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METAL INJECTION MOLDING (MIM) FEEDSTOCK PREPARATION WITH DRY AND WET MIXING: A RHEOLOGICAL BEHAVIOUR INVESTIGATION

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5.0 INTRODUCTION

Metal injection molding (MIM) is an advanced technology for processing net-shaped components that is experiencing commercial acceptance. In this process, a metal powder is mixed with an organic binder to produce a mixture, or feedstock, which has sufficiently low enough viscosity that can be molded using a high-pressure screw injection-molding machine [1, 2]. Once molded, the binder is removed from the components. This step is called debinding and can be performed by different techniques such as solvent debinding, thermal debinding, catalytic debinding, etc. [3]. In order to improve the brown part mechanical properties, the part will be sintered [4]. The process combines plastic injection molding technology to form the desired shapes and conventional powder metallurgy technology to sinter the molded parts. It is therefore capable of producing parts with complex shapes at relatively low processing cost [1, 5].

The major advantages of this manufacturing technology include high product density, more intricate shape, higher mechanical properties, and better surface finish than the traditional powder metallurgy products. Moreover, an inherent advantage of MIM is that the molding parts are hard enough to meet any needs for secondary machining. However, the acceptance for this process as a common production routine was extremely slow until recent years, but now it is gaining popularity due to some satisfactory understanding of several basic aspects of the process that have been achieved [6].

It is known that sinterable metal powder compact can be mixed with thermoplastic binders to form molding compounds and processed to form molded components by processes such as injection molding, extrusion or hot pressing. The successful of the processing depends upon powder characteristics, formulation of binders, good mixing and rheological behaviour, and proper filling of the mould [7].

The most important rheological property in MIM is viscosity, which relates shear stress to shear rate. It is well known that a high viscosity of a feedstock makes molding difficult [7; 8]. The particle size distribution, particle shape and the density of the powder also influence the viscosity of the molded part. The viscosity of the molding compact is also reduced by additives such as stearic acid and by plasticizers [9].

An experiment to study the influence of stearic acid addition on the properties of injection molded 316L stainless steel powder using a polyethylene glycol (PEG) and polymethyl methacrylate (PMMA) binder system was conducted by Mohd Alfian Omar [9]. The study found that the addition of small amounts of stearic acid in the formulation allows higher metal powder loading. Besides, it reduces the molding temperature of the feedstock while having unfavourable consequences of reducing the as-molded and as-leached strengths of the molding.

In addition, parameters such as flow behaviour indexes, n ; activation energy, E ; and moldability parameter, α are also

important in the feedstocks rheological investigation [6; 7; 10; 11; 12].

Consequently, Karatas et. al. [7] has conducted an investigation to the rheological properties of the ceramics feedstock, using polyethylene (PE) and three waxes (carnauba, bees wax and paraffin) mixed with steatite. The experiment concluded that the binder formulation and the feedstocks exhibits pseudo plastic flow behaviour and suitable for injection molded. The addition of steatite powder to the binder formulation increased the viscosity of the feedstocks.

The rheological behaviour of alumina feedstocks containing PEG, polyvinylbutyral (PVB) and stearic acid has been studied by Krauss et. al. [10]. Some of the feedstocks studied were pseudo plastic ($n < 0$). The results indicate that the feedstock containing lower powder loading displayed the best rheological behaviour.

Furthermore, experiment for evaluating the influence of TiC addition to the rheological behaviour and stability of 316L stainless steel powder injection molding feedstock has been presented by Khakbiz et. al. [11]. They found that the rheological behaviour of the feedstocks highly depends on the blend composition. The addition of TiC particles to the stainless steel powder increases the viscosity of feedstock at relatively low shear rates, i.e. $< 500 \text{ s}^{-1}$. Moreover, the feedstock instability increases, particularly at higher solid loading. Nevertheless, with increasing shear rate and temperature, the viscosity decreases and the instability of feedstocks improved.

Additionally, the investigation conducted by Faiz Ahmad [12] on the flow properties of composite mixes comprised of aluminum powder and glass fibers compounded into plastic binder shows the viscosity of the composite mixes decreases in the shear rate range required for powder injection molding. The optimum level of fiber content that would decrease the relative viscosity of the composite mix was also determined. Composite mixes containing longer fibers resulted in higher viscosity.

