RHEOLOGICAL CHARACTERIZATION OF WATER ATOMISED STAINLESS STEEL POWDER FOR MICRO METAL INJECTION MOLDING

M.H.I Ibrahim[a], N. Muhamad[b], A.B. Sulong[b],K.R Jamaludin[c], N.H.M Nor[b], S. Ahmad[a]

[a]Dept. Of Mechanical Engineering, Universiti Tun Hussein Onn Malaysia(UTHM), 86400 Parit Raja, Batu Pahat, Johor, Malaysia

[b]Precision Process Research Group,Dept. of Mechanical and Materials Engineering, Faculty of Engineering,Universiti Kebangsaan Malaysia (UKM),43600 Bangi, Selangor, Malaysia

[c]College of Science & Technology, Universiti Teknologi Malaysia, Int. Campus, 54100 Kuala Lumpur, Malaysia
Email : mdhalim@uthm.edu.my

ABSTRACT

In this paper, the performance of feedstock characteristics for micro metal injection molding (μMIM) is investigated by optimum power loading variation and rheological characterization. Due to the highly stringent characteristics of μMIM's feedstock, the study has been emphasized on the powder and binder system in which stainless steel SS316L powder are mixed with composite binder, which consists of PEG (Polyethelena Glycol), PMMA (Polymethyl Methacrilate) and SA (Stearic Acid) by variation of powder loading concentration. The rheology properties are investigated using Shimadzu Flowtester CFT-500D capillary rheometer. The geometry of water atomised stainless steel powder are irregular shape, therefore it is expected significant changes in the rheological results that can influence the microcomponent, surface quality, shape retention and resolution capabilities. The optimization of the μMIM rheological properties as a function of stainless steel powder loading concentration are evaluated by flow behavior exponent, activation energy and moldability index. Results show that 61.5%vol contributes a significant stability over a range of temperature and the best powder loading from a critical powder volume percentage (CPVP) and rheological point of view.

KEYWORDS: micro metal injection molding, water atomised metal powder, rheological characteristics, critical powder volume percentage.

1. INTRODUCTION

MIM has been well established as it inherit many features compared to conventional injection molding such as low production cost at large quantity, good tolerance and mechanical properties, shape complexity, applicability to many materials and involves very little waste of material. Due to the versatility and enormous potential, it is currently being explored by researchers in some aspects such as mold technology, structure and morphology, special machine, production process, filling performance analysis and numerical simulation. As the technology being developed, micro metal injection molding takes place to fulfill the needs of complex miniaturized components or microstructured components with features in the micrometer or submicrometer regime.

Micro Metal Injection Molding(μMIM) process begins with fine powder with particles typically less than 10μm in diameter. The basic processing steps in the μMIM are similar to MIM, these involved the mixing of powder with a binder to produce the feedstock, injection molding of the feedstock to replicate geometrical details in the mold, debinding to remove the binder components and sintering to obtain the final mechanical properties[4]. However, there is a limitation in the μMIM process such as feedstock preparation, debinding and sintering. Besides that, there are some additional requirements for binder properties for μMIM. For example, a low viscosity feedstock is desirable for filling the micro details during injection molding rapidly before the feedstock solidified [13,14]. It is well known that a high viscosity of a feedstock makes difficulty in molding [1,2]. Feedstock characteristic can only be determined by rheology test where the rheological behavior is measured in terms of viscosity, which relates to shear stress and shear rate. Therefore, it is clearly defined that rheological behavior and stability of feedstock is the main important role for successful manufacturing.

However, before the feedstock being developed under different powder loading, critical powder volume percentage (CPVP) of the powder itself should be done using modified ASTM D-281-31 which is oil absorption method [16]. The packing density of a powder is a first predictor of the critical powder loading. Usually fine powders would results in slightly lower critical powder loading due to the higher interparticle friction. Futhermore, fine powders will lead to difficulties in attaining a high packing density because of particle agglomeration and slowing down the debinding process. The infinitely high viscosity will make molding impossible using a feedstock formulated at the critical solids loading.

Although water atomised stainless steel powder can provide good shape retention due to mechanical interlocking, its irregular shape particles yield relatively low packing density and exhibit higher resistance to flow. Besides that, the poor packing of irregular powders leads to a lower green density, which translates into higher shrinkage that often results in greater distortion and less sintering densification [5]. Suri et al.[24] investigates the correlation between mixing and particle characteristic to improve the homogeneity of the feedstock using agglomerated and deagglomerated tungsten powder.

