© Universiti Tun Hussein Onn Malaysia Publisher's Office

IJIE

http://penerbit.uthm.edu.my/ojs/index.php/ijie
ISSN : 2229-838X e-ISSN : 2600-7916

The International Journal of Integrated Engineering

Rheological Analysis of Zirconia-Hydroxyapatite with Bi-Modal System of Binders; Low-Density Polyethylene and Palm Stearin

Muhammad Mohamed Amin[1], Nur Syamimi Zainal Adelin[1], Abu Bakar Sulong[1], Norhamidi Muhamad[1*]

[1]Department of Mechanical and Manufacturing Engineering, Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, MALAYSIA

*Corresponding Author

DOI: https://doi.org/10.30880/ijie.2023.15.05.019
Received 01 August 2023; Accepted 15 August 2023; Available online 19 October 2023

Abstract: The two component micro-powder injection molding (2C-µPIM) process has evolved from µPIM process because of the increasing demand for multi-functional micro-components applications. In this research work, the selected materials to fabricate micro-sized bi-material parts are zirconia (ZrO2) and hydroxyapatite (HA). ZrO2 is chosen for structural integrity and bio-inert, while HA is mainly chosen for bio-active properties. The reason of employing the multi-component binders is to ensure the flowability of the feedstock. Feedstock rheological characteristics needs to be carefully investigated to avoid any undesirable and inhomogeneous mixture between powder and binder. A common binder system which is comprised of palm stearin and low-density polyethylene (LDPE) were mixed with individual ZrO2 and HA powder particles to prepare for ZrO2 and HA feedstocks. Typically, the feedstocks were obtained ZrO2 and HA powders independently with a binder ratio of 60 wt.% of palm stearin and 40wt.% low-density polyethylene (LDPE). The mixing was carried out in Brabender mixer. Before mixing, critical powder volume percentage (CPVP) analysis was carried out to determine the optimal powder loadings required to prepare the ZrO2 and HA feedstocks. In this research work, the obtained CPVP of ZrO2 and HA powders were 47.0 and 59.0 vol.%, respectively. Based on CPVP analysis, six feedstocks with optimal powder loadings of 43, 44 and 45 vol.% for ZrO2 and 54, 55 and 56 vol.% for HA were prepared. The rheological analysis involving viscosity, shear rate, flow behavior index, activation energy and moldability index was investigated using capillary rheometer. Based on the obtained rheology result, it shows that the overall shear rate and viscosity are within the 2C-µPIM process recommended range. All tested composition shows pseudoplastic behavior. The results of the study found that ZrO2 and HA with optimal powder loadings of 55 vol.% and 44 vol.% have good rheological properties compared to feedstocks with other powder loadings. This is because both materials meet the criteria of good rheological properties which are low viscosity, high shear rate, flow behavior index less than one, low activation energy and high moldability index.

Keywords: Zirconia, hydroxyapatite, palm stearin, low density polyethylene, rheology, injection moulding, shear rate, viscosity, pseudoplastic behaviour

1. Introduction

The powder injection moulding process consists of four major stages which are mixing, injection moulding, debinding and sintering [1]. The two-component micro-powder injection moulding (2C-µPIM) process has evolved from the standard powder injection moulding (PIM) process in large part due to the worldwide trend concerning to the reduction size of the products and the necessity requirements or guidelines to incorporate various functional capabilities

**Corresponding author: norhamidi@ukm.edu.my*

within one micro-component [2], [3]. Two incompatible materials can be bonded utilizing the 2C-μPIM excellent manufacturing technology, providing a smooth gradient interface using an identical injection moulding machine, thanks to the considerable material consumption and low production costs [4], [5]. For 2C-μPIM, green dual-material micro-parts are often produced using a sequential method that involves giving each type of feedstock as granules to the same machine of injection moulding [6]. After the injection moulding procedure, the green part is removed from the mould cavity during the demolding procedure. In order to remove the binders from the green dual-material micro part, solvent and thermal debinding methods are applied [7]. Finally, the debound part is then undergo the sintering process to create the desired physical and mechanical characteristics [8].

The mechanical characteristic of the finished part is significantly affected by the binder system, which is why the binder system is so crucial to the powder injection moulding process [9], [10]. Therefore, it is essential to select the proper binders. Optimal flow behavior, positive interaction with powder, superior binder extraction properties, non-toxicity, and affordability are all essential characteristics of good binders [11], [12]. The primary and secondary binders that were utilized as the system for binders in this study were palm stearin and low-density polyethylene (LDPE), respectively. Palm stearin was chosen for this research due to its dual role, since it serves as both a and a lubricant at the same time [13]. The usage of palm stearin binders in the research area of powder injection moulding is also supported by the literature; [14], [15]. Binder removal is a delicate procedure; if this sensitive procedure are not performed carefully, a high probability of the formation of cracks or defects will develop as the process is going on [16], [17].

The materials chosen for this study are zirconia (ZrO2) and hydroxyapatite (HA). In a few engineering disciplines and sectors, the joining of ceramics is regarded as an excellent solution. This is because ceramics exhibit durable mechanical and thermal capabilities at high temperatures in addition to having strong resistance to corrosion and wear [18]. The initial step in implementing the 2C-μPIM process into practice is combining the two powders separately with palm stearin and LDPE to create feedstocks that are homogenous. Next, rheological analysis is done on the feedstocks. This is crucial for producing successful injection-molded components [19]. The objective of this study are to perform a rheological analysis of the feedstocks for ZrO2 and HA in order to successfully complete the micro powder injection moulding process and create dual-material green parts of ZrO2 and HA [20]. The rheological analysis involving of viscosity, shear rate, flow behavior index, activation energy and moldability index was analyzed to determine the best powder loading of individual ZrO2 and HA.

2. Experimental

2.1 Materials

The materials used in this research were Zirconia (ZrO2) and Hydroxyapatite (HA). ZrO2 powder was obtained from Inframat Advanced Materials LLC in Manchester, Connecticut, USA while HA were obtained from Sigma Aldrich in St. Louis, Missouri, USA. The XRD analysis for powders were accomplished utilizing diffractometer with a radiation of over a 2-theta range from 10-90 degrees. The binder system used for this experiment was low-density polyethylene (LDPE) and palm stearin. 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 Calorimetry). The tests were conducted 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). For both tests, 10 °C/min were used as the heating rate.