The present paper investigates the author's hypothesis that the PMMA powder has to be in the emulsion form before they are

mixed with another binders and powder metal. The authors postulated that, if PMMA were not in the emulsion form, it would be dispersed from the feedstock dough during granulation (crushing). Furthermore, the authors believed that emulsion has an ability to improve the feedstock paste homogeneity. In addition to the hypothesis, the non-emulsion PMMA enable the production of pseudo plastic feedstock but the thermal sensitivity is lesser than the one prepared with the emulsion PMMA. On the other hand, the compact prepared with the non-emulsion PMMA is weaker because PMMA, which will act as a backbone, was already dispersed out during granulation. However, it can still be injection molded as long as the flow behaviour index is less than one.

Moreover, literature [13] presents the influence of the PMMA content in the PMMA and PEG binder system. The study shows that reduction in the PMMA content allows injection molding to be carried out at a lower temperature, while having the unfavourable consequences of reducing the stiffness and the green and brown strengths of the molding. The feedstock in the investigation is prepared with PMMA emulsion. In addition, experiment presented in literature [9] was also prepared with PMMA emulsion but none of them explain the significance of the PMMA emulsion compared to fine powder PMMA.

5.1 EXPERIMENTAL PROCEDURE

Gas atomized stainless steel powder grade (SUS 316L) from ANVAL 316 of a mean size of 12 μm was used in the investigation. Table 5.1 shows the powder characteristic and Table 5.2 shows the chemical composition of the powder in the investigation.

Table 5.1 Stainless steel (SUS 316L) powder characteristic

Characteristics	
Identification	SUS 316L
Powder source	Anval 316 Stainless Steel, Sweden
Tap density, g/cm³	4.09
Apparent density, g/cm³	2.82
Pynometer density, g/cm³	7.96

Table 5.2 Stainless steel powder chemical composition

Elements	wt%
C	0.09
Si	0.32
Mn	0.80
P	0.041
S	0.016
Cr	16.40
Ni	12.40
Mo	2.31



Figure 5.1 Sigma type blade mixer

Combination of PEG, PMMA and stearic acid was used as a binder. The binder comprised of 73% of PEG; 25% of PMMA; and 2% stearic acid based on the volume fraction. The powder volume fraction was 61% and 65%, while the critical powder loading is 69 % [14]. The volume fraction of 61 % and 65 % of metal powder was mixed with the binders at 70 °C for 95 minutes using sigma type blade mixer as shown in Figure 5.1. Figure 5.2 shows the mixing sequence. Two types of feedstock were prepared; the first one is prepared with PMMA emulsion (ace61 and ace65). The PMMA was dissolved in acetone at 1 gram of PMMA for each 4 ml acetone. Nevertheless, the acetone evaporates during the mixing process and the PMMA emulsion will fully covers the powder particles matrix until the mixing process completed. The second feedstock was prepared without the PMMA emulsion (wo61 and wo65). Fine PMMA powder was dry mixed in the mixer with powder metal and stearic acid at the room temperature for 15 minutes before PEG was added into the mixture.

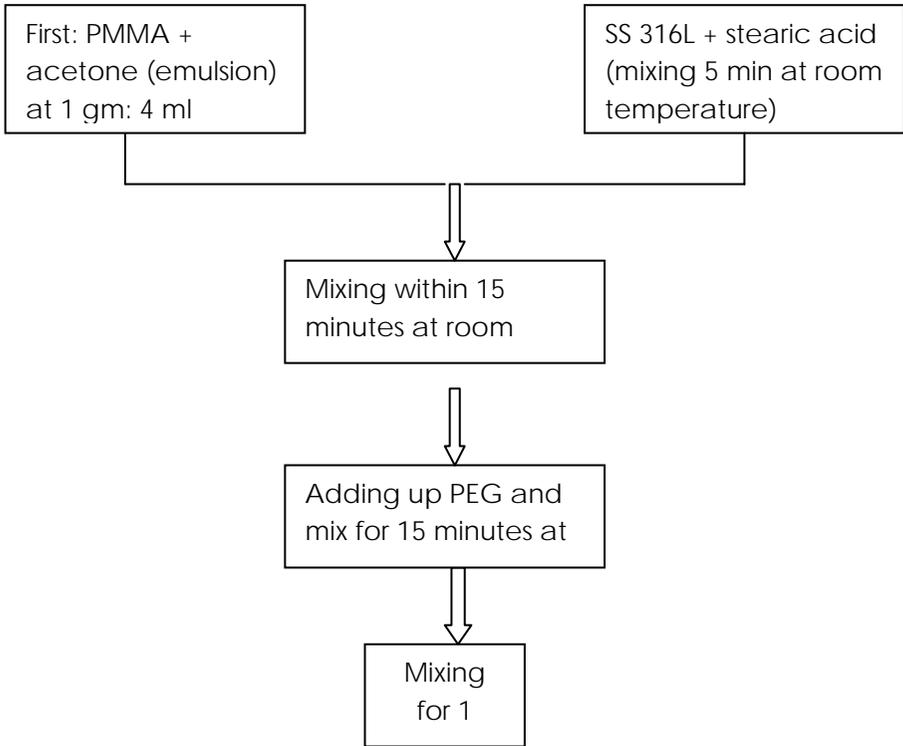


Figure 5.2 Feedstock mixing process flow chart

After mixing, the dough will be removed from the mixer and left at room temperature. Subsequently, when the dough temperature drops to 60 °C, the dough will be fed into a strong crusher for feedstock granulation.

