%, respectively, were mixed using brabender mixer. The rheological properties of feedstock such as flow behaviour index, flow activation energy, and mouldability of the feedstocks were determined with a capillary rheometer. It was found that, all feedstocks exhibited pseudoplastic flow, which is an important requirement in PIM. The three feedstock flow behaviour indexes were n (0.16-0.24), and flow activation energies; E at shear rate at 1000s^{-1} was 5.36, 6.91 and 14.35 kJ/mol. In addition, F3 was found to be able to be injected in a wide range of

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temperature due to its low-flow behaviour index, low activation energy, and high mouldability index gathered from the rheological test.

Introduction

Hydroxyapatite Ca10(PO4)6(OH)2 is an inorganic component that is chemically and crystallographically identical to a natural bone. The hydroxyapatite (HA) is an extremely compatible material for the biomedical applications, especially the orthopedic implantation. It is a greatly bioactive materials that allows new bones to grow from the natural bone at the implant [1]. In vivo, study shows that the biological apatite layer was found on the surface of hydroxyapatite implant. This study also reported that an apatite deposition was found either interacting or interlocking between the synthetic hydroxyapatite and natural bone tissue existed [2]. The excellent capabilities of HA cause this material to become an important bioceramic material for the implantation purpose. In powder metallurgy (PM), the processing of HA is mostly associated with plasma spraying [3], cold or hot isostatic pressing [4] and powder injection moulding (PIM) [5]–[7].

Due to increasing demands, it was found that PIM was the most suitable processing due to its mass production and complexity shaping of parts [8]. Moreover, the injectable of HA depends on the selection of binder systems, in which several studies have reported the used of high density polyethylene (HDPE), polyetheretherketone (PEEK), poly methyl methacrylate (PMMA), poly (L-lactide) (PLLA), palm stearin (PS), stearic acid (SA), paraffin wax (PW), EVA and collagen [5]–[7]. Khor et. al [9] reported that the use of HA polymer matrix (HA/HDPE) with 40% volume HA achieved a good dispersion through extensive equipment such twin screw extruder and centrifugal milling machine. Meanwhile, the HA/PLLA composite provides sufficient mechanical support during the healing period. However, such composite is not resistant under high loading condition. In addition, it is reported that HA/PMMA composite shows poor mechanical properties of structure [10], which is due to the interfacial adhesion between the HA particles and the polymer matrix [5]. Other than that, the situation is also believed to take place because of higher absorption of HA than metal during the mixing process.

Many studies have reported on the selection and function of binders in PIM. Karatas et al. [11], reported that rheological properties and behaviours of PE, PW and SA as a binder formulation system mixed showed a good feedstock behaviour with 50 vol% of steatite powder. Furthermore, Meng et al. [12], found that the feedstocks of 50 to 56vol% sub micron Al_2O_3 powder with a formulated binder system of LDPE, EVA, PW, and SA exhibited a pseudo-plastic behaviour in a temperature range of 130^{o}C to 160^{o}C. Foudzi et. al [13] has reported that the dilatant flow behaviour whose viscosity ranges from 10 to 40 Pa.s was obtained when 50 nm yttria stabilized zirconia (YSZ) powders with palm stearin (PS) and polypropylene (PP) at different powder loadings of 37 to 43vol%. The ability of palm stearin in providing a capillary route for removing the polymer during the debinding stage prior to sintering has been confirmed. In addition, the low cost, wide availability and good properties of palm stearin made it a suitable binder system [13]–[15].

The rheological studies have been conducted on the HA mixed with polymers (HDPE) have shown that the feedstock exhibits pseudoplastic flow at low to moderate shear rates and a second pseudoplastic region at high-shear rates [16]. The calcination and subsequent milling of HA led to an improvement in the rheological properties of HA/binder suspensions. It follows from this dependence that the suspension had rheological properties where it is suitable for injection moulding, even with HA content of up to 60 vol% [7]. The rheological properties of commercialized HA powder with 70 wt% PS and 30 wt% PE binder reported that pseudoplastic was existed and the feedstock can be injected as low as 150°C to 200 °C [17] .

The knowledge of the rheological properties of HA is still at a primary stage, as this material flow property through PIM processing has been less reported. Currently, several research work have been studied in improving a bio-ceramic injection moulding process [18]. The purpose of this study is to analyse the rheological behaviour of HA with a binder system of PS and PE at various volume percentage of powder loadings. The effects of flow behavior index, flow activation energy and mouldability with different powder loadings will be analysed for injection moulding purposes.

