Properties and Rheological Behavior of Nano-Sized Cemented Carbide Injection Molding Feedstocks with Different Percentages of Grain Growth Inhibitor

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***Abstract*—A homogenous distribution of powder particles and binders in metal injection molding (MIM) feedstock, and good flowability, are important characteristics as these help to reduce powder-binder separation and achieve isotropic reduction after sintering. To avoid problems in these areas, this paper focuses on determining feedstock properties and studying the effect of TaC powder as a grain growth inhibitor on the rheological behavior of MIM feedstock. A raw material of WC-6%Co, together with palm stearin and a polyethylene binder system, was used as feedstock, tailored with different TaC loadings of 0.4%, 0.8%, and 1.2% by weight. The homogenous feedstock, mixed by ball milling and with a Brabender mixer, was subjected to rheology testing at different temperatures. The results indicated that all feedstock formulations exhibited good pseudoplastic behavior within acceptable ranges in MIM, with a TaC content of 0.8 wt% giving the optimum rheological properties.**

***Index Terms*—MIM, feedstock, rheology, grain growth inhibitor**

I. Introduction

Metal injection molding (MIM) has proven to be a promising technology for producing cemented nanostructured carbides, tailored with grain growth inhibitors, for applications requiring particles with fine grain sizes below 1 µm [1]. In MIM, selected powders and a binder are initially mixed in the correct proportions (referred to as feedstock) and then injection molded into desired shapes. The binder is removed by debinding, and the sample is finally sintered at an elevated temperature to produce a high final density [2].

Feedstock preparation for MIM is a crucial step, since deficiencies in the quality of the feedstock cannot be corrected by subsequent processing adjustments. It is thus important that the feedstock is homogeneous and free of powder-binder separation and particle segregation. Furthermore, the formulation of a binder is an important characteristic since this promotes the fluidity and rigidity of the feedstock, especially during mixing, injection molding, and debinding [3], [4]. Besides this, there are additional requirements for MIM binder properties. For example, a low-viscosity feedstock is desirable for rapidly filling micro-details during injection molding, before the feedstock solidifies [5], [6]. It is well known that a high-viscosity feedstock makes molding difficult [7].

Feedstock characteristics can be determined by rheology testing, where the rheological behavior is measured in terms of viscosity, which relates to shear stress and shear rate. Thus, this study aims to discover the rheological properties of WC-Co with tantalum carbide, TaC, as grain growth inhibitor (GGI) and palm stearin, PS, and polyethylene, LDPE, as a binder component in producing WC-Co components via MIM technology. There is limited documentation on the rheological behavior of hard metals with a GGI and binder system.

II. Methodology

A. Starting Materials

The metal powder used in the study was WC-6%Co as the main constituent together with TaC at 0.4 wt%, 0.8 wt%, and 1.2 wt% as GGI. The characteristics and SEM images of the powder are as shown in Table I and Figure 1(a) and (b).

Manuscript received January 7, 2018; revised June 9, 2018.

doi: 10.18178/ijmerr.7.4.338-342

TABLE I. METAL POWDER DETAILS

Powder	WC-Co	TaC
Supplier	Vistec Technology Services Sdn. Bhd	Vistec Technology Services Sdn. Bhd
Grain Size	40–80 nm	950 nm
Morphology	Nearly spherical	Cubic
True Density	14.7 g/cm^3	13.9 g/cm^3