In order to study the feedstock rheology properties, the rheology testing was conducted with CFT-500D Shimadzu flow tester capillary rheometer. In order to monitor flow over the shear rate range of 1000 to 10,000 s⁻¹, a die (L/D = 10) was attached to the bottom of the extruder barrel. The test was conducted at constant capillary temperature of 130 °C and the load applied to the tester was from 30 kgf to 60 kgf.

The barrel was filled with the feedstock and then pressed lightly with the piston, and allowed to attain thermal equilibrium. This required a period of 10-15 minutes. The pressure drop across the die was recorded in order to calculate the shear stress at the die wall. The flow rate through the capillary was calculated using the relation provided by Japanese Industrial Standard, JIS K7210 [15]:

$$Q = \frac{0.4}{t} (cm^3) \quad (1)$$

where t is the time for the piston to travel from 3 mm point to 7 mm point in the barrel. The shear rate, $\dot{\gamma}$ was calculated using the relation:

$$\dot{\gamma} = \frac{32Q}{\pi D^3} 10^3 (s^{-1}) \quad (2)$$

where D is the die diameter (1mm). The tester will display the viscosity (Pas), shear rate (s⁻¹) and the flow rate (cm³/s). The viscosity versus shear rate was plotted. The slope (n-1) as shown in equation (3) was calculated from the graph to determine the flow behaviour index, n for each mixture.

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

where η is the viscosity, K is the constant. The activation energy, E for the samples is determined using Arrhenius's equation [7; 8; 11]:

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

where R is the gas constant, T is the temperature, η is the mixture viscosity and shear rate and η_o is the viscosity at reference temperature. Large values of activation energy show a high sensitivity of viscosity to temperature.

5.2 RESULT AND DISCUSSION

5.2.1 Feedstock preparation

Figure 5.3(a) shows the feedstock prepared without PMMA emulsion and Figure 5.3(b) is the feedstock prepared with PMMA emulsion. Both feedstocks do not show any existence of acetone as it has evaporated during mixing.

The feedstock shown in Figure 5.3(a) remains in the powder form but is slightly coarser than the fresh powder metal due to the existence of PEG and stearic acid that cover the powder particles. On the other hand, feedstock prepared with the PMMA emulsion (Figure 5.3(b)) is in granule shape thus this feedstock is suitable to be injection molded with the screw extruder.



a) Feedstock without acetone

b) Feedstock with acetone

Figure 5.3 MIM feedstock

Feedstock shown in Figure 5.3(a) is not in a granular form, as PMMA is not covering the powder since PMMA is still in powder form. However, PEG and stearic acid are covering the metal powder since their melting temperatures are lower than the mixing temperature. On the other hand, feedstock in Figure 5.3(b) is in a granular form because PMMA emulsion is covering its powder-binders matrix.

5.2.2 Rheological investigation

Figure 5.4 shows viscosity as a function of shear rate. Generally, each feedstock exhibits pseudo plastic behaviour; however, feedstock ace61 exhibit lower viscosity and higher shear rate compared to other feedstocks. These are due to high amount of plastic fraction in the feedstock matrix. On the other hand, feedstock wo61 is more viscous compared to the ace61 feedstock. The same phenomena also happened to the wo65 feedstock, which is more viscous than the ace65 feedstock.

The feedstocks viscosity, η_0 at shear rate 1000 s^{-1} and temperature $130 \text{ }^\circ\text{C}$ is shown in Table 5.3. The feedstock wo65 shows the highest viscosity (229.46 Pas) at shear rate 1000 s^{-1} and the lowest is exhibited by ace61. However, the feedstocks viscosity at this shear rate is still lower than the MIM limit (1000 Pas) [1].

By comparing the plots shown in Figure 5.4, the ace61 feedstock demonstrates very low viscosity at very high shear rate. However, the author believed it was still possible to be injection molded as the shear rate shown in Figure 5.4 is within 100 to 10,000 s^{-1} [1; 8]. The ace61 viscosity is low compared to other feedstock due to the excess of binder in the matrix. The curve is also located near to the binder curve, showing that the metal powder less influences ace61. It seems that the binder is dominating the viscosity and shear rate of the metal powder.

