Rheological Properties Of Titanium Alloy (Ti6Al4V) – Wollastonite (W) Composite Using Palm Stearin as Based Binder

Mohd Ikram Ramli
Abu Bakar Sulong
Norhamidi Muhamad
Andanastuti Muchtar
Mohd Yusuf Zakaria
Department of Mechanical and Materials Engineering,
Faculty of Engineering and Built Environment,
Universiti Kebangsaan Malaysia,
43600 Bangi, Selangor, Malaysia.

ABSTRACT

Powder injection molding (PIM) is a net-shaping process that can fabricate complex shaped of products in large quantities by using metal and ceramic powders. Biocompatible materials such as titanium alloy (Ti6Al4V) and wollastonite (W) have been widely used as bone implant's applications. However, no reports on a fabrication of Ti6Al4V-W composite using PIM process have been reported. In this study, the Ti6Al4V/W powders with the weight percentage (wt.%) ratio of 90:10, 80:20 and 70:30, were mixed with a binder system of palm stearin and polyethylene to obtain the feedstocks. It was found that for the feedstock of 90:10, the flow behavior at 130°C and 150°C is dilatant compared to 170°C where the flow is pseudoplastic. For the feedstocks of 80:20 and 70:30, the flow behavior was pseudoplastic. The rheological properties of such a feedstocks were analyzed using Shimadzu CFT-500D capillary rheometer. The lowest activation energy of 0.227 kJ/mol was obtained. All feedstocks were found to be in the range of injectability index for PIM process. There was a powder-binder separation phenomenon occurred on the green part of 90:10 wt.%while at 70:30 (wt.%), a good surface contact between the powder and binder was observed.

Keywords*:* *Powder Injection Molding, Metal-Ceramic Composite, Rheological Properties*

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Introduction

Powder injection molding (PIM) is a manufacturing process that combines plastic injection molding and powder metallurgy, which can produce high density, complex shapes, good mechanical properties and better surface finish of products compared to other powder metallurgy processes such as compaction and casting [1]. Such process consists of four main steps: mixing, injection molding, debinding and sintering respectively [2]. In such process, the viscous flow of feedstock is very important since it affects the shape forming process. In terms of homogeneity, the powders have to be well dispersed with the binder so that the shrinkage of the final sintered part is uniform and isotropic [2]. Therefore, feedstock having good rheological properties is required. The viscosity of feedstock is sensitive to temperature and shear rate [3]. Such viscosity can be observed by the rheology test where the powder-binder separation can be identified.

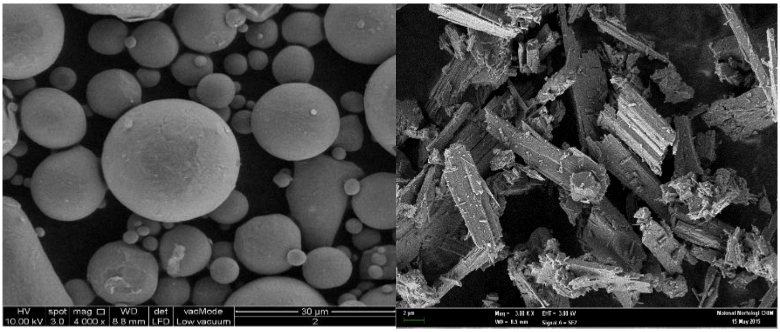
Generally, ceramic materials are known for theirs brittleness and poor mechanical properties, while metals have the opposite properties. Therefore, the combination of ceramic and metal seems promising to produce a new composite which may possessed improved mechanical properties. In the processing of such composites, methods that are commonly used are powder metallurgy and plasma spray [4]-[6]. In previous studies, Ti6Al4V and hydroxyapatite (HA) was used to produce metal-ceramic composites [2, 7]. It was reported that at high temperature, Ti6Al4V tends to oxidize and reacts with other materials while HA will be unstable and decomposed to different phases [8, 9]. Other than HA, glass-ceramics containing apatite and wollastonite crystals (A-W glass ceramics) has also been found as a suitable material candidate for the applications of artificial bone and dental root due to their good biocompatibilit. [10, 11].