Many experimental data about rheological characteristics of micro MIM feedstock are available in the technical literature [7, 8, 14, 20]. Recently Quinard et al.[19] has studied the properties and behavior using 16μm SS316L with LDPE and PP as a binder where the shrinkage in range from 12 to 15%. Besides, Liu et al.[13] and Supati et al.[22] studied the production and characterization of SS-TiC composites. Chuankrerkkul et al.[3] investigates the interaction between PEG/PMMA with WC-Co powder and it was found that PMMA only bonds to Co but not to WC. Nevertheless, there are limited data available particularly dealing with the characterization of feedstock for micro metal injection molding.

Taking above considerations into account and from an environmental point of view, binder systems based on PEG and PMMA are preferred in this study as it can be removed easily through solvent debinding and thermal debinding. PMMA works as primary binder to keep the component in shape after injection molding & debinding while secondary binder (PEG) helps decreasing the feedstock viscosity and then to increase the replication ability [19]. In order to improve the binder properties such as surface wetting, spreading, adsorption, and binder strengthening, the surfactant is often added as an additive that consists of a functional group adhering to the powder surface and an oriented molecular chain extending into the binder [10,11, 25] where Stearic Acid(SA) will be used in 2% amount of total weight binder. Critical powder volume percentage(CPVP) of the feedstock will be determined using Thermo Haake Rheomix in order to find the optimum powder loading that suites feedstock stability and avoid powder binder separation. Next validation using Shimadzu Capillary Rheometer through rheological characteristic by determining the viscosity, flow behavior index, activation energy and moldability index where low viscosity requirements are the important needs for μMIM feedstock to flow before it is solidified.

2. METHODOLOGY

2.1 Materials

For the replication of fine details, fine particles powder around 5 μm are mixed with a multi-component binder consist of water soluble binder PEG and PMMA. The main objective of using PMMA binder is that it can be removed from the mouldings in a comparatively short time [18]. Stearic acid will act as a surfactant and lubricant to the feedstock for improving powder wetting. Table 3 show properties of the binder used in the study.A 316L stainless steel water atomised powder (Epson Atmix Corp) with irregular shape was used as it is compatible with water leaching and high corrosion resistance. The characteristic of used powder are reported in Table 1 while Table 2 shows binder properties.

Table 1 : Stainless steel(SS316L) powder characteristic

Characteristic	Details
Identification	SS 316L, PF-10F
Powder Source	Epson Atmix Corp
Tap Density,g/cm^3	4.06
True pynometer density,g/cm^3	8.0471
Powder Size	D10=2.87μm D50=5.96μm D90=10.65μm

Table 2 : Binder properties

Binder	Type	Designation	Melting temperature, °C	Density, gcm^{-3}
Binder 1	Primary	Polymethyl Methacrilate(PMMA)	257.77	1.19
Binder 2	Secondary	Polyethelena Glycol(PEG)	63.32	1.23
Binder 3	Surfactant	Stearic acid(SA)	70.1	0.94

2.2 Critical powder loading

The mixing torque which is proportional to the work required to mix the powder and binder,is an indicator of the viscosity of the mixture. The uniformity of the mixture is estimated by the variation in the mixing torque over a period of time [4, 16]. Each metal powder will have difference mixing torque value which indicates maximum allowable powder loading, therefore it will be determine using ASTM D-281-31 using Thermo Haake Rheomix as shown in Figure 1. Critical powder volume percentage (CPVP) might show maximum torque evolution curves which states critical powder loading that can be used for metal powders. The critical loading is the point where all the particles are tightly packed and all voids between the particles are filled

with the binder. German & Bose[4] state that the optimum powder loading is kept approximately 2-5% lowers than the critical loading. This range will be using to make a feedstock and being analyse under rheological characteristic. The volume of oleic acid is added in 0.5ml for every 5 minutes and equation 1 was adopted to obtain the correlation between volume of oleic acid and torque value:-

$$CPVC = 100\, x \frac{V_f}{V_f + V_o}(\%) \quad (1)$$

2.3 Feedstock preparation and rheology

The binder system consists of 73 % PEG; 25 % PMMA and 2 % stearic acid based on the volume fraction. Stearic acid works as a surfactant where it acts as a lubricant that enhances the dispersion of powder in the binder during mixing, it enhanced powder loading and green strength [17] without sacrificing the flow

Figure 1: Thermo HAAKE Rheomix.

properties of the mixtures. The powder volume fraction using in the experimental was 61.5% and 62.5% which was kept 2-5% lower from the CPVC measured by Thermo Haake Rheomix. The feedstocks were prepared using a sigma type blade mixer with a rotation frequency of 26 rpm. The mixing temperature was set at 70ºC, which is within the highest melting temperature and the lowest degradation temperature of the binder system. After mixing, the dough will be removed from the mixer and left at the room temperature. Subsequently, when the dough temperature drops to 60ºC, it will be fed into a crusher to produce homogenized granules.