2.2 Optimal Powder Loading

During the experiment process, an oil absorption technique are used to determine the critical powder volume percentage (CPVP) value for both ZrO2 and HA materials with the following formulation of feedstock denoted as formulae (1) [21].

$$CPVC(\%) = \frac{Volume\ of\ powder}{Volume\ of\ powder + Volume\ of\ oil} x100 \qquad (1)$$

The powder loadings of 2, 3 and 4 vol.% less than the CPVP were individually mixed with the binders at the ratio of 60 wt.% ppalm stearin and 40 wt.% LDPE in a roller blade-type W50 EHT Brabender mixer (Brabender GmBH & Co. KG, Kulturstrasse, Duisburg, Germany) at a mixing temperature of 150 °C and at a speed of 25 rpm until the mixture becomes homogenous. Both ZrO2 and HA produced dough-like mixture. The homogenous mixture was crushed by a crusher tool before moving on to the rheological analysis.

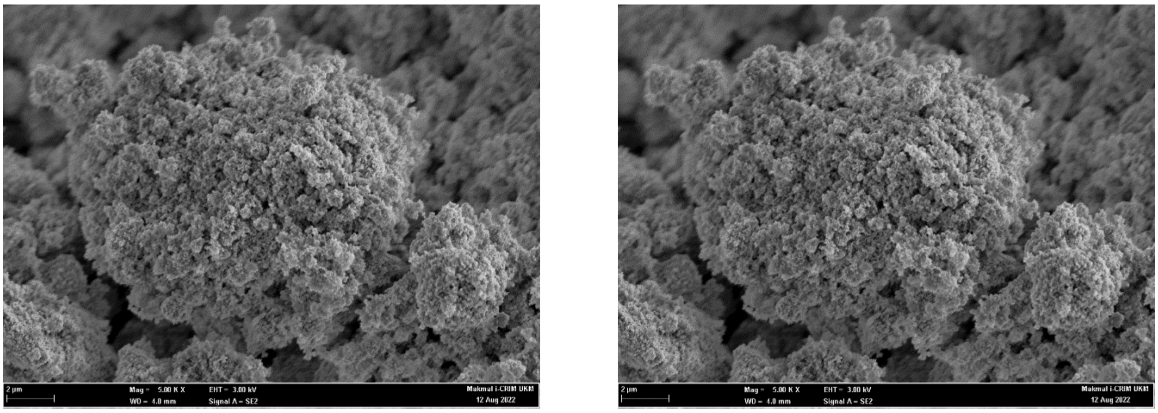
2.3 Rheological Analysis

The rheological behaviors of ZrO2 and HA feedstocks with different powder loadings was analyzed by using a capillary rheometer from Universiti Kebangsaan Malaysia. The machine used in the laboratory were Shimadzu CFT-500D from Shimadzu Corporation, Nakagyo-ku, Kyoto, Japan with a diameter of 1 mm and 10 mm long die. The temperatures used for both material were 140, 160, and 180 ◦C for ZrO2 meanwhile 150, 165, and 180 ◦C were used for HA, were implemented by the rheometer, and the Bagley correction was executed automatically by the capillary rheometer [22]. The viscosity against shear rate graph was obtained for each temperature from the rheometer and subsequently flow behavior index, activation energy and moldability index has been achieved.

3. Results and Discussion

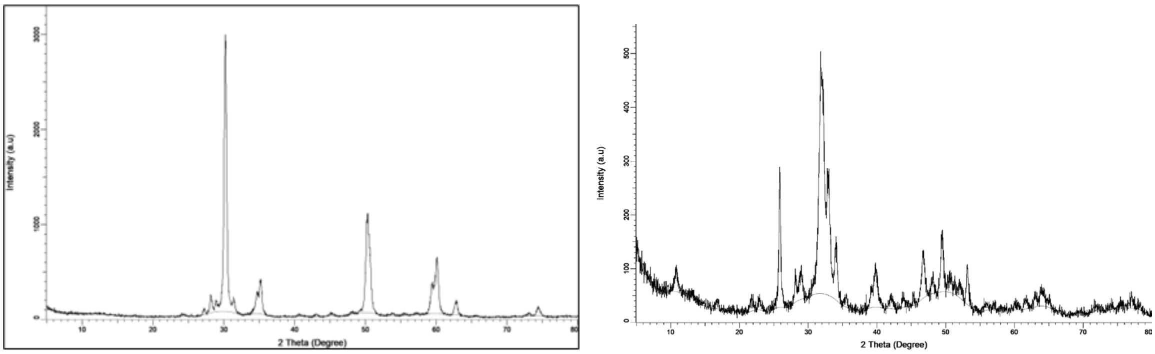
3.1 Raw Materials Characterization

Figure 1(a) and 1(b) shows the materials used in this research which are Zirconia (ZrO2) and Hydroxyapatite (HA) where both have irregular shape particles. The average particle sizes of ZrO2 and HA were 172.4 nm and 5.31 µm, respectively. The pycnometer densities were obtained using a helium gas pycnometer, and the results were 5.6387 g/cm^3 for ZrO2 and 3.3008 g/cm^3 for HA. The XRD analysis for powders were performed using diffractometer with radiation over a 2-theta range from 10-90 degrees as shown in Figure 2. The binder system designed for this experiment consisted of palm stearin and low-density polyethylene (LDPE). In order to improve the rheological properties and wettability, palm stearin are used in this research as the primary binder meanwhile LDPE are used to retain the shape of the component where it act as a backbone polymer after injection molding and debinding [23]. The DSC and TGA test for binders' system was carried out to obtain the melting temperatures for binders to determine the mixing temperatures as well as the solvent debinding temperature. A heating rate of 10 °C/min was used in both tests. Low density polyethylene and palm stearin melting temperatures were 109.2°C and 49.8°C as shown in Figure 3. The decomposition range temperatures were 397.8°C to 501.4 °C. and 355.8°C to 465.9 °C respectively, which can be shown in Figure 4. Table 1 below shows the properties of the binder components.



