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ORIGINAL ARTICLE

Rheological properties of titanium-hydroxyapatite with powder space holder composite feedstock for powder injection moulding

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Abstract
Metal-ceramic composites such as titanium-hydroxyapatite have been extensively studied as a new generation of implant material in medical application. The powder injection moulding (PIM) process is one the viable processing method in producing the titanium-hydroxyapatite composite which offers extreme geometry part at a lower cost of production. The final powder injection moulding (PIM) product was influenced by the feedstock rheological and thermal properties that related to the binder selection and the critical solids loading. The emphasis of this study was towards the rheological and thermal properties of Ti6Al4V-hydroxyapatite composite feedstock with the powder space holder using a low-density polyethene and palm stearin binder system. The critical solids loading for 90:10 of Ti6Al4V-hydroxyapatite with 20% of the space holder was selected for capillary rheometer tests. The solids loading was obtained at 73 vol.% with optimal solids loading in the range of 2–5% below the critical solids loading which were 68, 69 and 70 vol.%. All feedstocks exhibited shear thinning behaviour, with the shear rate and viscosity values in the range of the PIM feedstock. The work in this study found that the feedstock of 68 vol.% solids loading possessed the best rheological properties with a higher flow behaviour index.

Keywords Titanium Ti6Al4V · Hydroxyapatite · Feedstock · Powder injection moulding · Rheology · Binder system · Space holder

1 Introduction

Powder injection moulding (PIM) has become one of the feasible large-scale processing methods to produce titanium-hydroxyapatite composite as PIM offers a better net-shape product with a high tolerance at an affordable cost [1, 2]. In PIM, metal powders are mixed with a suitable binder usually a polymer, to form a feedstock which will be injected into the mould cavity with the desired shape [3]. The binder is then removed thermally via a debinding process and sintered into the final parts [4]. The selection of a suitable binder is crucial since the binder affects the feedstock homogeneity and the feedstock flow behaviour which influences the final product [5–7]. Moreover, inappropriate processing conditions such as the selection of the binder system might cause defects such as cracks, distortion and warpage in the final product [8, 9]. Therefore, the preparation of the feedstock such as the selection of the powder and binder system, including the powder to binder ratio, is necessary before commencing the mixing process [10]. Indeed, high solids loading of the Ti-HA composite feedstock can be achieved with loading as high as 78.21 vol.% as reported by Ariffin et al., using polyethene and palm stearin as a binder system [11]. Previous studies have also reported the lower solids loading of 60 vol.% using the PAN-250S binder system for the Ti-HA feedstock and PEG, poly(methyl methacrylate) (PMMA) and the stearic acid (SA) binder system for the Ti-HA feedstock with 20% of the space holder [12]. Therefore, the solids loading is within the suggested solids loading for Ti metal injection moulding, which is at 65 vol.% [13].

The feedstock properties are commonly described by the rheological measurement. Feedstocks with low viscosity, low flow behaviour index and low activation energy are also excellent rheological properties for PIM [14, 15]. This, therefore, shows that the binder system consisting of PE and palm stearin have good potential in PIM since the binder can provide

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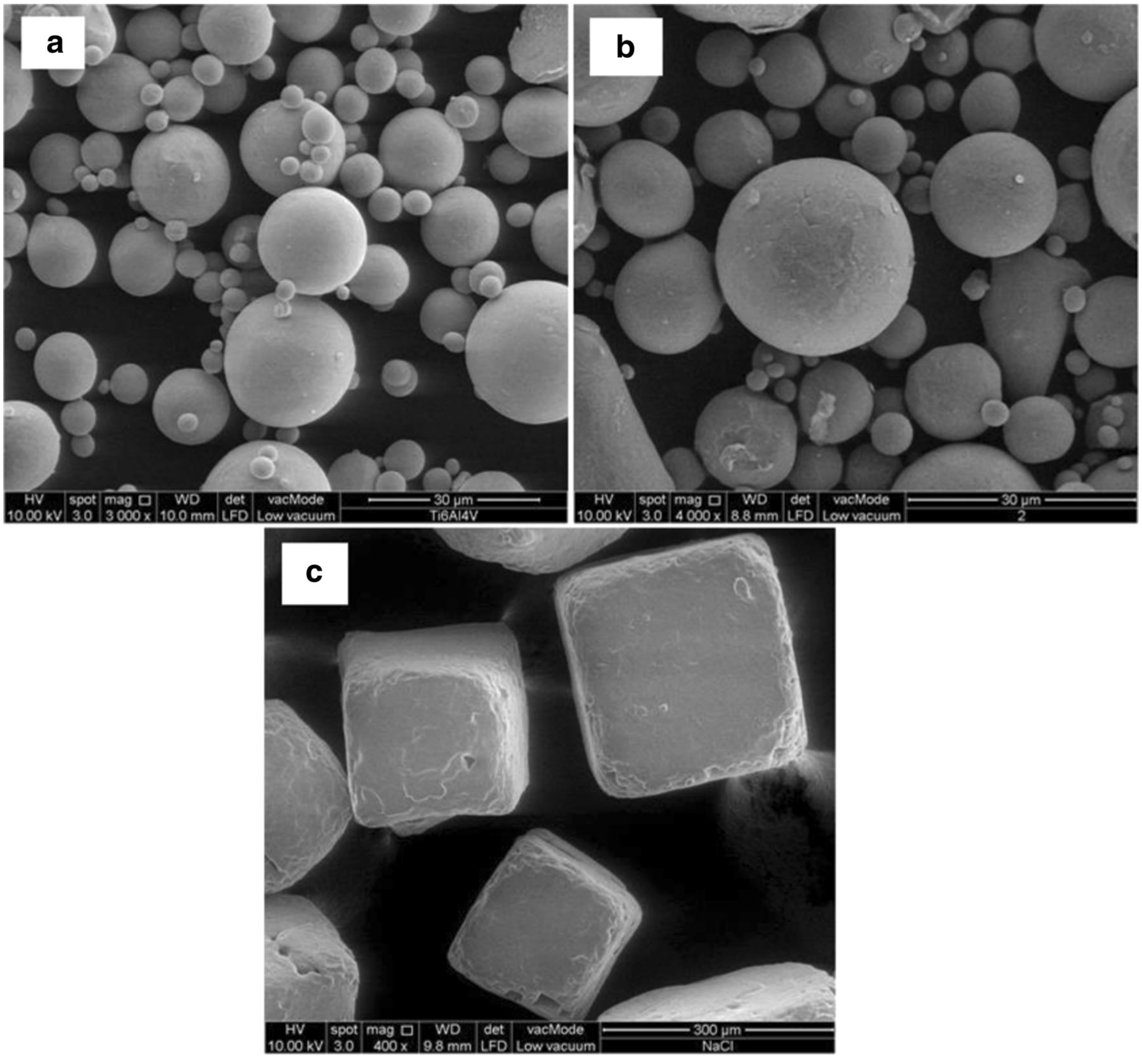