Feedstock behavior was tested using CFT-500D Shimadzu capillary rheometer which used to measures the viscosity resistance of feedstock when melted materials pass through the die orifice. As the powder to binder ratio increases, the viscosity becomes essentially infinite at the critical solids loading. In order to monitor the flow, a die (L/D=10) was attached to the bottom of

the extruder barrel. The measurement temperature was conducted at various capillary temperatures at 130ºC, 140ºC, 150ºC and the load was applied to the tester from 30kgf-110kgf. The barrel was filled with the feedstock and then pressed lightly with the piston. Feedstock was left in the barrel for about 10-15 minutes to attain thermal equilibrium. The pressure drop across the die was recorded in order to calculate the shear rate at die wall. Meanwhile, the flow rate through the capillary was calculated using the relation provided by Japanese Industrial Standard,JIS K7210[21]:

$$Q = \frac{0.4}{t}\left(cm^3 / s\right) \tag{2}$$

where t is the time for the piston to travel at 4 mm stroke in the barrel. The shear rate , $\dot{\gamma}$ was calculated using the equation:

$$\dot{\gamma} = \frac{32Q}{\pi D^3} 10^3 \left(s^{-1}\right) \tag{3}$$

where D is the die diameter, 1mm. The tester will display the viscosity(Pa.s), shear rate(s^{-1}) and the flow rate(cm^3/s), and the viscosity versus shear rate was plotted. The slope(n-1) was calculated from the graph based on the Power of Law equation to determine the flow behavior index. Since the binder formulation and feedstocks shown pseudo-plastic behavior, it should obey the following expression:

$$\eta = K\,\dot{\gamma}^{n-1} \tag{4}$$

where η is the viscosity, K is the constant. The activation energy,E for the samples is determined using the Arrhenius's equation:

$$\eta = \eta_o \exp\left(\frac{E}{RT}\right) \tag{5}$$

where R is the gas constant, T is the temperature in Kelvin unit, η is the mixture viscosity and η_0 is the viscosity at reference temperature. Large values of activation energy show a high sensitivity of viscosity to temperature. However, the value of E depends to the composition of binder formulation and feedstocks. Liu et al.[13, 14] stated that low viscosity is desirable for filling micro details beside low activation energy[2]. In order to establish a general molding

index, the Weir's model which proposed for polymers has been used including the main parameters as regards flow[26].

$$\alpha_{stv} = \frac{1}{\eta_0} \frac{\left|\frac{\partial \log \eta}{\partial \log \dot{\gamma}}\right|}{\eta_0 \quad \frac{\partial \log \eta}{\partial 1/T}} \tag{6}$$

where, η is the viscosity, η_0 is a reference viscosity, T is the temperature, $\dot{\gamma}$ is the shear rate and α_{stv} is the rheological index or moldability index. Simplifying the above equation:

$$\alpha_{stv} = \frac{1}{\eta_0} \frac{|n-1|}{E/R} \tag{7}$$

3.0 RESULTS & DISCUSSION

3.1 Critical powder loading

Variation in the mixing torque and the maximum solids volume fraction can be determined using a torque rheometer [16]. By determining the critical powder loading, the homogeneity mixture will be achieved as it correlates the density peak at the critical powder loading with the point where the viscosity becomes effectively infinite. In other words, mixture composition near the critical loading are amplified into large viscosity shifts. Figure 2 shows the mixing torque as a function of the mixing time at various levels of solids loading.