Experimental

Characterization of powder and binder

The hydroxyapatite (HA) is manufactured by Sigma, Aldrich. Figure 1 shows the SEM image of HA powder characteristic. The particle size of the non-calcined HA powder in agglomeration flake shape was measured using the Malvern particle size analyser. The distribution on the particle size and density for the HA powder average is 5.3 µm (D_{50}) and 3.3008 g/cm^3, respectively. Table 1 specifies the binder characteristic of PS and PE binder system [6]. The melting and decomposition range temperatures were gathered from DSC and TGA test conducted. The DSC test for binders system is according to ASTM D3418 (Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetric). The tests were carried out to obtain the melting temperatures for binders to determine the mixing temperatures as well as the solvent debinding temperature. The TGA test was conducted according to ASTM E1131 (Standard Test Method for Compositional

Analysis by Thermogravimetry). Such temperature is important to achieve the homogeneity of the feedstock during a mixing process.

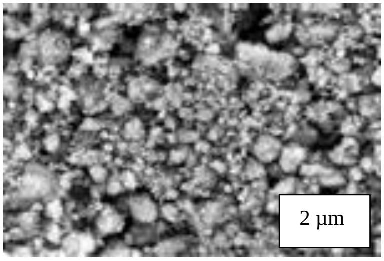

Figure 1: SEM image of HA powder

Table 1: Binder characteristic

Binder Types	**Density (g/cm^3)**	**Melting Point (^OC)**	**Decomposition Range (^OC)**
Palm Stearin	0.891	53.97	296.3 -459.1
Polyethylene	0.91	124.75	406.4-496.3

The preparation of feedstock

The critical powder volume percentage (CPVP) was obtained by using a capillary rheometer based on an ASTM standard D-281-12. It was found that the CPVP of the HA powder is 59 vol% powder loading. Since the optimal powder loading is 2-5 % of the critical power loading, the powder loadings of 54, 55 and 56 vol% were used during this study [19]. In this study, a binder system of PE and PS is used where the volume percentage is 60 vol% PE and 40 vol% PS, relatively [20]. The HA-PS/PE feedstock is prepared using the brabender mixer at temperature, time and speed of 150^{o}C, 2 hrs and constant speed 25 rpm, respectively. Table 3 shows the weight percentage (wt%) distribution at each powder loadings.

Table 3: HA-PS/PE binder systems feedstocks

Feedstock	**Powder Loading (vol%)**	**HA (wt%)**	**PE (wt%)**	**PS (wt%)**
F1	54	81.11	11.33	7.55
F2	55	81.72	10.97	7.31
F3	56	82.32	10.61	7.07

Rheology

A RH Rosand 2000 capillary rheometer was used to measure the viscosity of HA-PS/PE feedstocks. The rheology test was conducted at four temperatures different; 150ºC, 160 ºC, 170 ºC and 180 ºC with a capillary die with the diameter of 1mm and length of 10mm (L/D=10). The units for viscosity and shear rate are Pa.s and 1/s, respectively.

Results and Discussion

Flow Behaviour Index

The flow behaviour of a feedstock is preferably pseudoplastic where the viscosity decreased when the shear rate increased. Such behaviour can be calculated using Equation (1).

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

where η and K is the flow behaviour indexes for viscosity and constant. For a feedstock with pseudoplastic flow, the value of η is less than 1. The correlation between the viscosity and shear rate for each feedstock, F1, F2 and F3 based on Equation (1) is shown in Figure 2. The viscosity decreases at higher shear rate due to the shear thinning that occurs pseudoplastic flow [21]. The range of viscosity and shear rate is 10 to 1200 Pa.s and 50 to 5000 s^{-1}, respectively. Figure 3 shows the flow behaviour index, n at different temperatures; 150 ºC, 160 ºC, 170 ºC and 180 ºC for all the feedstocks (F1, F2 and F3). It is found that the n value is very less than 1 such value, indicating that the viscosity depends on upon shear rate [22]. The n value, 0.16 to 0.24 was consistently with commercialized HA powder reported by Subuki et al. [17]. In addition, it was found that the shear rate varies between 100 to 1000 s^{-1} and the flow is below than 1000 Pa.s which is required during injection moulding processing [11].