Fig. 1 Powder morphology of **a** Ti6Al4V, **b** hydroxyapatite and **c** NaCl space holder

the desired feedstock properties such as flowability and homogeneity at higher solids loading. However, the research of the binder system consisting of PE and palm stearin for Ti-HA with space holder material is not yet established. The suitable binder system is important with the presence of the space holder material to ensure homogeneous mixing can be produced. Furthermore, the porosity and the mechanical properties of the Ti-HA composite are influenced by a homogeneous mixing process. Thus, this study is focusing on the flowability of the Ti-HA with space holder feedstock using the binder system consisting of low-density polyethene (LDPE) and palm stearin for the powder injection moulding process.

Table 1 Material properties

Material	Density (g/cm^3)	Size (d_{50}) (μm)
Titanium (Ti6Al4V)	4.43	19.61
Hydroxyapatite (HA)	2.43	20
Sodium chloride (NaCl)	2.17	381.39

2 Experimental

2.1 Materials

The feedstock consists of spherical gas-atomised titanium alloy (Ti6Al4V) powder supplied by TLS Technik, Germany. The spherical hydroxyapatite (HA) fine powder was supplied from China, and the sodium chloride (NaCl) was supplied from Sigma-Aldrich, (Fig. 1). Table 1 lists the properties of each powder. Furthermore, the two-component binder system composed of low-density polyethene (LDPE) as the backbone binder was obtained from the Polyolefin Company (Singapore) Pte Ltd., and the palm stearin grade COSMOTHENE® G812 as a surfactant was purchased from Intercontinental Specialty Fats, Malaysia (Fig. 2). Table 2 lists

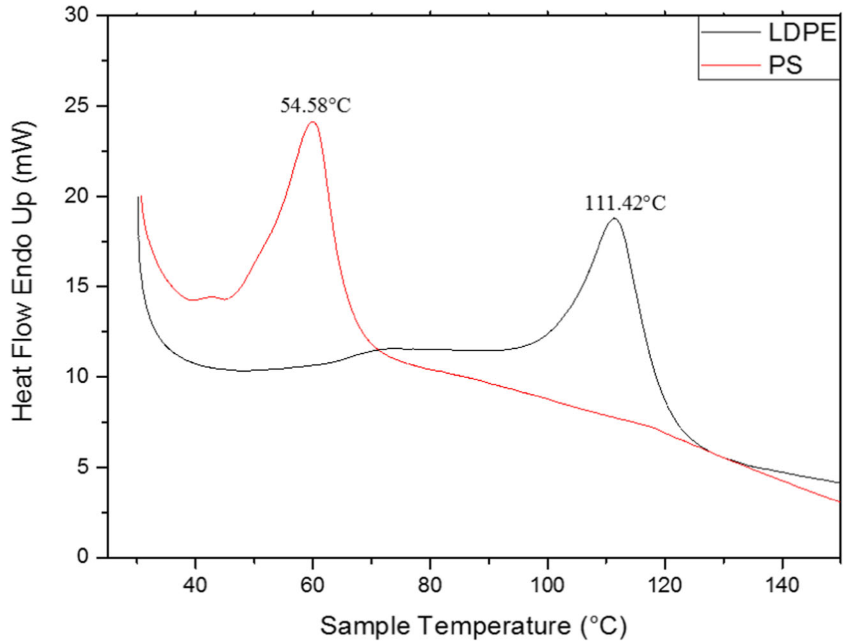

Fig. 2 DSC for LDPE and palm stearin

Table 2 Binder properties

Type of binder	Content (wt.%)	Density (g/cm^3)	Melting temperature (°C)
LDPE	40	0.98	111.42
Palm stearin	60	0.98	54.58

the thermal properties of the binder system obtained from the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) tests.