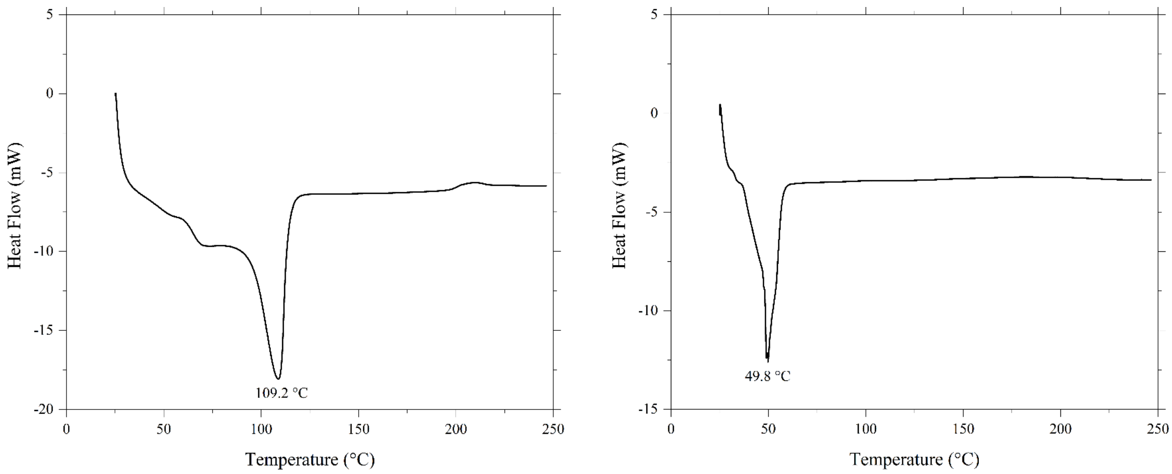
(a) (b)

Fig. 1 - Field Emission Scanning Electron Microscopy (FESEM) micrograph of (a) ZrO2; (b) HA powders



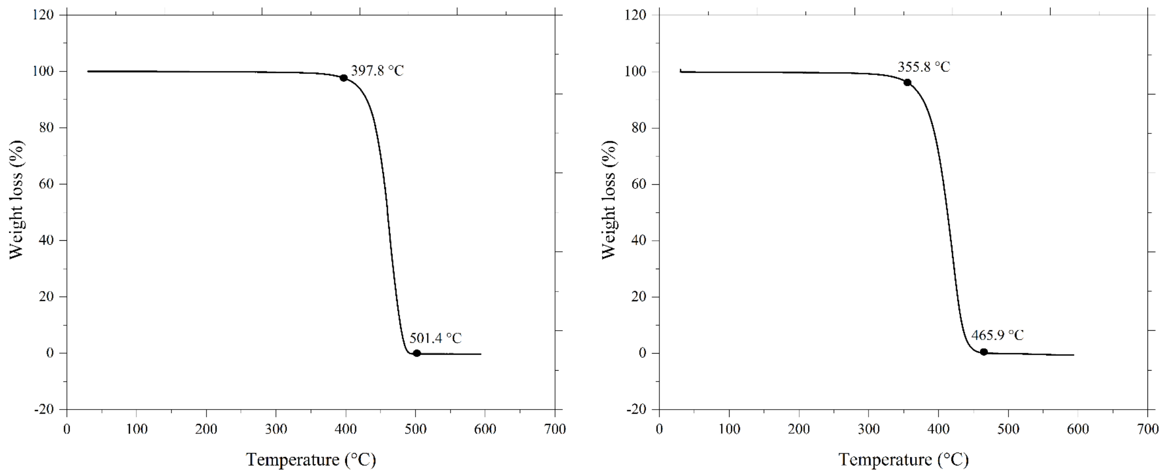
(a) (b)

Fig. 2 - X-Ray Diffraction Analysis (XRD) of (a) ZrO2; (b) HA powders



(a) **(b)**

Fig. 3 - Differential Scanning Calorimetry (DSC) of (a) LDPE and; (b) palm stearin binders



(a) **(b)**

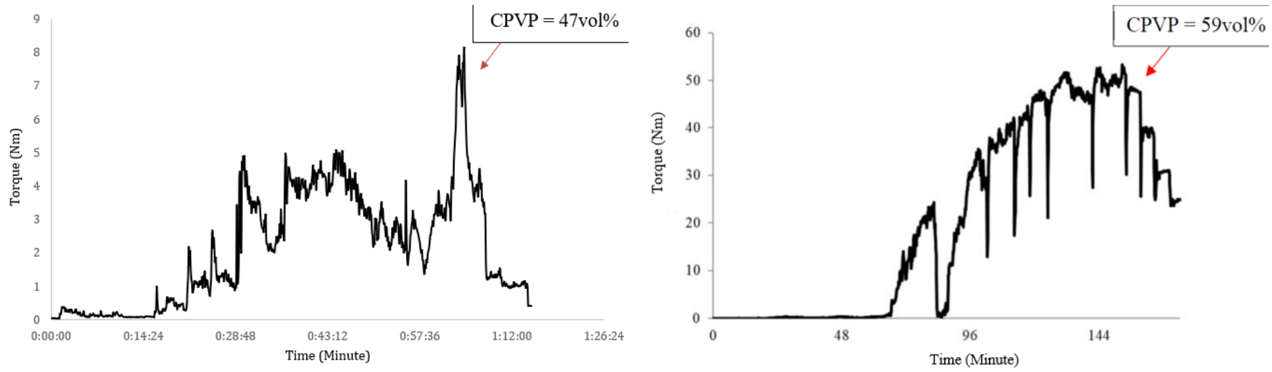
Fig. 4 - Thermogravimetric Analyzer (TGA) of (a) LDPE and; (b) palm stearin binders

Table 1 - Characterization of LDPE and palm stearin binders

Binders	Chemical Formula	Density (g/cm^3)	Melting Point (°C)	Decomposition temperature (°C)	Content (wt.%)
LDPE	$(C_2H_4)_n$	0.91	109.2	397.8-501.4	40
Palm Stearin	$CH_3(CH_2)_{14}COOH$	0.891	49.8	355.8-465.9	60

3.2 Optimal Powder Loading

The critical powder volume percentage (CPVP) is what mostly determines the range of optimal powder loadings. The CPVP of ZrO2 and HA were obtained when individual ZrO2 and HA was gradually put inside the brabender mixture with subsequent adding of oil in intervals of 3 minutes, until the mixture reached a maximum torque. Figure 5 (a) and (b) shows that every time oil is added, the torque increases. Eventually the maximum torque is reached whereby the oil concentration at the maximum torque is used to calculate the CPVP of individual ZrO2 and HA. When adding oil to the combination of ZrO2 and HA, it will increase the dilatation of the solid structure and improving the interparticle distance [24].