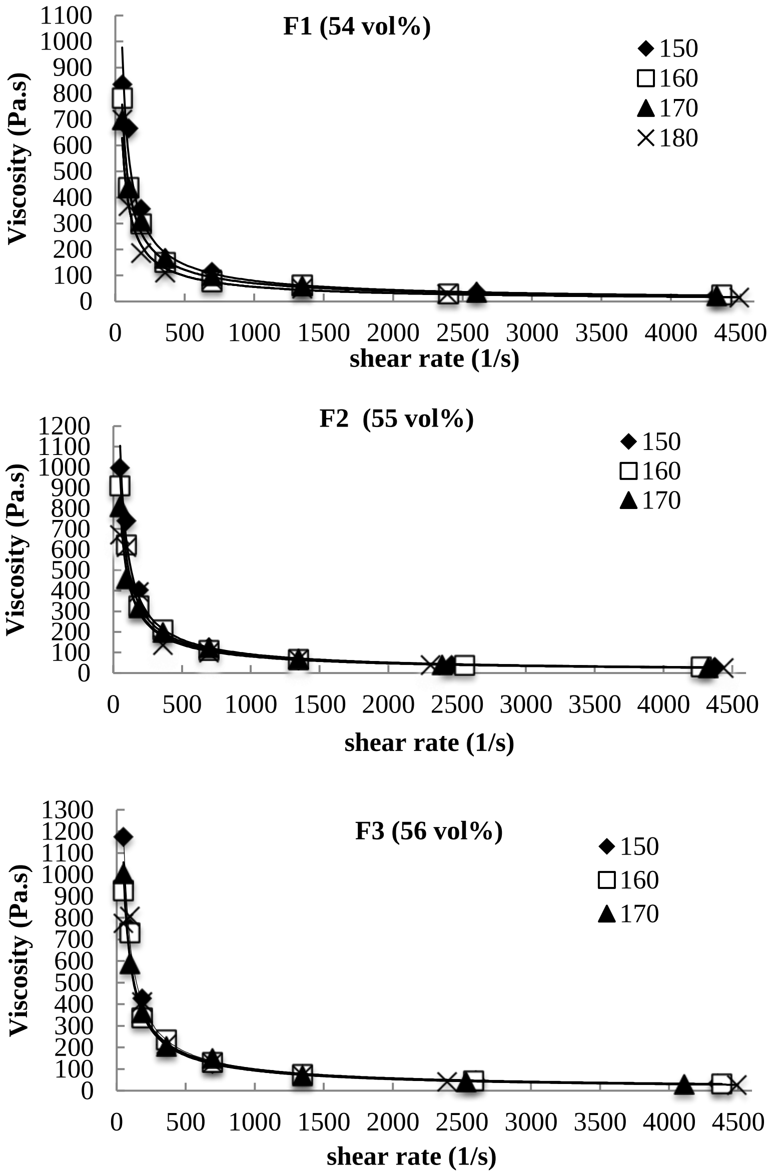

Figure 2: Correlation between viscosity and shear rate for all the feedstocks at different temperatures.

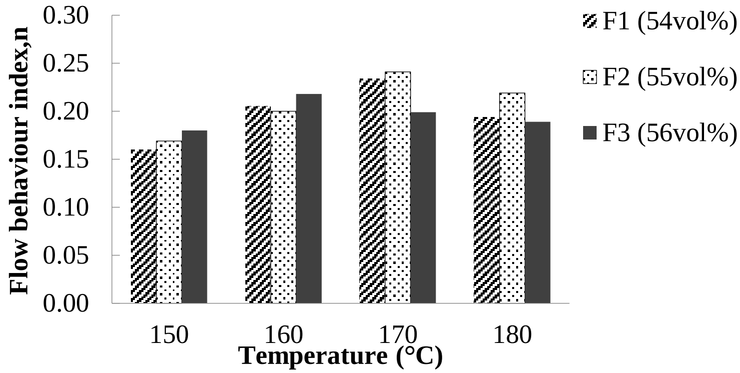

Figure 3: Variation of the flow behaviour index, n for all the feedstock at different temperatures.