2.2 Feedstock preparation

Before mixing, the critical solids loading was first determined using the oil absorption method based on ASTM D-281-31 for the ratio of 9:1 of Ti6Al4V and HA at 20% of the NaCl space

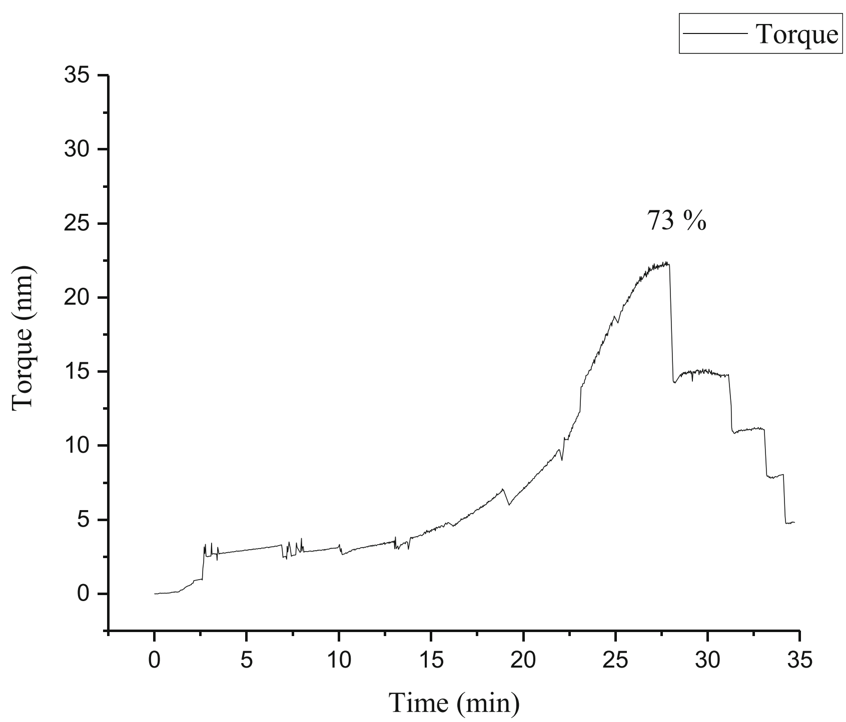

Fig. 3 Torque rheometer

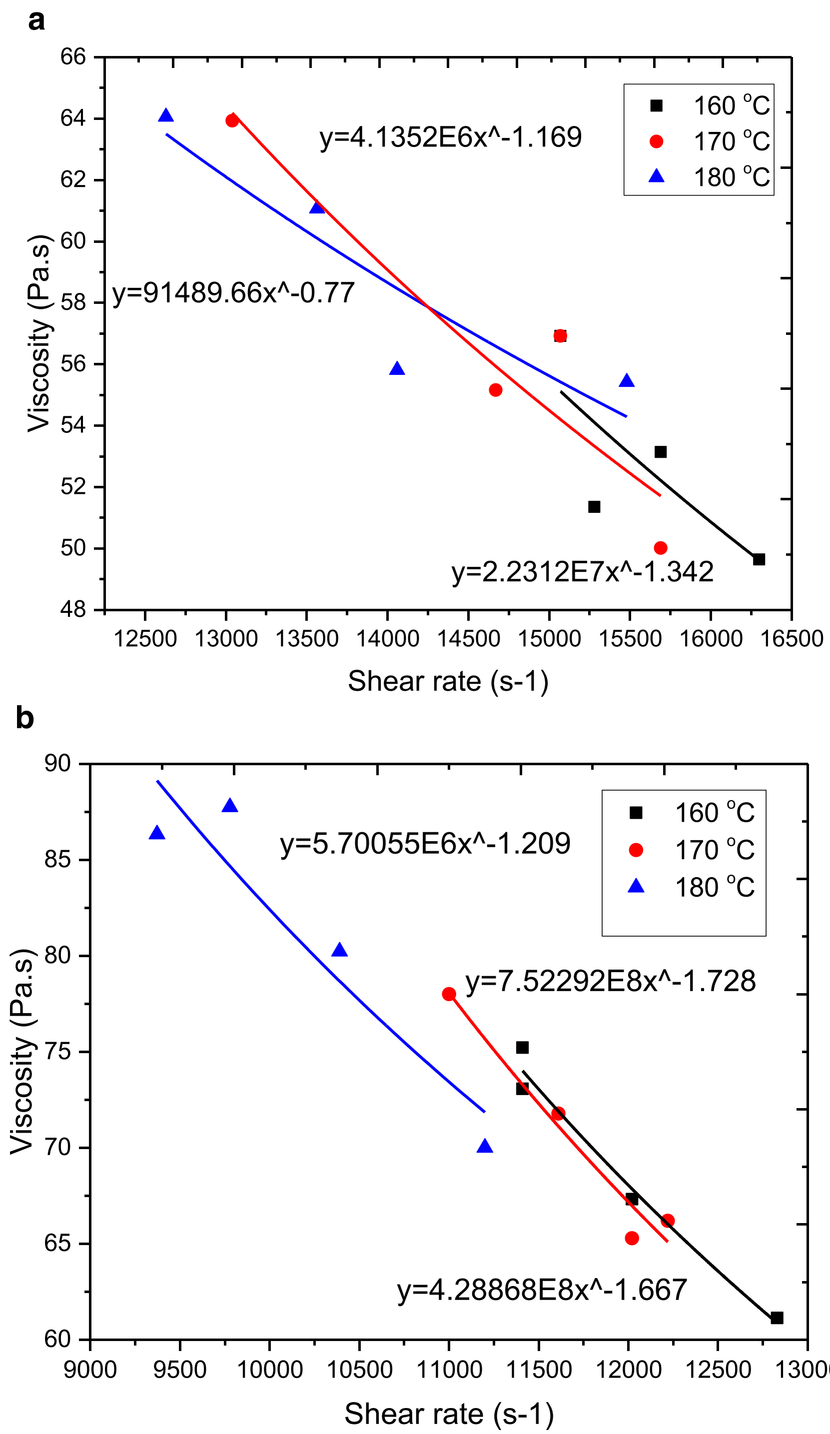

Fig. 4 Viscosity vs. shear rate for **a** 68 vol.%, **b** 69 vol.% and **c** 70 vol.% solids loading

holder. Next, the mixing process was performed at 150 °C, at 40 rpm for 60 min using a Brabender torque rheometry machine with a roller blade setup. Critical solids loading also known as the critical powder volume percentage (CPVP) can be calculated based on the Eq. (1) and the weight percentage for the powder and binder can be calculated using Eq. (2) as follows:

$$\mathrm{CPVP} = \frac{V_\mathrm{f}}{V_\mathrm{f} + V_\mathrm{o}} \times 100 \quad (1)$$

where V_f is the powder volume, and V_o is the oleic acid volume.

$$\mathrm{Weight} = \frac{\rho_\mathrm{p} \times \varphi}{\rho_\mathrm{p}\varphi + \rho_\mathrm{b}(1-\varphi)} \times 100 \quad (2)$$