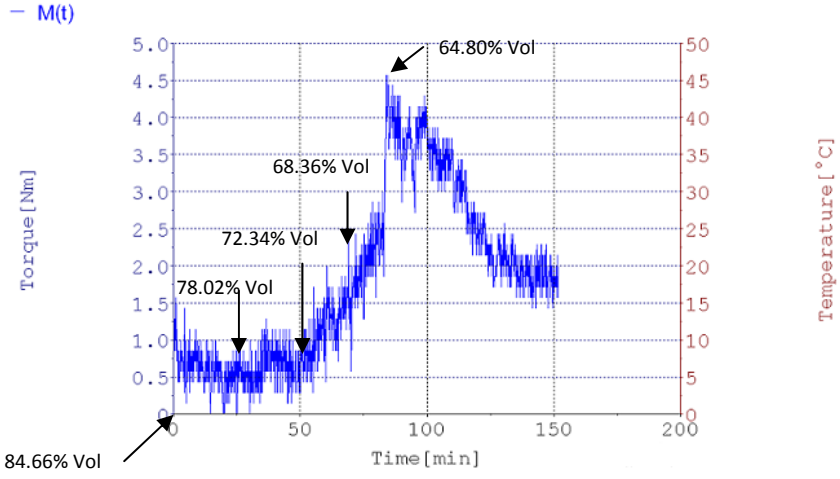


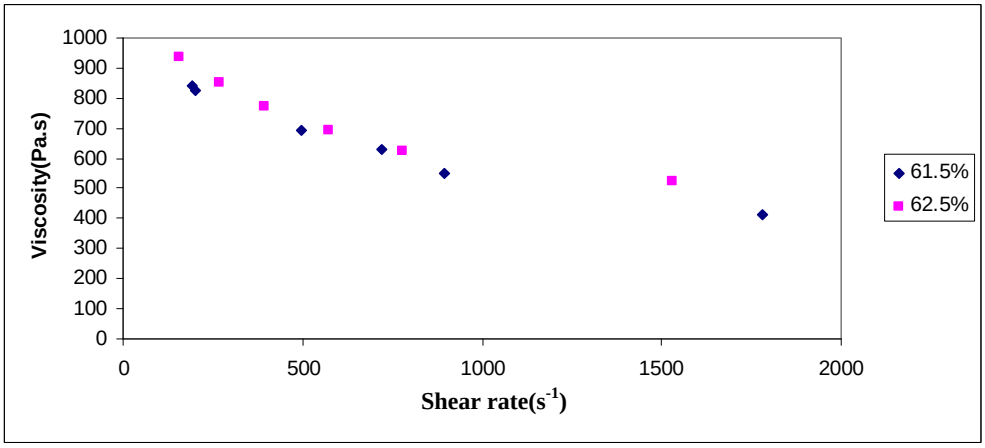
Figure 2 : Critical Powder Volume Concentration for SS 316L(PF-10F)

At each point where powder is added to the mixture, the mixing torque makes a jump and then settles to a lower steady state value associated with homogenization of the PIM mixture.

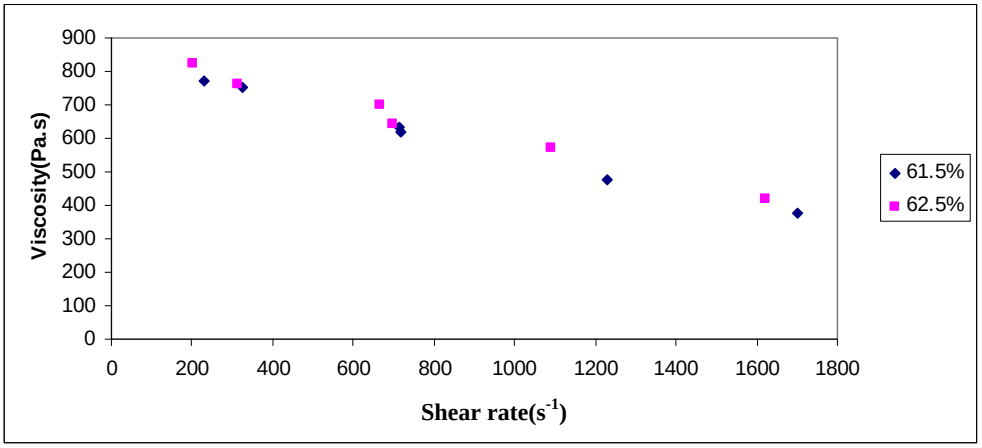
However once the critical powder loading is exceeded, the excessive loading makes the mixture unstable and from the figure, 64.8% vol is the critical powder loading as it shows the highest peak. Higher powder loading is in favour of the compact retention as it will enhance sintering and minimize shrinkage [4] however the feedstock will be difficult to mix and inhomogeneous mixture. Low powder loading is prone to powder binder separation under high pressure. Suri et al.[24] studied the variation in the mixing torque between agglomerated and deagglomerated powder in order to find the maximum solids volume fraction where agglomerated powder has higher powder loading compared to rod milled powder. Practically, the optimum powder loading content contains more binder than the critical content thus the optimum loading will be around 2-5% lower than a critical powder loading as mentioned by German & Bose [4]. In μMIM, it is important to use the powder loading as high as possible since it effects to the total shrinkage of the product after sintering process.