Flow Activation Energy

The flow activation energy plays an important role in PIM. It represents the influence of temperature on the viscosity of the feedstock. During the injection process, the flow activation energy of the feedstock is influenced by the temperature and can be determined by the Arrhenius equation as shown by Equation (2) where, η, η_o, E, R, and T represent mixture viscosity, viscosity at reference temperature, flow activation energy, gas constant and temperature in Kelvin, K, respectively.

$$\eta = \eta_o \exp(E/RT) \tag{2}$$

Based on Eq. (2), the shear rates for each feedstock of F1, F2, and F3 are 185.45 s^{-1}, 1000 s^{-1} and 2304 s^{-1}, respectively. Based on all feedstocks, such as shear rates influence the flow activation energy, E (kJ/mol) as shown in Figure 4. It shows that the higher value of shear rate gives lower value to the flow activation energy. Feedstock with low activation energy is a basic requirement for a good processing of PIM. Moreover, the smaller value of E indicates less sensitivity of the feedstock towards the temperature, where the formations of stress concentration, crack, and distortion of the molded part are reduced [13, 22].

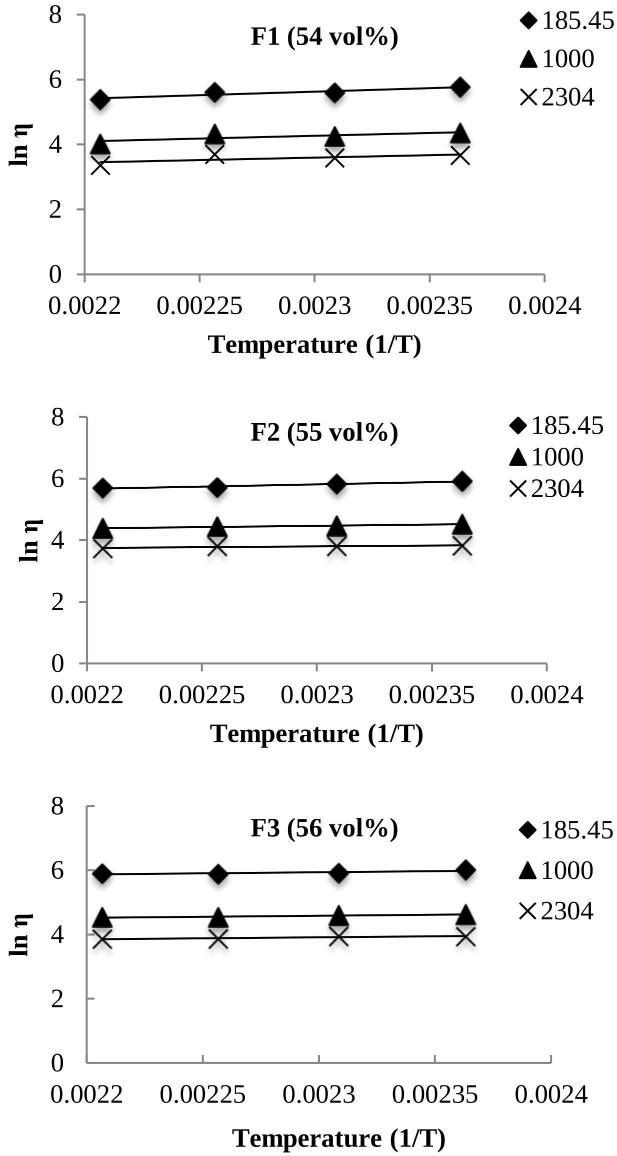

Figure 4: Correlation between the viscosity and temperature for all feedstocks at different shear rates (s^{-1})

Table 4: Flow activation energy, E kJ/mol for all feedstocks at different shear rate (s^{-1})

Shear rate (s^{-1})	**F1 (kJ/mol)**	**F2 (kJ/mol)**	**F3 (kJ/mol)**
185.45	17.97	12.11	5.63
1000	14.35	6.91	5.36
2304	12.56	4.34	5.21

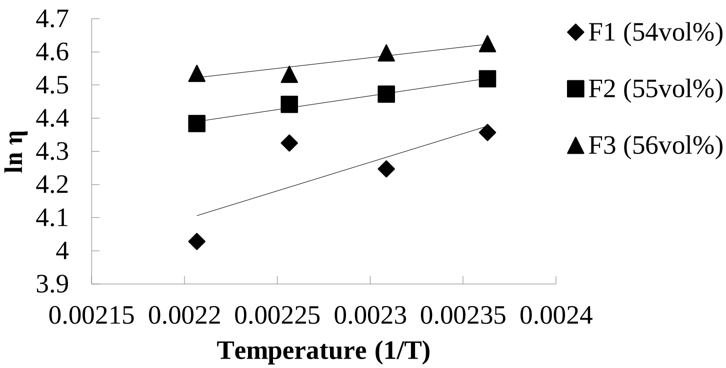

Figure 5: Relation between viscosity and temperature of feedstocks (F1, F2 and F3) at shear rate $1000s^{-1}$