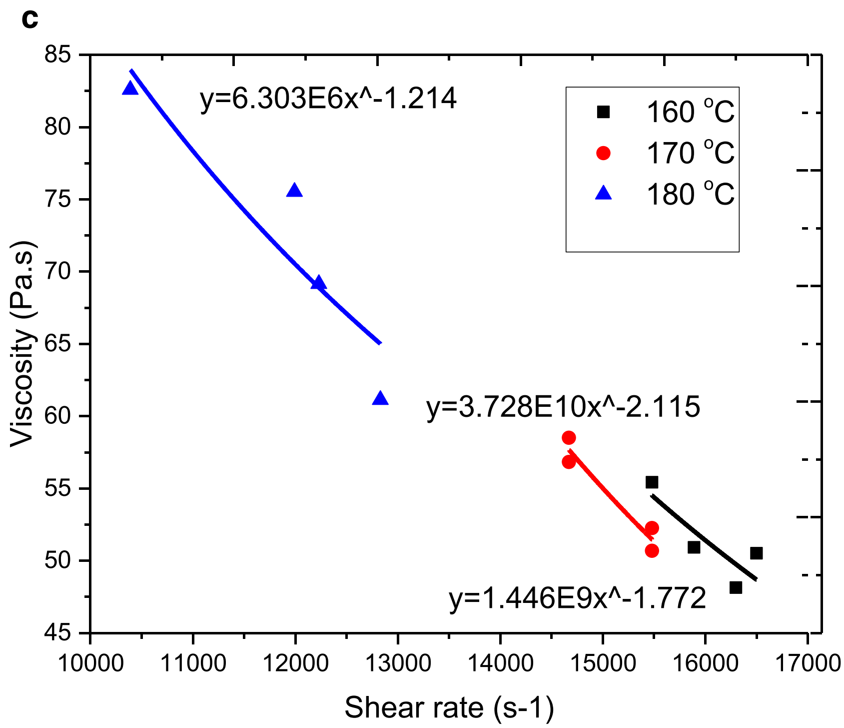

Fig. 4 (continued)

where ρ_p is the powder density, ρ_b is the binder density and φ is the volume fraction of the powder (solids loading).

2.3 Feedstock characterisation

The rheological properties of the feedstock were obtained using a Shimadzu CFT 500D capillary rheometer with a die size of 1 mm in diameter and length of 10 mm at various temperatures of 160 °C, 170 °C and 180 °C, respectively. The load cell ranging from 320 to 350 kN was then applied to obtain a broad range of shear rate and viscosity for all temperatures. Next, the randomly crushed samples were fed into the capillary barrel and preheated for 200 s. The DSM Xplore injection moulding machine was used for the injection moulding process with an injection parameter of 160 °C at ten bars, and the microstructural characterisation of the feedstock was examined using a TOSHIBA tabletop scanning electron microscope (SEM). The green part mechanical properties were obtained using a three-point bending test based on the ASTM D790.