3.2 Rheology

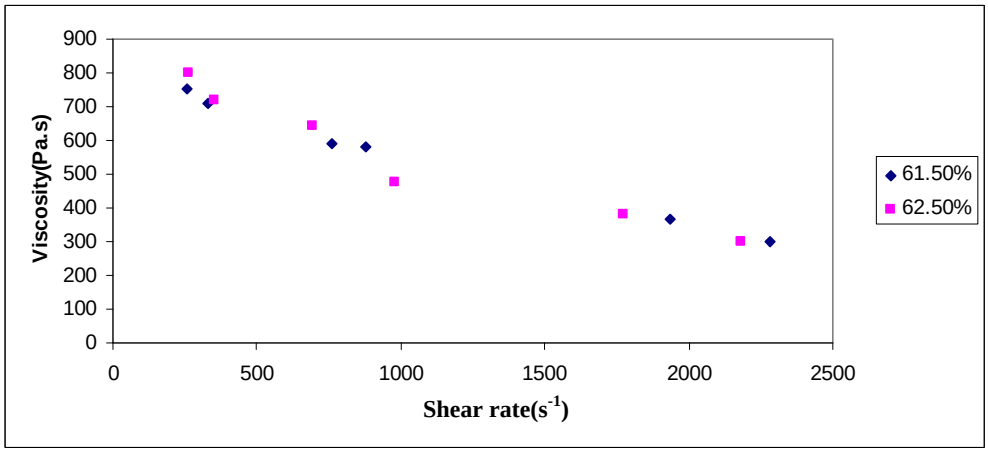
A homogeneous distribution of the powder particles and binder in feedstock is important as it helps to minimize segregation in the injection stage and then to obtain an isotropic shrinkage after sintering. Futhermore, homogeneity are required to prevent wear of the mixing equipment and lower contamination of feedstock. Based from the figure, feedstock with 61.5% and 62.5% were made as small errors in formulating a feedstock will cause molding sensitivities because of the rapid viscosity change in solids loading. The evaluation of the feedstock rheological properties is based on the viscosity and its shear sensitivity and temperature sensitivity [12]. Viscosity of the feedstock is greatly influence by particle size distribution, particle shape and density of the powder [8, 9] stated that viscosity is the single most important predictor of feedstock quality that influences the success of molding stage. In achieving the low viscosity, Supriadi et al.[23] suggested that binder selection is important especially for very micron powders. Results show that all the feedstock exhibits a shear thinning or pseudoplastic behavior, which is desirable for not only MIM but also in μMIM. This could be due to particle orientation and ordering with flow as well as breakage of particle agglomerates with release of fluid binder [4]. Figures 3(a),(b) and (c) show the variation of viscosity as increasing shear rate at temperatures 130 ºC, 140 ºC and 150 ºC at 61.5% and 62.5% powder loading respectively.



(a) 130ºC



(b) 140ºC



(c) 150ºC

Figure 3 Correlation of viscosity and shear rate at (a)130ºC, (b)140ºC and (c)150ºC

From figure 3, it indicates a pseudoplastic flow behavior at which viscosity of the feedstock decreases with shear rate. No dilatant behavior that is viscosity increasing with shear rate is observed, figuren indicating there are no powder binder separation. As shown in all figure, 62.5% exhibit higher viscosity than 61.5%. Li et al.[10, 11] also experienced the same phenomenon where the viscosity of the feedstock increase with the powder loading value. However, when the temperature was increased to 150ºC, the viscosity is reducing. This is due to powder volume reduction which arising from larger binder expansion and disentanglement of the molecular chain during heating [15]. As reported, flow exhibiting a viscosity of less than 1000 Pa.s in the shear rate range of 10^2 to 10^5 s^{-1} is necessary for MIM [4].

With the increase of the solid powder loading in the binder matrix, it is a rational result of the decrease of the flowability and the increase of the viscosity. The lower the value of the viscosity, the easier it is for a feedstock to flow. In other words, the viscosity data indicate the flowability of the feedstock. Besides that, the flowability of the feedstock can be measured from the Power of Law equation stated in equation (3). The value of flow behavior exponent,n indicates the degree of shear sensitivity. The lower the value of n, the faster the viscosity of feedstock changes with shear rate. 61.5% shows a lower value of n which is better compared to 62.5%.It is desirable in μMIM that the viscosity of the feedstock should decrease fast with increasing shear rate during molding. High shear sensitivity is important to produce a complex, delicate and miniaturized parts.