(a) (b)

Fig. 5 - Evaluation of torque as a function of time for (a) ZrO2 and; (b) HA powders

The CPVP of ZrO2 and HA powders were 47 vol.% and 59 vol.%, respectively. A few circumstances may differentiate CPVP value. These are the differences in size of particles, how the materials were handled and technique of measurement. Usually, 2 to 5 vol.% fewer than the CPVP value is deemed as the optimal powder loading [11]. Based on this, the chosen powder loadings for ZrO2 were 43 vol.%, 44 vol.% and 45 vol.%. 54 vol.%, 55 vol.% and 56 vol.% powder loadings were selected for HA. The ZrO2 and HA powder loadings were separately mixed with the LDPE and palm stearin binders at a percentage of 60 wt.% palm stearin and 40 wt.% LDPE in the Brabender mixer at a mixing temperature of 150 °C and at a speed of 25 rpm until the mixture becomes homogenous. All ZrO2 and HA feedstocks were homogenous. The homogenous feedstocks were crushed by a crusher tool before moving on to the rheological analysis.

3.3 Rheological Analysis

3.3.1 Relationship Between Shear Rate and Viscosity

Rheological analysis of the feedstock is an important method to determine the flowability of the feedstock that will flow into the mold cavity throughout the 2C-μPIM process [25]. Feedstocks that have pseudoplastic properties are suitable for use in the PIM process [1]. In this study, the rheological property test was carried out according to the viscosity profile of the feedstock based on viscosity against shear rate. For ZrO2 feedstocks with a powder loading of 43, 44 and 45 vol.%, the rheological properties test for the relationship between viscosity and shear rate was conducted at three various temperatures, namely 140, 160 and 180°C while for HA feedstock it was conducted at 140, 165 and 180°C. Feedstocks that have a high viscosity and shear rate can cause the separation of powders and binders during the injection process [22].

Figure 6 (a), (b) and (c) and Figure 7 (a), (b) and (c) show the relationship between the viscosity (η) and the resulting shear rate (s^{-1}) for feedstocks with different powder loadings. During the flow process in the fluid state, pseudoplastic feedstock occurs due to the presence of shear thinning. For ZrO2 feedstock with powder loading of 43, 44 and 45 vol.%, the correlation between viscosity and shear rate at three different temperatures (140, 160, and 180 °C) is shown in Figure 6 (a), (b) and (c). Based on the figure, the viscosity of the feedstock decreases when the shear rate increases. This condition is called pseudoplastic behaviour or shear thinning. Therefore, this pseudoplastic property can be detected for ZrO2 feedstock. The results of this study contradict previous studies conducted by [26], who stated that during rheological analysis, nano-sized ZrO2 feedstock with powder loading ranging from 37 to 43 vol.% showed shear thickening or dilatant flow. Separation of powders and binders is aided by dilatant properties, where viscosity increases as the shear rate increases. According to [27], the powder injection molding process can be carried out when the shear rate is in the range of 100 s^{-1} to 10000 s^{-1} and the viscosity is below 1000 Pa.s. Based on Figure 6 (a), (b) and (c), although the viscosity decreases as the temperature increases, the range of viscosity for the ZrO2 45 vol.% feedstock at temperatures of 140, 160 and 180°C is very high compared to the ZrO2 43 vol.% and 44 vol.%.

For HA feedstock, the studied rheological properties were shown in Figure 7 (a), (b) and (c). Similar to the ZrO2 feedstock based on Figure 6, pseudoplastic properties can also be observed for the HA feedstock with powder loadings of 54, 55 and 56 vol.% when the applied temperature increases from 150, 165 to 180°C. When the temperature was at 180°C all of the three feedstocks for viscosity were decreased ranging from 200 to 800 Pa.s. Apart from temperature, powder loading percentage can also affect feed viscosity. The results of the study that has been conducted have the same results as the results of the study that has been conducted by [28] stating that, when the temperature increase and the volume of powder loading decrease, the viscosity for the feedstock will be lower.