3 Results and discussion

3.1 Critical solids loadings

The critical solids loading also known as 'critical powder volume percentage' (CPVP) is the state in which the powders are closely packed, and the remaining space is filled with the binder which influences the homogeneity of the feedstock. The critical solids loading is determined based on the relationship between torque and time (Fig. 3). The maximum torque peak occurred at 73 vol.%, indicating the critical solids loading for the composition. The torque value drops after the critical point to a steady state which reflects the homogenisation of the composition. The optimal solids loading generally lies between 2~5% below the critical solids loading. In this study, the critical solids loading is higher compared to the critical solids loading of single Ti feedstock in the range of 66–69 vol.% [16]. However, the higher solids loading for the Ti-HA feedstock can be as high as 78 vol.% using different morphologies of the HA powder with the same binder system.

Table 3 Flow behaviour index and activation energy

Feedstock (vol.%)	Flow behaviour index, n			Activation energy, E_a (kJ/mol)
	160 °C	170 °C	180 °C	
68	− 0.342	− 0.169	0.23	126.04
69	− 0.667	− 0.728	− 0.209	93.84
70	− 0.772	− 1.115	− 0.214	191.44

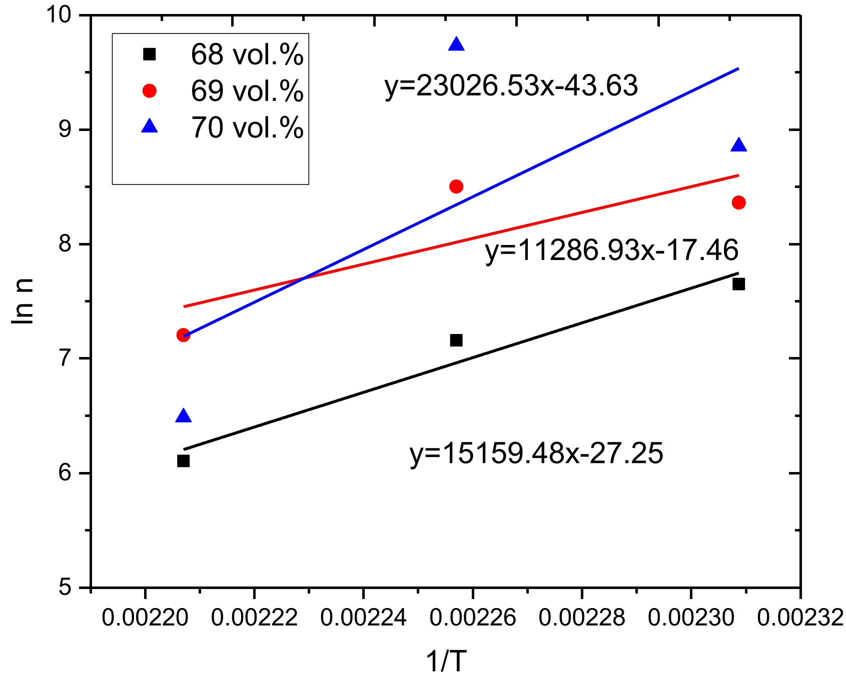

Fig. 5 Viscosity and temperature relation

Therefore, this result demonstrates that powder morphology affects the critical solids loading which is crucial in the preparation of the feedstock for the PIM process. Also, the optimal solids loading is determined based on the rheological