Titanium alloy (Ti6Al4V) has been widely used in biomedical implants for load bearing applications due to its ability in retaining its shape after the physical activities of patients. Ti6Al4V is well known for its biocompatibility, low modulus and resistance to corrosion [12]. Wollastonite (W) is a natural calcium silicate ceramic ($CaSiO_3$) that has been extensively used in regenerating bone tissues due to superior bioactivity and biocompatibility compared to hydroxyapatite (HA) [13]. It was reported that the formation of apatite on wollastonite is faster than that of bioglass and glass-ceramic as observed in the simulated body fluid (SBF) [14,15]. It is expected that the combination of Ti6Al4V and W can produce biocompatible composites having good mechanical properties. Such promising criteria seems interesting to be applied on the bone implant applications.

Binder system is important in the PIM process as it provides the flowability and formability for the powders during the injection process. Previously, palm stearin has been successfully used as a based binder system due to its low cost and wide availability [16]. Palm stearin is the derivation from palm oil which is environmentally friendly and act as a lubricant and surfactant in the injection process [7]. In addition, it provides capillary pores during the binder removal in the debinding stage before sintering. Such binder has been successfully used for stainless steel 316L (SS316L), Ti6Al4V, magnesium alloy, yttria stabilized zirconia (YSZ) and Ti6Al4V-HA composite [17]-[20]. Due to its good performance, the objective of this study is to analyze the rheological behavior of Ti6Al4V-W composites for the powder injection molding process using palm stearin as the binder system.

Experimental Setup

The scanning electron micrograph of Ti6Al4V and W are shown in Figures 1(a) and (b), respectively. Ti6Al4V powder having the average particle size of 19.6 μm from TLS Technik GmbH & Co, Germany, is mixed with wollastonite (W) powder having the average particle size of 8.7 μm from CNPC, China at three different weight percentage (wt.%) compositions of 90:10, 80:20 and 70:30, respectively. The binder system that consists of palm stearin (PS) and polyethelene (PE) at ratio of 60:40 wt.% is used. Both powders and binders are mixed at 150°C with a constant speed of 25 rpm for 2 h using the Brabender mixer. The mixed composition is known as feedstock and by using a crusher machine, the feedstock is then crushed into small and uniform sized of pallets. The rheological behavior of such feedstock is tested using the Shimadzu CFT-500D capillary rheometer with a die of 1 mm diameter. The temperatures for rheology test are 130°C, 150°C, and 170°C, respectively. Such range of temperature are chosen based on the highest melting temperature of the binders. Loads of 20, 30, 40 and 50 kN are used.



(a) (b)

Figure 1: SEM micrographs of (a) Titanium alloy (Ti6Al4V) powder and (b) Wollastonite (W) powder

The graph of viscosity against shear rate is plotted. By using the Power Law equation (Equation 1), the flow behavior index for each feedstock is analyzed based on the slope (n^{-1}) of the graphs. The Power Law equation:

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

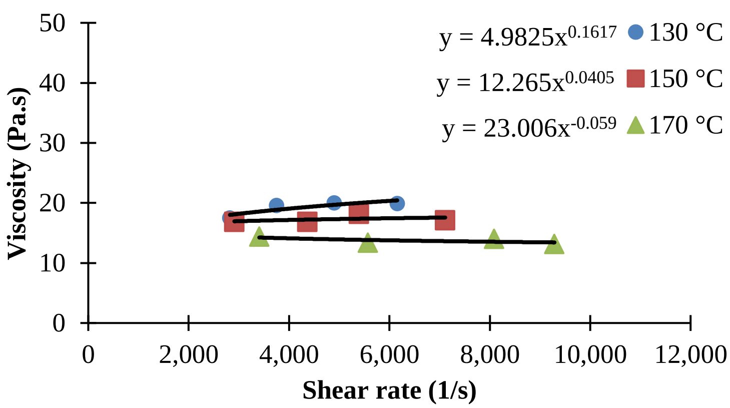
where $\eta, K, \gamma,$ and n are the viscosity, constant, shear rate, and flow behavior index, respectively. The activation energy of the feedstocks is determined by Arrhenius's equation (Equation 2):