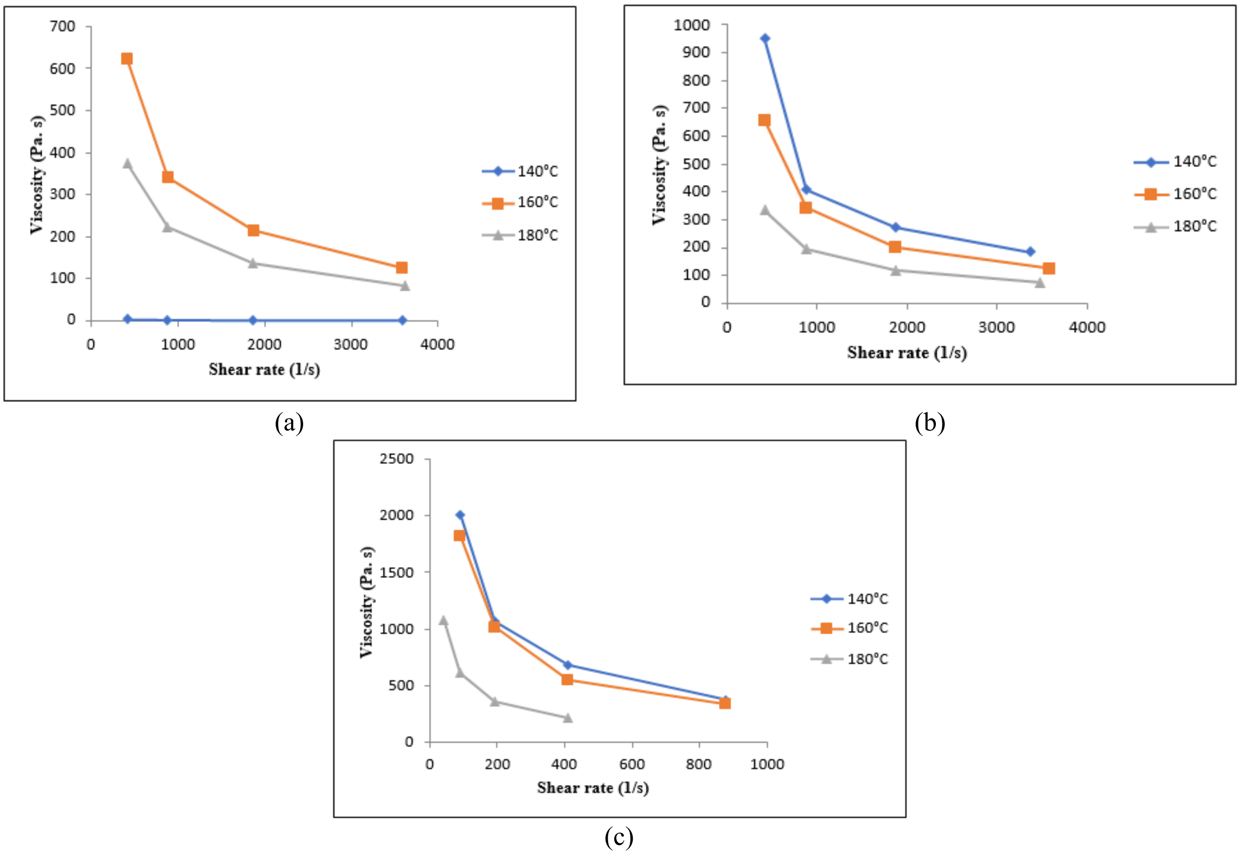


Fig. 6 - Graph of viscosity in relation to shear rate of ZrO2 (a) 43; (b) 44 and; (c) 45 vol.%

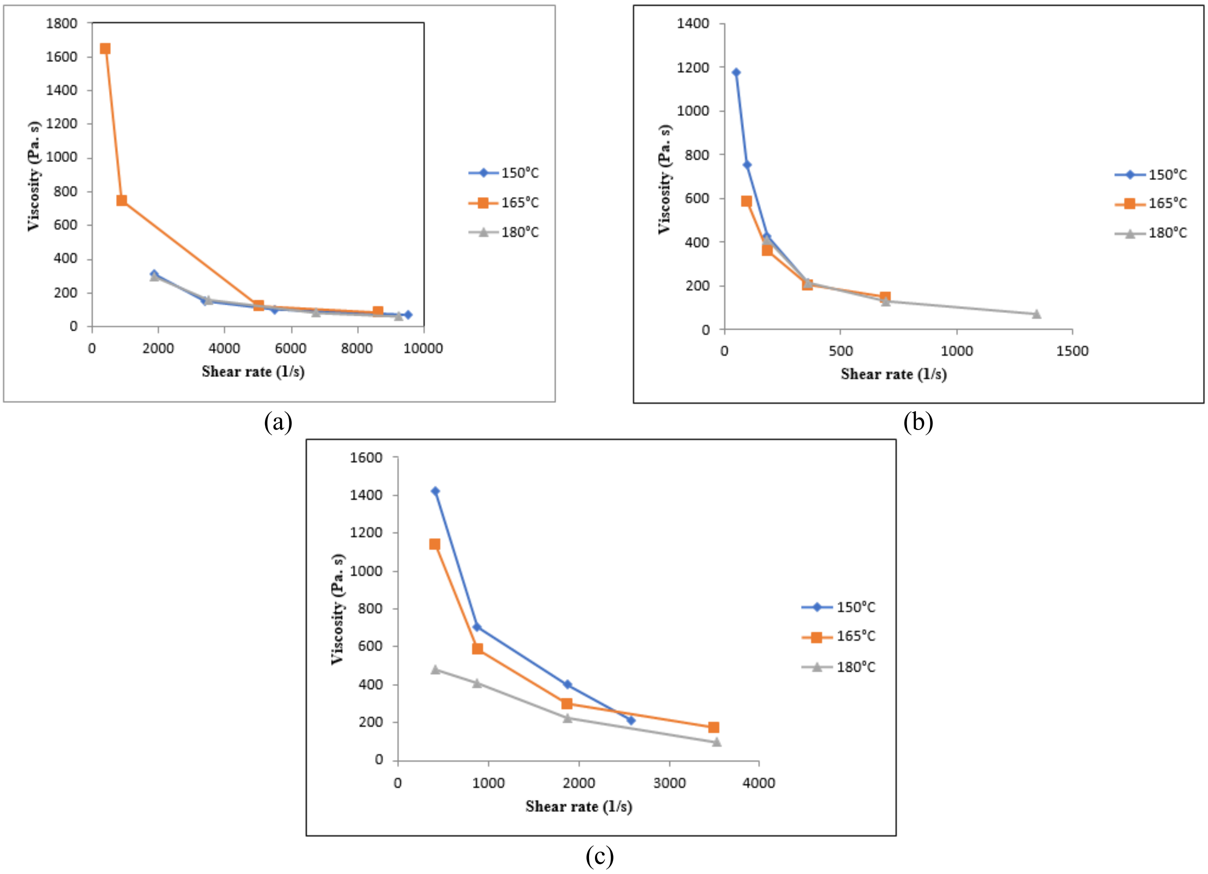


Fig. 7 - Graph of viscosity in relation to shear rate of HA (a) 54; (b) 55 and; (c) 56 vol.%

3.3.2 Flow Behaviour Index, n

In this study, to study the properties of ZrO2 and HA feedstocks, an analysis of the flow behavior index, n, needs to be carried out. Generally, values of n less than 1 indicate pseudoplastic properties of the feedstock. Table 2 shows flow behavior index values, n at varying temperatures for ZrO2 and HA feedstocks. Based on Table 2, the average value of n for ZrO2 feedstock at powder loading of 43, 44 and 45 vol.% is between 0.01-0.27, 0.24-0.30 and 0.15-0.40. While for HA feedstock the average value for powder loading of 54, 55 and 56 vol.% is -0.01-0.27, 0.17-0.25 and 0.14-0.43. According to [29], shear thickening occurs when a high value of n will cause separation between the powder and the binder. Therefore, the range of n for both feedstocks provides an indication of the capabilities of the injection moulding process.