Mouldabiltiy Index

A mouldability index α_{stv}, is one of the rheological criteria that can estimate the flow efficiency of the feedstocks into the mold. The index can be obtained using weir Equation (3) where n, η_o, E and R are flow behaviour index, viscosity at reference temperature, activation energy and gas constant, respectively.

$$\alpha = (10^9 (n))/ \eta_o(E/R) \qquad (3)$$

Figure 6 shows the correlation of mouldability index with the temperature at shear rate 1000 s^{-1}. It shows that the feedstock of 56 vol% (F3) gives bigger value of the mouldability index compared to the other feedstocks (F1 and F2). This finding is consistent with the previous study where the higher value of the mouldability index, (α_{stv}) the better rheological properties of the feedstocks [23]

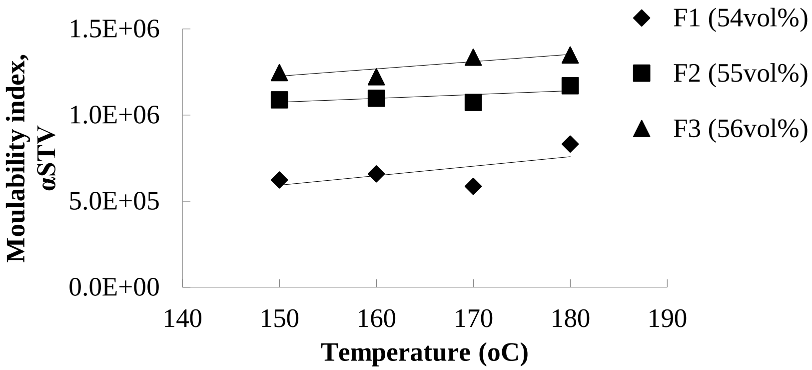

Figure 6: Correlation of mouldability index dependence to temperatures

Conclusion

The rheological properties for all the feedstocks of HA-PE/PS exhibit are suitable for the PIM processing. The flow behaviour index, n range over 0.12-0.2 where $n < 1$ indicates that the pseudoplastic behaviour existed. Furthermore, the flow activation energy, E for F1, F2, and F3 was 14.35, 6.91 and 5.36 kJ/mol at shear rate 1000 s^{-1}, respectively. The F3 at 56 vol% of powder loading would be the best feedstock compared with the others. It has low value of n where the faster the viscosity of feedstock changes with shear rate. The low activation energy, E of F3 is recommended for injection as it would have lower sensitivity of viscosity to the temperature in the range of 150°C to 180°C. The mouldability index shows that F3 is a potential feedstock that can be injected and moulded through the temperature range studied.

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References

[1] A. Ravaglioli, A. Krajewski, V. Biasini, R. Martinetti, C. Mangano, and G. Venini, “Interface between hydroxyapatite and mandibular human bone tissue,” Biomaterials, vol. 13, no. 3, pp. 162–167, 1992.

[2] Z. Xia, X. Yu, X. Jiang, H. D. Brody, D. W. Rowe, and M. Wei,

"Fabrication and characterization of biomimetic collagen-apatite scaffolds with tunable structures for bone tissue engineering," Acta Biomater., vol. 9, no. 7, pp. 7308–7319, 2013.

[3] G. Bolelli, D. Bellucci, V. Cannillo, L. Lusvarghi, A. Sola, N. Stiegler, P. Müller, A. Killinger, R. Gadow, L. Altomare, and L. De Nardo, "Suspension thermal spraying of hydroxyapatite: Microstructure and in vitro behaviour," Mater. Sci. Eng. C, vol. 34, pp. 287–303, 2014.

[4] Y. Yang, K. H. Kim, C. M. Agrawal, and J. L. Ong, "Interaction of hydroxyapatite-titanium at elevated temperature in vacuum environment," Biomaterials, vol. 25, no. 15, pp. 2927–2932, 2004.

[5] M. S. Abu Bakar, P. Chenag, and K. a. Khor, "Mechanical properties of injection molded hydroxyapatite-polyetheretherketone biocomposites," Compos. Sci. Technol., vol. 63, no. 3–4, pp. 421–425, 2003.