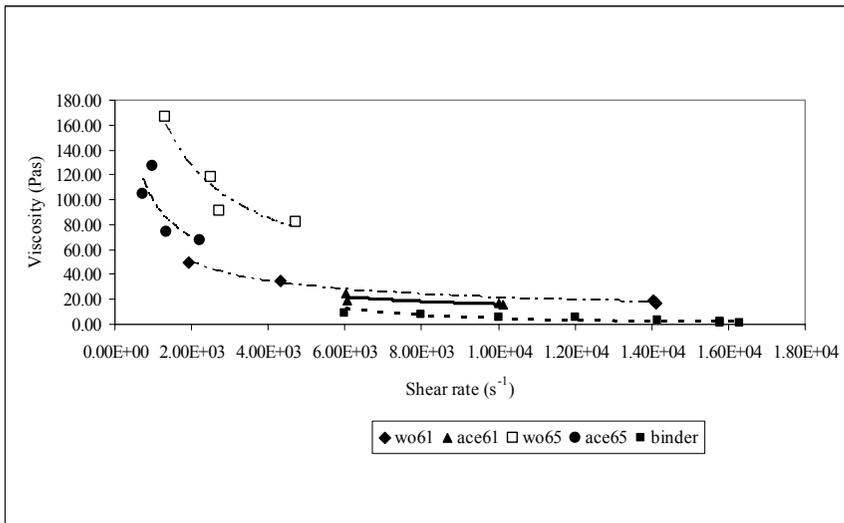


Figure 5.4 Feedstock and binder's viscosity as a function of shear rate at temperature 130°C

Table 5.3 Feedstock at shear rate 1000 s^{-1} temp $130 \text{ }^\circ\text{C}$

Feedstock	η_o(Pas)	E (kJ/mole)	n	α
w061	69.92	18.52	0.48	3.08
ace61	65.82	5.044	0.3905	9.7796
w065	229.46	2.322	0.424	6.6165
ace65	98.66	15.72	0.49	2.6269
Binder	424.78	n/a	-0.99	

Referring to Table 5.3, the w065 feedstock is more viscous than the ace65 feedstock. This is because the PMMA emulsion covers the binder-powder matrix of the ace65, while the w065 has only PEG and stearic acid. Stearic acid will act as a lubricant to the feedstock [9]. The PMMA powder was dispersed out from the dough during crushing. Thus the authors believe that the compact part produced with these feedstock (w061 and w065) might lost its strength after solvent bath debinding as PMMA is required to act as the back bone binder which will hold the powder particles until pre-sintering stage.

Flow activation energy of the tested feedstock as a function of shear rate at 1000 s^{-1} is shown in Figure 5.5. The gradients of the plot are E/R where the relationship is as shown by equation (4). The activation energy obtained from the graph shown in Figure 5.5 is listed in Table 5.3.