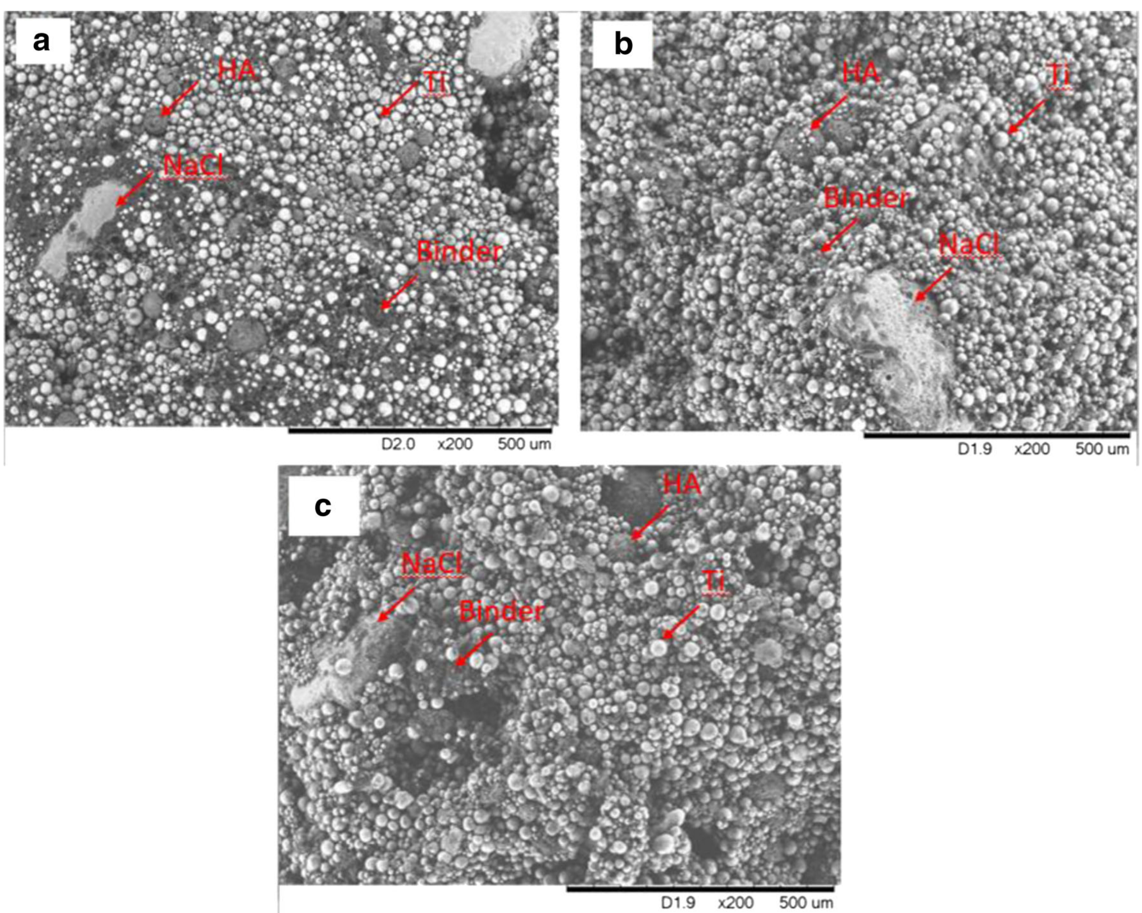

Fig. 6 SEM image of the feedstock for **a** 68 vol.%, **b** 69 vol.% and **c** 70 vol.%, respectively

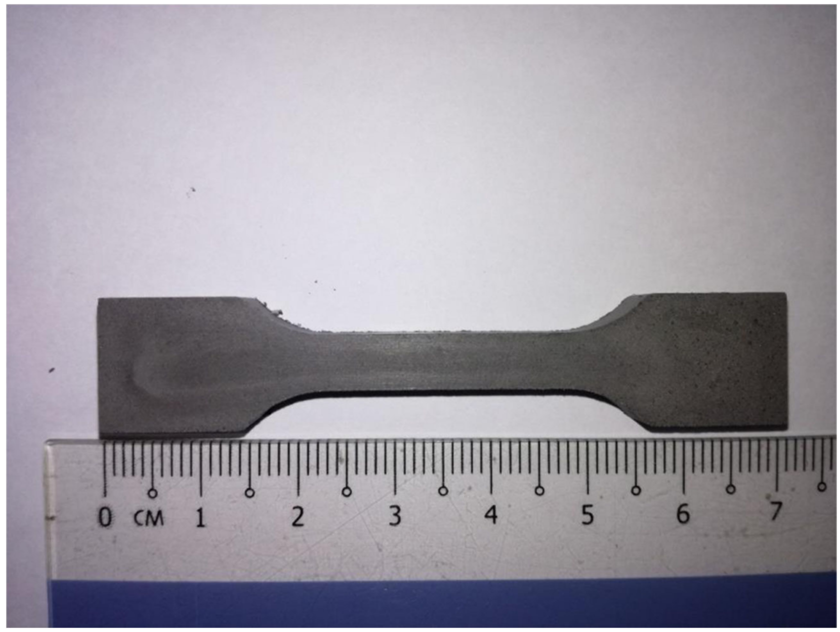

Fig. 7 Injected green part with a tensile bar shape

properties of the selected solids loading at 68, 69 and 70 vol.%, respectively, which is 2~5% below the critical solids loading of this study at 73 vol.%.

3.2 Rheological properties

Feedstock rheological properties in the PIM process are one of the main attributes where the properties affect the mould filling process. Therefore, it is crucial to obtain the best rheological properties of the PIM feedstock to avoid any moulding defects such as short-shot, flash, crack, bubble and powder-binder separation phenomena. The relationship between viscosity and shear rate is the preferred, if not the best way to describe the rheological properties of the PIM feedstock based on the power law equation as given below:

$$\eta = K\gamma^{n-1} \quad (3)$$

where η is the feedstock viscosity; γ is the shear rate; K is a constant; n is the feedstock flow behaviour index. All the viscosity and shear rate data from the capillary rheometer test to suit the equation empirically, and the relation of the viscosity and shear rate is illustrated in Fig. 4.

Figure 4 shows the relationship between viscosity and the shear rate for the feedstocks with 68, 69 and 70 vol.% solids loadings at various temperatures of 160, 170 and 180 °C, respectively. All feedstocks exhibit shear thinning, known as pseudo-plastic behaviour where the viscosity decreases with increases in shear rate. Notwithstanding, this behaviour demonstrates that the small particles will fill the gaps between the large particles when the shear is increased resulting in uniform particle distribution. This is shown in Fig. 6 where the Ti, HA and NaCl particles for all feedstocks are randomly dispersed.