$$\eta = \eta_o \exp(\frac{E}{RT}) \qquad (2)$$

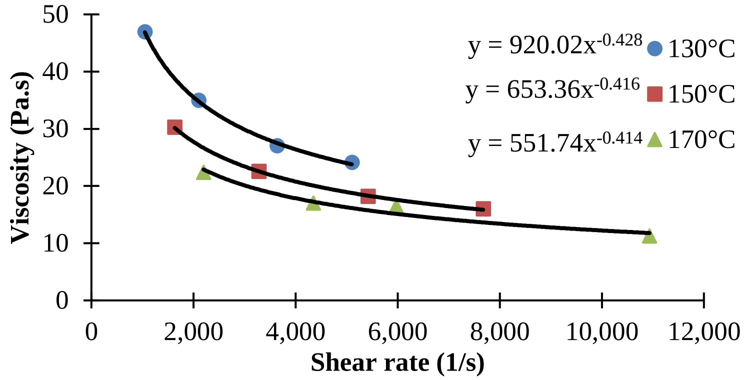
where η_o, E, R and T are viscosity at the reference temperature, activation energy, gas constant, and temperature in Kelvin, respectively. Take note, at a shear rate of 1000 s^{-1}, the graph for the activation energy is plotted. The activation energy, E can be obtained by the slope of graph.

Results and Discussions

PIM feedstocks are basically considered as pseudoplastic fluids where the viscosity decreases as the shear rate increases [16, 21]. Figure 2 shows graphs of viscosity against shear rate for all the compositions. In Figure 2(a), dilatant flow is observed at 130°C and 150°C, respectively. Dilatant flow occurs when the viscosity increase with the increasing shear rate. However, as the temperature increases to 170°C, the flow behavior changed to pseudoplastic flow behavior. For Figures 2(b) and (c), pseudoplastic flow behaviors are observed, which are suitable for the PIM process.



(a)



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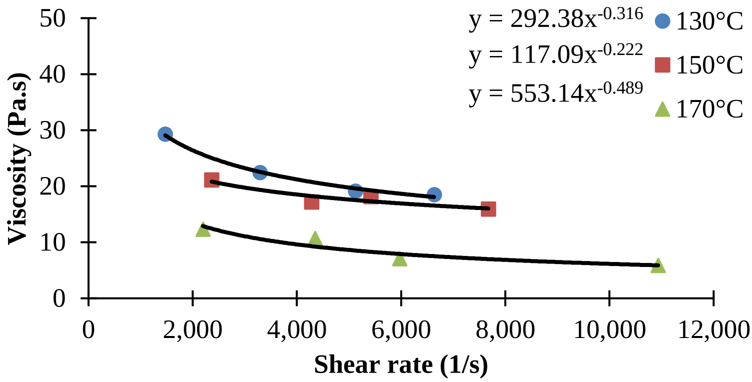


(c)

Figure 2: Graphs of viscosity against shear rate for the Ti6Al4V/W feedstocks at weight percentage (wt.%) ratio of (a) 90:10, (b) 80:20 and (c) 70:30, respectively

Although the 90:10wt.% feedstock shows dilatant flow behavior, the viscosity and shear rate for such feedstock are still in the injectability range for the PIM process; viscosity <1000 Pa.s and shear rate ranging from 10^2-10^5 s^{-1}. The measured viscosity and shear rate are 13-20 Pa.s and 2×10^3 to 1×10^4 s^{-1}, respectively. Such consistency of flow behavior may result from the feedstock that was not fully melted due to the higher fraction of powder (Ti6Al4V). Such ratio leads to higher friction at the capillary die during the rheology test. In addition, it is found that as the temperature increases, the viscosity of feedstock decreases [16].

Table 1 shows the value of flow behavior index, *n* for all the compositions. Such *n* values can also determine the flow behavior of the feedstocks. For pseudoplastic, the value of *n* is less than 1 and vice versa for the dilatant flow. Based on Table 1, for the 90:10wt.% feedstock at 130°C and 150°C, the values of *n* indicate that such feedstock has a dilatant flow.

Table 1: Flow behavior index for the Ti6Al4V/W feedstocks

Temperature (°C)	**Composition (wt.%)**		
	90:10	**80:20**	**70:30**
130	1.16	0.57	0.68
150	1.04	0.58	0.78
170	0.94	0.59	0.51

The sensitivity of the feedstocks towards pressure and the temperature is determined by the Arrhenius equation where the activation energy, *E* (kJ/mol) can be obtained. In PIM feedstock, a small value of *E* is preferable since less defects will be produced due to such sensitivity [19]. Figure 3 shows the activation energy for the three different compositions where the *E* values are 0.27 kJ/mol, 15.45 kJ/mol and 1.84 kJ/mol, respectively. These values are smaller compared to the previous research reported by Foudzi et. al [16], where free-defect samples were successfully injected with the activation energy of 37.91 kJ/mol. Such finding is very important because defects such as cracks and deteriorations can be avoided.