Table 2 - Values of flow behaviour index, n for ZrO2 and HA feedstocks at varying temperatures

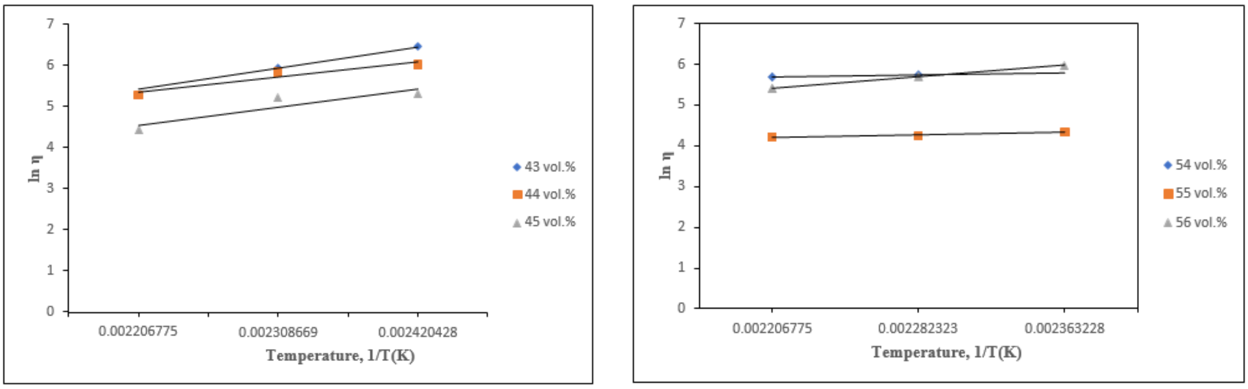
Feedstocks	Powder Loadings (vol.%)	Temperature (°C)	Flow Behavior Index (n)
ZrO2	43	140	0.01
		160	0.25
		180	0.27
	44	140	0.24
		160	0.24
		180	0.30
	45	140	0.15
		160	0.25
		180	0.40
HA	54	150	0.27
		165	0.01
		180	0.02
	55	150	0.22
		165	0.17
		180	0.25
	56	150	0.14
		165	0.03
		180	0.43

3.3.3 Flow Activation Energy, E

In general, a high flow activation energy, E value indicates a more obvious sensitivity of the viscosity of the feedstock to temperature. This can promote solidification of feedstock during the PIM process according to [1]. [26] stated that a high E value of the feedstock will result in the body breaking or warping during the molding process. A high E value of the feedstock tends to change the viscosity as the temperature decreases according to [30], This makes temperature control important during the injection molding process. Furthermore, uneven flow due to inconsistent mold temperature will cause inter-particle pressure or so-called particle pressure.

Table 3 - Flow activation energy, E for ZrO2 and HA

Feedstocks	Powder Loadings (vol.%)	Flow Activation Energy, E (kJ/mol)
ZrO2	43	37.85
	44	28.36
	45	33.99
HA	54	5.51
	55	7.02
	56	30.47



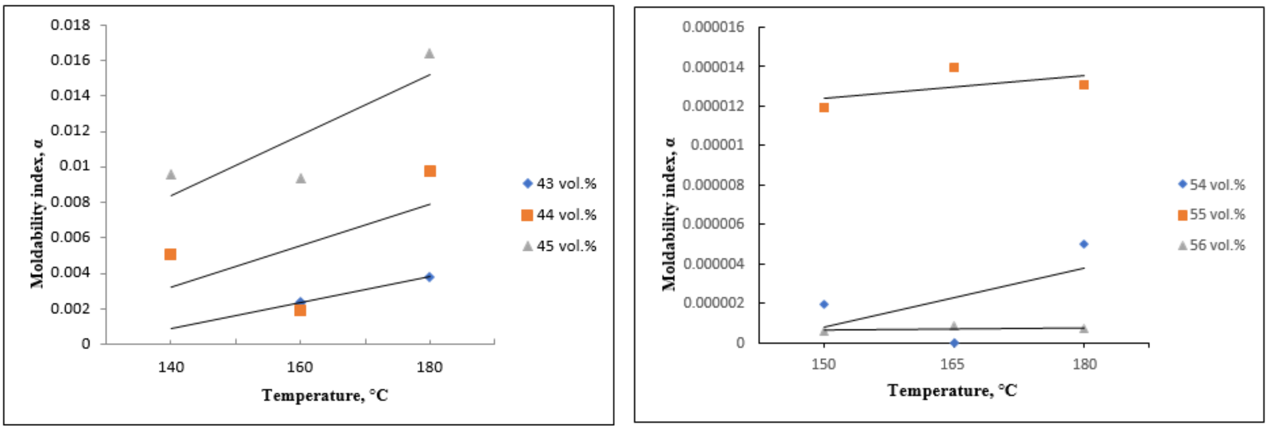
(a) (b)

Fig. 8 - Gradient of ln η vs 1/T of (a) ZrO2 and; (b) HA feedstocks

The temperature dependence of the viscosity of the feedstock plays an important role in analyzing flow properties of the feedstock which were achieved through the calculation of the activation energy, E using the equation of Arrhenius. The value of E is determined from the product between the value of the slope of the plotted graph and the value of R which is the gas constant. According to [20], [31], a low E value will facilitate the feedstock to flow to the mold to reduce defects of the green part. In Figure 8 (a) and (b) shows the graph of the relationship between viscosity and temperature for feedstock ZrO2 and HA. Table 3 shows the value of E for ZrO2 feedstock with a powder loading of 43, 44 and 45 vol.% is 37.51, 28.36 and 33.99 kJ/mol while for HA feedstock with a powder loading of 54, 55 and 56 vol.% produced E values of 5.51, 7.02 and 30.47 kJ/mol. Both feedstocks showed an increase in E value as the powder loading increased.