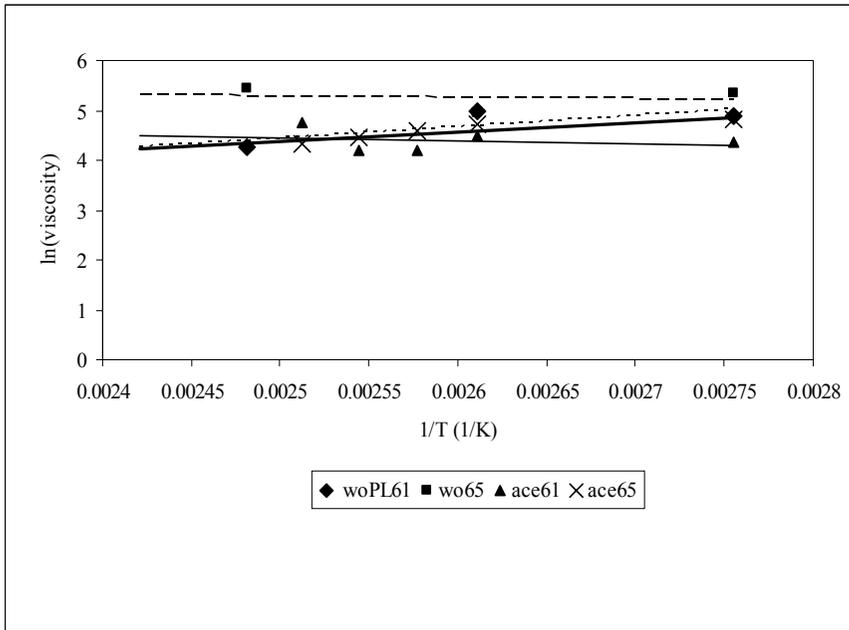


Figure 5.5 Feedstock correlation with temperatures

As shown in Table 5.3, the activation energy of wo61 is the highest. This shows that the wo61 viscosity is highly sensitive to temperature. Furthermore, the feedstock that is highly sensitive to temperature is also sensitive to pressure. As pressure increases, the feedstock becomes more viscous [1]. Thus, this is the reason why wo61 viscosity increases when the tester load is increased. When the feedstock is too sensitive, binder-powder separation might occur during rheology testing at high temperature and pressure. However, less sensitivity feedstock (less activation energy) will minimize stress concentration, cracks and distortion in the molded part [11]. Thus, ace61, wo65 and ace65 are suitable to be injection molded, as these feedstocks are less sensitive to temperatures.

Table 5.3 also shows the flow behaviour index, n which is smaller than 1 which indicates shear thinning occurs on the pseudo plastic materials. The value of n , which indicates the degree of shear sensitivity, gives an important insight about the rheological characteristics of MIM feedstocks. The lower the value of the flow behaviour index the more viscous dependence it is to the shear rate [11]. If the value of n is greater than 1, it indicates the behaviour of dilatants. In this case, powder and binder will separate under high pressure. However, a pseudo plastic system may also act as dilatants when subjected to a high shear rate [7]. The flow behaviour indexes for these feedstocks show good pseudo plastic behaviour.

Table 5.4 Flow behaviour index, n and activation energy, E from literatures

Literature	Feedstock formulation	n	Activation energy (kJ/mole)
Iriany [8]	Temp: 160 °C: 92.5 PW-30 PS-	0.36	28
	60 PP- 10 PE	0.3	29
	92.5 PW-40 PS- 50 PP- 10 PE	0.34	42
	92.5 PW-50 PS- 40 PP- 10 PE		
Yimin et. al. [16]	Temp: 150 °C: 79 PW-20 EVA -1	0.377	32.5
	SA	0.345	31.8
	79 PW-20 HDPE- 1 SA	0.319	22.0
	79 PW-10 EVA- 10 HDPE-1SA		

By comparing n and E in Table 5.3 (from the investigation) against the values from literatures (Table 5.4) shows that the values are significant and the authors believed that the feedstocks have an ability to serve as MIM feedstock. However, in comparing with Table 5.4, wo61 is much more sensitive to the temperature and pressure. In addition, comparison of wo65 to the literatures (Table 5.4) shows that wo65 is less sensitive and this might lead to difficulties in the molding process.

Moldability parameter, α of MIM feedstocks are calculated from equation (5) as proposed by Weir [7]:

$$\alpha = \frac{10^9 (n)}{\eta_o (E/R)} \quad (5)$$

where η_o is the apparent viscosity at the reference shear rate (1000 s^{-1}). The result obtained from Weir equation is tabulated in Table 5.3. On the other hand, Mutsuddy and Khan [17] studied the applicability of Weir model on ceramic powder feedstocks and reported that, due to the interactions between filler particles, the Weir model is not applicable onto such systems. According to Mutsuddy and Khan, fluidity at processing temperature is more related to moldability [17].

In the absence of problems such as jetting or high residual stresses, the higher value of α is desirable since feedstocks with low n values are prone to powder-binder separation. If $\alpha=1$ is assumed as a hypothetical reference feedstock [11], the relative values of examined feedstocks, the α values of examined feedstock at $130 \text{ }^\circ\text{C}$ at reference shear rate 1000 s^{-1} , would be seen in Table 5.3. The result shows that feedstocks are able to produce no defect compact since the α is optimum.

5.3 CONCLUSIONS

From the experiment carried out, it was concluded that the MIM feedstocks were of pseudo plastic flow behaviour and suitable for MIM. PMMA emulsion will help the existence of PMMA in the powder-binder matrix and thus reduce viscosity. The result shows that the ace61 and wo65 were less sensitive to temperature and pressure compared to wo61 and ace65. However, binder separation may possibly occur in ace61 because its flow behaviour index is the lowest. This is due to the excess binder in the matrix. ace65 is an optimum feedstock although the sensitivity is less than as shown in the literatures. The sensitivity of wo61 is possibly caused by the PEG and stearic acid that covers the metal powder while the existence of PMMA in ace61 reduces its sensitivity as the PMMA melting temperature is high ($\approx 170^{\circ}$ C). Although wo61 and wo65 exhibit pseudo plastic behaviour, these feedstocks are not suitable to be injection molded with screw type extruder.

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