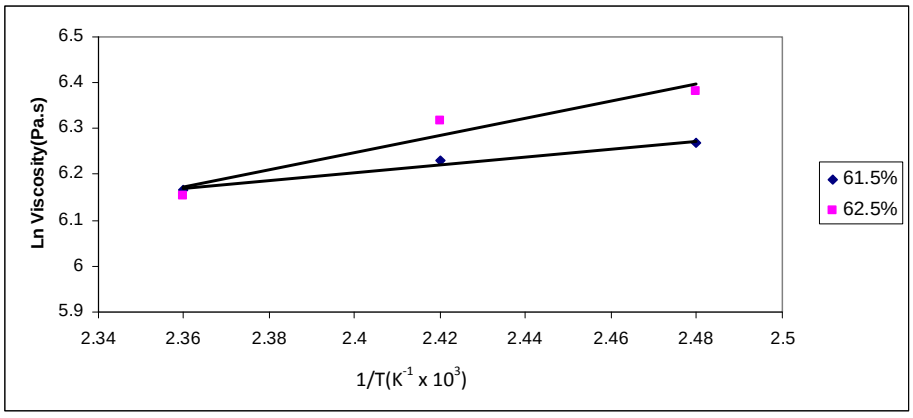


Figure 4 Correlation of viscosity and temperature for feedstocks with different powder loading.

Figure 4 show the feedstock viscosity dependence on temperature which measures a value of flow activation energy, E. It shows that 62.5% have a broad viscosity range compared to 61.5% and the viscosity value seems to decrease when the extrusion pressure and test temperature increase regardless. The value of E expresses the effect of temperature on the

viscosity of the feedstock. Powder loading of 61.5% exhibits a low value of E which means the viscosity is not so sensitive to temperature variation. Therefore, any small fluctuation of temperature during molding will not result in sudden viscosity change. A sudden viscosity change could cause undue stress concentrations in molded parts, resulting in cracking and distortion [10,11]. Table 3 shows a comparison of the feedstock at shear rate 1000 s^{-1}.

The higher the value of α_{stv}, the better the rheological properties. According to the table 4, 61.5% feedstock gives the highest rheological index and therefore it would be the best candidate from a rheological point of view. Besides that,it indicates the best powder-binder ratio to get quick powder repacking and binder molecule orientation during molding. On the other hand, 62.5% gives the lowest value and it could be considered to be the lowest candidate for injection molding in terms of flowability.

Feedstock	Temp(ºC)	n	E(kJ/mol)	η(Pa.s)	α_{stv}
61.5%	130	0.6975	7.0	527.615	677.06
	140	0.6542	7.0	507.471	804.7
	150	0.6037	7.0	476.633	981.88
62.5%	130	0.7362	15.6	590.395	238.34
	140	0.7124	15.6	554.050	276.89
	150	0.5596	15.6	471.457	498.28

Table 3 Comparison of n, E, η and α_{stv} at shear rate 1000 s^{-1}.

4.0 CONCLUSION

The critical powder volume percentage (CPVP) has been investigated due to critical requirement in μMIM which concern in low viscosity, homogeneous mixture, minimize shrinkage and better shape retention. Based from the CPVP, the optimal loading has been established due to rapid viscosity variation near the critical loading where molding problems can be encountered when attempting to work with compositions too near with the critical loading. Furthermore, validation through rheological test of SS 316L water atomized feedstock has been conducted in terms of viscosity, flow behavior exponent, flow activation energy and rheological index at two optimal powder loadings, 61.5% and 62.5% with three different temperatures of 130ºC, 140ºC and 150ºC. All the feedstock show a pseudoplastic behavior which is suitable to be injection molded and no dilatant behavior is observed which indicates powder binder separation.

However, with some characterization stated above, 61.5% powder loading would be the best compared to 62.5% in terms of the lowest viscosity for easier flowability and low value of flow behavior exponent, n for rapid viscosity changes with shear rate. Low activation energy at 61.5% is desirable for injection as it would lower the sensitivity of viscosity due to temperature variation. Thus 61.5% feedstock is stable and it would be the best over the wide range of temperature.

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