3.3.4 Moldability Index, α

Moldability index, α is one of the rheological processes that need to be analyzed to predict the effectiveness of the feedstock flow into the mold for the molding process to be carried out. The value of α can be calculated using the moldability index equation introduced by *Weir* where ηo, n, E, and R are constants for viscosity at reference temperature, flow behavior index, activation energy and gas constant [31]. Figure 9 (a) shows the moldability index for ZrO2 feedstock against melting temperatures from 140°C to 180°C. At a ZrO2 powder loading of 45 vol.%, it showed a high impact compared to the feedstock at a powder loading of 44 and 43 vol.%. In Figure 9 (b) it shows the moldability index for HA feedstock against the melting temperature from 150°C to 180°C and at a powder loading of 55 vol.% showing a high impact compared to the feedstock at a powder load of 54 and 56 vol.%. The feedstock has high moldability which were able to load up the mold cavity well and can give a high density value in addition to being able to influence the mechanical and physical characteristics of the sintered part. [32] reported that a high moldability index indicates that the feedstock has good rheological properties.



(a) (b)

Fig. 9 - Moldability index of (a) ZrO2 and; (b) HA feedstocks

4. Conclusion

In this study, the viability of producing bi-material green micro-parts from ZrO2 and HA powder were examined. Firstly, the raw material characterization shows that the mean particle sizes of ZrO2 and HA were 172.4 nm and 5.31 µm, respectively. Both were irregular shape according to FESEM images, the pycnometer densities were 5.6387 g/cm^3 for ZrO2 and 3.3008 g/cm^3 for HA. Furthermore, LDPE and palm stearin melting temperatures were 109.2°C and 49.8°C, respectively. While the decomposition range temperatures for 397.8°C to 501.4 °C for LDPE and 355.8°C to 465.9 °C for HA. The CPVP was 47vol.% for ZrO2 and 58vol.% for HA. The ideal powder loadings—43, 44, and 45 vol.% for ZrO2 and 54, 55, and 56 vol.% for HA—that were chosen based on the CPVP were taken into consideration for rheological measurements. According to the study's findings, all ZrO2 and HA feedstocks synthesized utilizing the ideal powder loadings exhibited pseudoplastic behaviour which means that each feedstock's viscosity decreased as temperature increased. The best rheological properties with respect to low viscosity, high shear thinning, low activation energy and high moldability index were exhibited by the ZrO2 and HA feedstocks with powder loadings of 44 vol.% and 55 vol.%, respectively. Therefore, this optimal powder loading is suitable for use in producing a defect-free 2C-μPIM process.

Acknowledgements

The authors gratefully acknowledge Universiti Kebangsaan Malaysia and the Ministry of Higher Education Malaysia through the Fundamental Research Grant Scheme with grant number FRGS/1/2021/TK0/UKM/01/3 for the financial support.

References

[1] R. M. German and A. Bose, *Injection Molding of Metals and Ceramics*. Metal Powder Industries Federation, 1997. [Online]. Available: https://books.google.com.my/books?id=jXINAAAACAAJ

[2] J. Rajabi, H. Zakaria, N. Muhamad, A. B. Sulong, and A. Fayyaz, "Fabrication of miniature parts using nano-sized powders and an environmentally friendly binder through micro powder injection molding," *Microsyst. Technol.*, vol. 21, no. 5, pp. 1131-1136, 2015, doi: 10.1007/s00542-014-2272-y.

[3] J. M. Torralba, J. Hidalgo, and A. Jiménez-Morales, "Powder injection moulding: Processing of small parts of complex shape," *Int. J. Microstruct. Mater. Prop.*, vol. 8, no. 1-2, pp. 87-96, 2013, doi: 10.1504/IJMMP.2013.052648.

[4] A. Ruh, V. Piotter, K. Plewa, H. J. Ritzhaupt-Kleissl, and J. Hausselt, "Development of Two-Component Micropowder Injection Molding (2C-MicroPIM)-Process Development," *Int. J. Appl. Ceram. Technol.*, vol. 8, no. 3, pp. 610-616, 2011, doi: 10.1111/j.1744-7402.2009.02468.x.

[5] A. Rota, M. Wiegmann, and A. Material, "Getting better bonding at tiny interfaces," no. March, pp. 31-34, 2007, [Online]. Available: https://doi.org/10.1016/S0026-0657(07)70064-4

[6] A. Basir, A. B. Sulong, N. H. Jamadon, and N. Muhamad, "Feedstock properties and debinding mechanism of yttria-stabilized zirconia/ stainless steel 17-4PH micro-components fabricated via two-component micro-powder injection molding process," *Ceram. Int.*, vol. 47, no. 14, pp. 20476-20485, 2021, doi: 10.1016/j.ceramint.2021.04.057.

[7] G. Aggarwal, I. Smid, S. J. Park, and R. M. German, "Development of niobium powder injection molding. Part II: Debinding and sintering," *Int. J. Refract. Met. Hard Mater.*, vol. 25, no. 3, pp. 226-236, 2007, doi: 10.1016/j.ijrmhm.2006.05.005.

[8] S. H. Choi, S. D. Kang, Y. S. Kwon, S. G. Lim, K. K. Cho, and I. S. Ahn, "The effect of sintering conditions on the properties of WC-10wt%Co PIM compacts," *Res. Chem. Intermed.*, vol. 36, no. 6-7, pp. 743-748, 2010, doi: 10.1007/s11164-010-0176-8.

[9] D. Checot-Moinard, C. Rigollet, and P. Lourdin, "Powder injection moulding PIM of feedstock based on hydrosoluble binder and submicronic powder to manufacture parts having micro-details," *Powder Technol.*, vol. 208, no. 2, pp. 472-479, 2011, doi: 10.1016/j.powtec.2010.08.045.

[10] C. F. Escobar and L. A. dos Santos, "New eco-friendly binder based on natural rubber for ceramic injection molding process," *J. Eur. Ceram. Soc.*, vol. 35, no. 13, pp. 3567-3575, 2015, doi: 10.1016/j.jeurceramsoc.2015.06.006.

[11] J. Gonzlez-Gutirrez, G. Beulke, and I. Emri, "Powder Injection Molding of Metal and Ceramic Parts," *Some Crit. Issues Inject. Molding*, 2012, doi: 10.5772/38070.

[12] D. Lin *et al.*, "Rheological and thermal debinding properties of blended elemental Ti-6Al-4V powder injection molding feedstock," *Powder Technol.*, vol. 311, pp. 357-363, 2017, doi: 10.1016/j.powtec.2016.12.071.

[13] A. Basir, A. B. Sulong, N. H. Jamadon, and N. Muhamad, "Bi-material micro-part of stainless steel and zirconia by two-component micro-powder injection molding: Rheological properties and solvent debinding behavior," *Metals (Basel).*, vol. 10, no. 5, 2020, doi: 10.3390/met10050595.