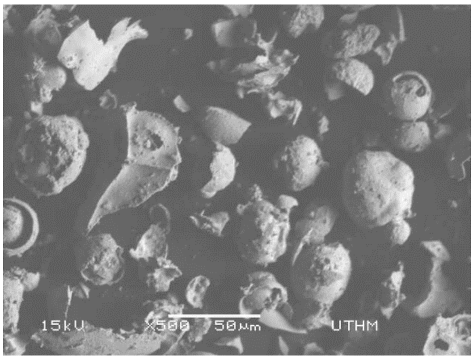


Figure 1(a). SEM image of WC-Co Powder

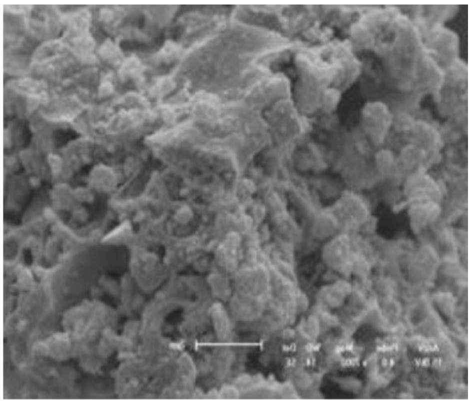


Figure 1(b). SEM image of TaC Powder

A multi-component binder system was used to prepare the feedstock. The characteristics of the binder components are given in Table II. The major fraction (60%) of the binder system consists of PS and the minor fraction (40%) consists of LDPE.

TABLE II. PROPERTIES OF BINDER COMPONENTS

Type	Density (g/cm^3)	T melt (℃)	T decompose (℃)
PS	0.891	54.3	398.5–598.8
LDPE	0.95	127	389.6–501.6

B. Critical Powder Loading

The critical powder loading of the WC-Co powder was measured according to the modified American Society for Testing and Materials Oil Absorption Test, ASTM D-28-31. A 0.5 ml volume of oleic acid was added every 5 minutes into the powder, and Equation (1) was adopted to obtain the correlation between the volume of oleic acid and the torque value (critical powder volume concentration, CPVC):

$$CPVC\ \% = \frac{V_f}{V_f + V_0} \times 100 \qquad (1)$$

V_f–Volume of powder $\quad V_o$–Volume of oleic acid

C. Feedstock Compounding

WC-Co powder was mixed with TaC powder by a dry ball milling method. To avoid or minimize contamination by other elements, the container and balls were treated with chemicals and dried in an oven for 48 hours. The overall weight of the balls used was 134.5 g, while the milling ratio was 0.4 wt%, 0.8 wt%, and 1.2 wt% of TaC powder with WC-Co powder. Mixing experiments were conducted in a Brabender Plastograph at 140 ℃ and a speed of 40 rpm for 1 hour or until a homogenous mixture was obtained.

D. Rheology Characterization

Feedstock behavior was tested by using an RH2000 rheometer to measure the viscosity resistance of the feedstock when melted materials pass through the die orifice. To monitor the flow, a die (L/D = 5) was attached to the bottom of the extruder barrel. The measurement was conducted at capillary temperatures of 130 ℃, 140 ℃, and 150 ℃. The following equations were used to quantify the rheological parameters:

$$\eta = K\,\gamma^{n-1} \qquad (2)$$

where η is the viscosity at a shear rate of γ, K is a constant, and n is a flow behavior index. The activation energy, E, for the samples is determined using the Arrhenius equation:

$$\eta = \eta_o \exp\frac{E}{RT} \qquad (3)$$

where R is the gas constant, T is the temperature in Kelvin units, η is the mixture viscosity, and η_o is the viscosity at a reference temperature. To establish a general molding index, Weir's model, proposed for polymers, was used, including the main parameters with respect to flow.

$$\alpha_{stv} = \frac{1}{\eta_o}\frac{\left|\frac{\partial \log\eta}{\partial \log\gamma}\right|}{\eta_o \frac{\partial \log\eta}{\partial 1/T}} \qquad (4)$$

where η is the viscosity, η_o is a reference viscosity, T is the temperature, γ is the shear rate, and α_{stv} is the rheological or moldability index. The above equation is simplified as shown below:

$$\alpha_{stv} = \frac{1}{\eta_o}\frac{|n-1|}{E/R} \qquad (5)$$

III. RESULTS AND DISCUSSION

A. Feedstock Characterization

The characteristics of the binder components were examined using differential scanning calorimetry and thermogravimetric analysis (TGA). The melting points of the binders, PS and PE, were 54.3 ℃ and 127 ℃, respectively, based on Figure 2(a) and (b). The mixing and molding temperatures should be set above the melting point of the highest melting component (LDPE 127 ℃) of the binder to ensure that all the binders will melt and the mold will be homogenously filled with the feedstock. The mold temperature should be kept below the melting point of the minor binder (PS 54.3 ℃) to prevent the molded part from sticking in the mold cavity [8]. The melting and decomposition temperatures given in Table II were used as a guideline during the mixing process.