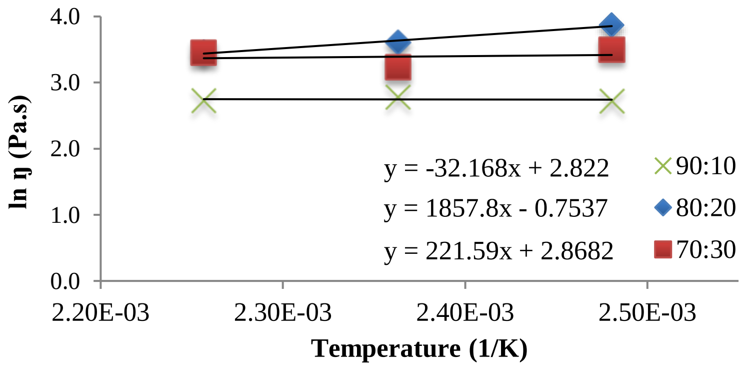
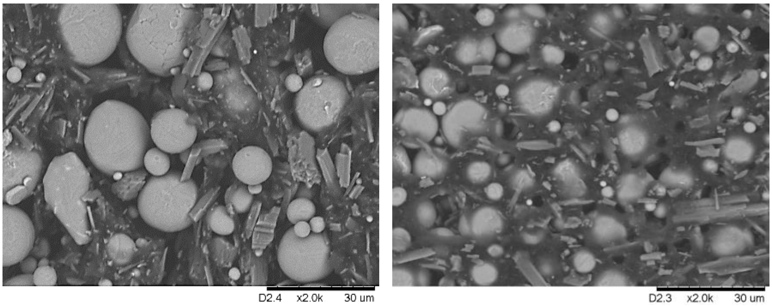


Figure 3: Graph of the activation energy for the Ti6Al4V/W feedstocks at all compositions.

All Ti6Al4V/W feedstocks are successfully injected with no defects. The parameters for such injection are 150 °C, 80 °C, 10 bar and 8 seconds, each for the injection temperature, mold temperature, injection pressure and holding time, respectively. Figure 4 shows the injected part (green part) with a single gate at one end.

Figure 4: Green part for Ti6Al4V/W composite at composition 70:30

The distribution and dispersion for powder and binder are investigated on the green part by the SEM micrographs as shown in Figures 5(a) and (b) for the feedstock at 90:10wt.% and 70:30wt.%, respectively. The powder-binder separation phenomenon may occurred as shown by Figure 5(a) where some of the Ti6Al4V powder particles are clustered and not coated by the binders. Such poor coating between the powder and binder may caused the 90:10wt% feedstock to have a dilatant flow. For the 70:30wt.% feedstock as shown by Figure 5(b), it is clearly observed that the contact surface between the powder and binder is good where the powder particles are coated with the binder. Therefore, no powder-binder separation phenomenon occurred for such feedstock. In addition, such good contact helps the injected part to retain its shape and prevent from cracking or other damages during the debinding and sintering processes [21].



(a) (b)

Figure 5: Feedstock of Ti6Al4V/W for composition of (a) 90:10wt.% and (b) 70:30wt.%, at 2000X magnification.

Conclusions

The flow behavior of Ti6Al4V/W feedstocks for all the three compositions are mostly pseudoplastic. Although, some of the feedstocks show a dilatant flow, the values of viscosity and shear rate are in the range of injectability for the powder injection molding process. From the activation energy, it shows that the feedstocks are less sensitive towards pressure and temperature changes which result to less defects during the injection process. Therefore, it can be concluded that the Ti6Al4V/W feedstocks are able to be injected. For the 90:10wt% feedstock, a powder-binder separation phenomenon occurred due to the dilatant flow of the feedstock compared to other feedstocks at 80:20wt.% and 70:30wt.% which have a better contact surface between the powder and binder.

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