[14] M. I. Ramli, A. B. Sulong, N. Muhamad, A. Muchtar, and M. Y. Zakaria, "Effect of sintering on the microstructure and mechanical properties of alloy titanium-wollastonite composite fabricated by powder injection moulding process," *Ceram. Int.*, vol. 45, no. 9, pp. 11648-11653, 2019, doi: 10.1016/j.ceramint.2019.03.038.

[15] U. B. Emeka, A. B. Sulong, N. Muhamad, Z. Sajuri, and F. Mohd Salleh, "Two Component Injection Moulding of Bi-material of Stainless Steel and Yttria Stabilized Zirconia - Green Part," *J. Kejuruter.*, vol. 29, no. 1, pp. 49-55, 2017, doi: 10.17576/jkukm-2017-29(1)-07.

[16] W. J. Tseng and C. K. Hsu, "Cracking defect and porosity evolution during thermal debinding in ceramic injection moldings," *Ceram. Int.*, vol. 25, no. 5, pp. 461-466, 1999, doi: 10.1016/S0272-8842(98)00061-3.

[17] M. R. Raza, F. Ahmad, M. A. Omar, and R. M. German, "Effects of cooling rate on mechanical properties and corrosion resistance of vacuum sintered powder injection molded 316L stainless steel," *J. Mater. Process. Technol.*, vol. 212, no. 1, pp. 164-170, 2012, doi: 10.1016/j.jmatprotec.2011.08.019.

[18] F. M. Salleh, A. B. Sulong, N. Muhamad, I. F. Mohamed, N. N. Mas'Ood, and B. E. Ukwueze, "Co-Powder Injection Moulding (Co-PIM) Processing of Titanium Alloy (Ti-6Al-4V) and Hydroxyapatite (HA)," *Procedia Eng.*, vol. 184, pp. 334-343, 2017, doi: 10.1016/j.proeng.2017.04.103.

[19] F. M. Salleh *et al.*, "Flow behaviour characterization of Hydroxyapatite for powder injection moulding (PIM)," *J. Mech. Eng.*, vol. SI 3, no. 1, pp. 77-88, 2017.

[20] B. Huang, S. Liang, and X. Qu, "The rheology of metal injection molding," *J. Mater. Process. Technol.*, vol. 137, no. 1-3, pp. 132-137, 2003, doi: 10.1016/S0924-0136(02)01100-7.

[21] A. Fayyaz, N. Muhamad, A. B. Sulong, H. S. Yunn, S. Y. M. Amin, and J. Rajabi, "Micro-powder injection molding of cemented tungsten carbide: Feedstock preparation and properties," *Ceram. Int.*, vol. 41, no. 3, pp. 3605-3612, 2015, doi: 10.1016/j.ceramint.2014.11.022.

[22] G. Thavanayagam, K. L. Pickering, J. E. Swan, and P. Cao, "Analysis of rheological behaviour of titanium feedstocks formulated with a water-soluble binder system for powder injection moulding," *Powder Technol.*, vol. 269, pp. 227-232, 2015, doi: 10.1016/j.powtec.2014.09.020.

[23] C. Quinard, T. Barriere, and J. C. Gelin, "Development and property identification of 316L stainless steel feedstock for PIM and μPIM," *Powder Technol.*, vol. 190, no. 1-2, pp. 123-128, 2009, doi: 10.1016/j.powtec.2008.04.044.

[24] J. J. Reddy, M. Vijayakumar, T. R. R. Mohan, and P. Ramakrishnan, "Loading of Solids in a Liquid Medium: Determination of CBVC by Torque Rheometry," *J. Eur. Ceram. Soc.*, vol. 16, no. 5, pp. 567-574, 1996, doi: 10.1016/0955-2219(95)00165-4.

[25] M. Y. Zakaria, M. I. Ramli, A. B. Sulong, N. Muhamad, and M. H. Ismail, "Application of sodium chloride as space holder for powder injection molding of alloy Titanium-Hydroxyapatite composites," *J. Mater. Res. Technol.*, vol. 12, pp. 478-486, 2021, doi: 10.1016/j.jmrt.2021.02.087.

[26] 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, 2013, doi: 10.1016/j.ceramint.2012.09.033.

[27] C. Karatas, A. Kocer, H. I. Ünal, and S. Saritas, "Rheological properties of feedstocks prepared with steatite powder and polyethylene-based thermoplastic binders," *J. Mater. Process. Technol.*, vol. 152, no. 1, pp. 77-83, 2004, doi: 10.1016/j.jmatprotec.2004.03.009.

[28] A. Arifin, A. B. Sulong, N. Muhamad, J. Syarif, and M. I. Ramli, "Material processing of hydroxyapatite and titanium alloy (HA/Ti) composite as implant materials using powder metallurgy: A review," *Mater. Des.*, vol. 55, pp. 165-175, 2014, doi: 10.1016/j.matdes.2013.09.045.

[29] M. H. Ismail, R. Goodall, H. A. Davies, and I. Todd, "Porous NiTi alloy by metal injection moulding/sintering of elemental powders: Effect of sintering temperature," *Mater. Lett.*, vol. 70, pp. 142-145, 2012, doi: 10.1016/j.matlet.2011.12.008.

[30] I. Agote *et al.*, "Rheological study of waste porcelain mixtures for injection molding," *Bol. la Soc. Esp. Ceram. y Vidr.*, vol. 40, no. 3, pp. 195-200, 2001, doi: 10.3989/cyv.2001.v40.i3.744.

[31] J. P. Choi, J. S. Park, E. J. Hong, W. S. Lee, and J. S. Lee, "Analysis of the rheological behavior of Fe trimodal micro-nano powder feedstock in micro powder injection molding," *Powder Technol.*, vol. 319, pp. 253-260, 2017, doi: 10.1016/j.powtec.2017.06.056.

[32] S. Ahn, S. J. Park, S. Lee, S. V. Atre, and R. M. German, "Effect of powders and binders on material properties and molding parameters in iron and stainless steel powder injection molding process," *Powder Technol.*, vol. 193, no. 2, pp. 162-169, 2009, doi: 10.1016/j.powtec.2009.03.010.