Therefore, the results show that all feedstocks possess viscosity below 1000 Pa.s and a shear rate above 10,000 s^{-1} which is necessary for PIM feedstock. Furthermore, the flow behaviour index n, for all the feedstock, is $n < 1$ thereby demonstrating non-Newtonian shear thinning flow behaviour. However, a lower n value is undesirable for the injection to avoid a jetting defect because the feedstock is more viscosity dependent on the shear rate [17]. In this study, feedstock with 68 vol.% was found to be the best feedstock, possessing a higher value of n at 0.23 as compared to the 69 and 70 vol.% feedstock.

Table 3 summarises the flow activation energy, E, for all the feedstocks based on the relationship of the temperature and viscosity as illustrated in Fig. 5, which represents the sensitivity of the feedstock towards the change in temperature. This relation is obtained based on the Arrhenius equation as given below:

$$\eta = \eta_o \exp\left(\frac{E}{RT}\right) \quad (4)$$

Furthermore, low activation energy is required for PIM feedstock since maintaining the feedstock homogeneity is important during the moulding process to avoid the possibility of any defects. In this case, the feedstock with 69 vol.% solids loading possesses the lower activation energy which is desirable for PIM feedstock. Also, having a slightly higher value of activation energy, the feedstock of 68 vol.% was chosen as having the best rheological properties due to the higher flow behaviour index which is crucial during the injection process (Fig. 6). While the sensitivity of the feedstock during the temperature changes can still be controlled by optimising the injection and mould temperature.

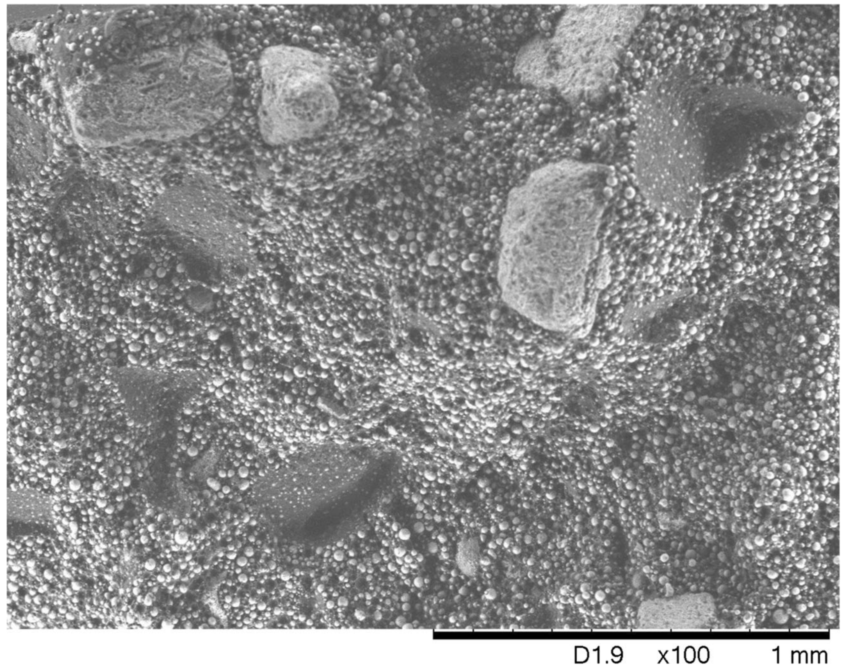

Fig. 8 The fracture surface of the green part

3.3 Green part produced from the optimum feedstock

Despite the entire feedstock exhibiting shear thinning behaviour, the feedstock with 68 vol.% was selected for the injection process due to the feedstock possessing a lower viscosity range between 48 and 66 Pa.s and a higher shear rate ranging between 12.4 × 10^3 and 16.5 × 10^3 s^{-1}. Indeed, this is desirable for the injection moulding process compared to 69 vol.% and 70 vol.% feedstock as described in the previous section. The green part was successfully injected without any apparent defects as displayed in Fig. 7.

A certain amount of strength is required for the green part to retain the shape and to ensure that the next PIM step, such as debinding and sintering, is performed without any issues. The maximum flex stress obtained is at 2.92 MPa which is lower than the suggested value of 10 MPa by German [13]. Accordingly, the lower strength possessed by the green part is a result of the larger size of NaCl space holder as shown in the SEM image of the fracture surface of the green part (Fig. 8). Indeed, this amount of strength is considered sufficient for the green part to retain the shape during the debinding and sintering stages.