[6] 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," Mater. Des., vol. 65, pp. 1028–1034, 2015.

[7] J. Cihlář and M. Trunec, "Injection moulded hydroxyapatite ceramics," Biomaterials, vol. 17, no. 19, pp. 1905–1911, 1996.

[8] I. Doo, J. Min, J. Yu, T. Gon, S. Jo, and S. Jin, "ScienceDirect Particle size effect on the magneto-rheological behavior of powder injection molding feedstock," Mater. Charact., vol. 94, pp. 19–25, 2014.

[9] K. A. K. C.P. Sim, P. Cheang, M.H. Liang, "Injection moulding of hydroxyapatite composites," J. Mater. Process. Technol., vol. 136, pp. 75–78, 1997.

[10] K. Hirota, H. Kurosawa, and H. Tanaka, "Pressure sintering of apatite-collagen composite," Biomed. Mater. Eng., vol. 3, no. 3, pp. 147–151, 1993.

[11] C. Karatas, A. Kocer, H. I. Ünal, and S. Saritas, Rheological properties of feedstocks prepared with steatite powder and polyethylene-based thermoplastic binders, vol. 152, pp. 77–83, 2004.

[12] J. Meng, N. H. Loh, G. Fu, B. Y. Tay, and S. B. Tor, "Micro powder injection moulding of alumina micro-channel part," J. Eur. Ceram. Soc., vol. 31, no. 6, pp. 1049–1056, 2011.

[13] F. Mohd Foudzi, N. Muhamad, A. Bakar Sulong, and H. Zakaria, "Yttria stabilized zirconia formed by micro ceramic injection molding: Rheological properties and debinding effects on the sintered part," Ceram. Int., vol. 39, no. 3, pp. 2665–2674, Apr. 2013.

[14] M. A. Omar, I. Subuki, N. Abdullah, and M. F. Ismail, "The Influence Of Palm Stearin Content On The Rheological Behaviour Of 316L Stainless Steel MIM Compact," J. Sci. Technol., vol. 2, no. 2, pp. 1–14, 2011.

[15] N. H. Mohamad Nor, N. Muhamad, K. R. Jamaludin, S. Ahmad, and M. H. I. Ibrahim, “Characterisation of Titanium Alloy Feedstock for Metal Injection Moulding Using Palm Stearin Binder System,” Adv. Mater. Res., vol. 264–265, pp. 586–591, 2011.

[16] R. Joseph, W. J. McGregor, M. T. Martyn, K. E. Tanner, and P. D. Coates, “Effect of hydroxyapatite morphology/surface area on the rheology and processability of hydroxyapatite filled polyethylene composites,” Biomaterials, vol. 23, no. 21, pp. 4295–4302, 2002.

[17] I. Subuki, N. H. M. Ali., M. H. Ismail, Rheological Properties of Hydroxyapatite synthesized clamshell mix with palm stearin binder system, Advanced Material Research, vol. 911, pp. 366-370, 2014

[18] M. Maas, U. Hess, and K. Rezwan, “The contribution of rheology for designing hydroxyapatite biomaterials,” Curr. Opin. Colloid Interface Sci., vol. 19, no. 6, pp. 585–593, 2014.

[19] R. German, A. Bose, Injection molding of metals and ceramics, Metal Powder Industries Federation, 1997

[20] Iriany. Rheology Properties Study on The Feedstock Contains Palm Stearin for Metal Injection Molding, Doctor of Philosophy Thesis, National University of Malaysia, 2002.

[21] I. Agote, A. Odriozola, M. Gutierrez, A. Santamarıa, J. Quintanilla, Coupelle, and J. Soares , "Rheological study of waste porcelain feedstocks for injection moulding", Journal of the European Ceramic Society, 21(16), pp.2843-2853, 2001.

[22] S. Y. M. Amin, N. Muhamad, K. R. Jamaludin, S. Abdullah, B. Pahat, Rheological Investigation Of Mim Feedstocks Prepared With different particle sizes, pp. 5–9, 2007.

[23] Park, S.J., Wu, Y., Heaney, D.F., Zou, X., Gai, G. and German, R.M., 2009. Rheological and thermal debinding behaviors in titanium powder injection molding. Metallurgical and Materials Transactions A, 40(1), pp.215-222.