4 Conclusion

In this study, the rheological properties of Ti6Al4V-hydroxyapatite with powder space holder were characterised. The critical solids loading for the Ti-HA (90:10) with 20% of NaCl space holder was obtained at 73 vol.%, where three solids loadings were selected with 68, 69 and 70 vol.% for the rheology tests. The rheology results determined that all the feedstock exhibit shear thinning behaviour which is necessary for the injection moulding process. The feedstock with 68 vol.% possessed the best rheological properties with a higher flow behaviour index at a lower viscosity range between 48 and 66 Pa.s and a higher shear rate ranging between 12.4 × 10^3 and 16.5 × 10^3 s^{-1} which are desirable for the PIM. As a result, the injected green part was successfully injected without apparent defects with a 2.92-MPa maximum flexural stress. These results indicate that the binder system consisting of LDPE and palm stearin is suitable in producing Ti-HA composite with the presence of the space holder material as a feedstock for the PIM. Besides, the binder system was able to randomly disperse the space holder material which is crucial in producing a porous Ti-HA composite for the implant purpose. Future studies need to be carried out in order to study the debinding and sintering behaviour as well as its mechanical and porosity properties in order to justify as a new generation of implant material.

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References

1. Aslam M, Ahmad F, Yusoff PSMBM, Altaf K, Omar MA, German RM (2016) Powder injection molding of biocompatible stainless steel biodevices. Powder Technol 295:84–95. https://doi.org/10.1016/j.powtec.2016.03.039

2. Dehghan-Manshadi A, Bermingham MJ, Dargusch MS, StJohn DH, Qian M (2017) Metal injection moulding of titanium and titanium alloys: challenges and recent development. Powder Technol 319(Supplement C):289–301. https://doi.org/10.1016/j.powtec.2017.06.053
3. Dehghan-Manshadi A, StJohn D, Dargusch M, Chen Y, Sun JF, Qian M (2018) Metal injection moulding of non-spherical titanium powders: processing, microstructure and mechanical properties. J Manuf Process 31:416–423. https://doi.org/10.1016/j.jmapro.2017.12.004
4. Kate KH, Enneti RK, McCabe T, Atre SV (2016) Simulations and injection molding experiments for aluminum nitride feedstock. Ceram Int 42(1, Part A):194–203. https://doi.org/10.1016/j.ceramint.2015.08.079
5. Thavanayagam G, Pickering KL, Swan JE, Cao P (2015) Analysis of rheological behaviour of titanium feedstocks formulated with a water-soluble binder system for powder injection moulding. Powder Technol 269:227–232. https://doi.org/10.1016/j.powtec.2014.09.020
6. Bleyan D, Hausnerova B, Svoboda P (2015) The development of powder injection moulding binders: a quantification of individual components' interactions. Powder Technol 286:84–89. https://doi.org/10.1016/j.powtec.2015.07.046
7. Fang W, He X, Zhang R, Yang S, Qu X (2014) The effects of filling patterns on the powder–binder separation in powder injection molding. Powder Technol 256:367–376. https://doi.org/10.1016/j.powtec.2014.01.065
8. Park DY, Shin DS, Cho H, Park SJ (2017) Effects of material and processing conditions on powder-binder separation using the Taguchi method. Powder Technol 321:369–379. https://doi.org/10.1016/j.powtec.2017.07.091
9. Park DY, Oh Y, Hwang HJ, Park SJ (2017) An experimental approach to powder-binder separation of feedstock. Powder Technol 306:34–44. https://doi.org/10.1016/j.powtec.2016.11.008
10. Choi J-P, Lyu H-G, Lee W-S, Lee J-S (2014) Investigation of the rheological behavior of 316L stainless steel micro-nano powder feedstock for micro powder injection molding. Powder Technol 261:201–209. https://doi.org/10.1016/j.powtec.2014.04.047
11. Arifin A, Sulong AB, Muhamad N, Syarif J, Ramli MI (2015) Powder injection molding of HA/Ti6Al4V composite using palm stearin as based binder for implant material. Mater Des 65:1028–1034. https://doi.org/10.1016/j.matdes.2014.10.039
12. Raza MR, Sulong AB, Muhamad N, Akhtar MN, Rajabi J (2015) Effects of binder system and processing parameters on formability of porous Ti/HA composite through powder injection molding. Mater Des 87:386–392. https://doi.org/10.1016/j.matdes.2015.08.031
13. German RM (2013) Progress in titanium metal powder injection molding. Materials 6(8):3641–3662. https://doi.org/10.3390/ma6083641
14. Hidalgo J, Jiménez-Morales A, Barriere T, Gelin JC, Torralba JM (2015) Capillary rheology studies of INVAR 36 feedstocks for powder injection moulding. Powder Technol 273:1–7. https://doi.org/10.1016/j.powtec.2014.12.027
15. Hayat MD, Cao P (2016) A new lubricant based binder system for feedstock formulation from HDH-Ti powder. Adv Powder Technol 27(1):255–261. https://doi.org/10.1016/j.apt.2015.12.017
16. Lin D, Sanetrnik D, Cho H, Chung ST, Kwon YS, Kate KH, Hausnerova B, Atre SV, Park SJ (2017) Rheological and thermal debinding properties of blended elemental Ti-6Al-4V powder injection molding feedstock. Powder Technol 311:357–363. https://doi.org/10.1016/j.powtec.2016.12.071
17. Sri Yulis MA, Khairur Rijal J, Norhamidi M (2009) Rheological properties of SS316L MIM feedstock prepared with different particle sizes and powder loadings. Journal - The Institution of Engineers, Malaysia (Vol. 71, No.2, June 2009)