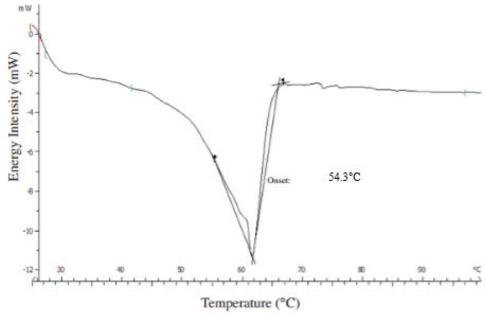


Figure 2(a). Palm stearin (PS)

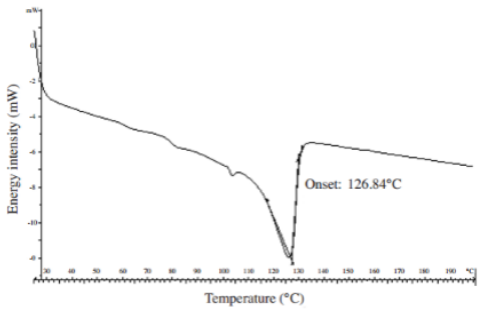


Figure 2(b). Polyethylene (LDPE)

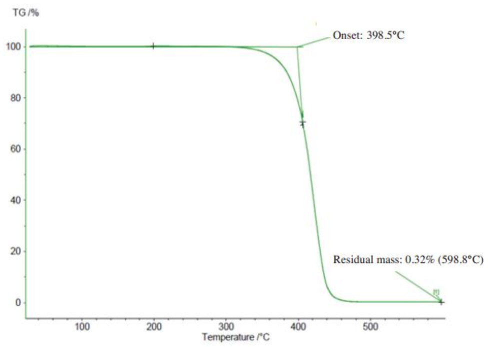


Figure 3(a). Palm stearin (PS)

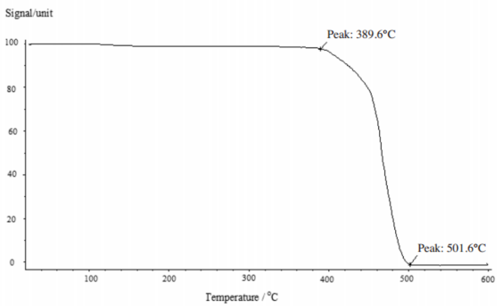


Figure 3(b). Polyethylene (LDPE)

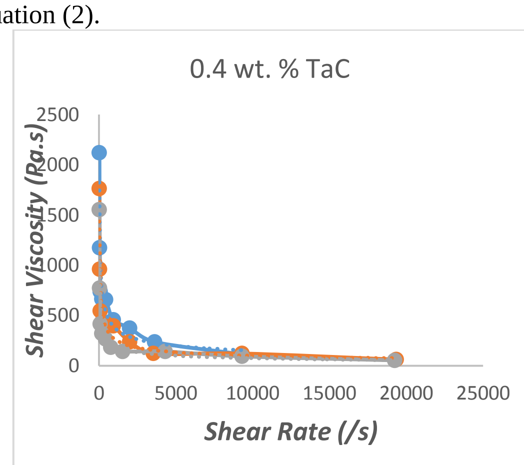
Based on the TGA curves shown in Figure 3(a) and (b), PS decomposed between 398.5 ℃ and 598.8 ℃, whereas LDPE decomposed between 398.6 ℃ and 501.6 ℃ [8]. German & Bose (1997) state that molding and mixture temperatures must be below the binder composition temperature to prevent binder degradation. TGA analysis showed that a wide decomposition range is important for fast debinding and a defect-free product. Luo et al. (2009) stated that the temperature should not be raised too quickly to avoid defects, such as bubbles and cracks.

The CPVC showed maximum torque evolution curves, which gave the critical powder loading 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 (1997) stated that the optimum powder loading is maintained at approximately 2–5% lower than the critical loading. This range will be used to produce feedstock and analyze the rheological characteristics [9]. The powder volume fraction was 43%, which was below the critical powder loading of 45%.

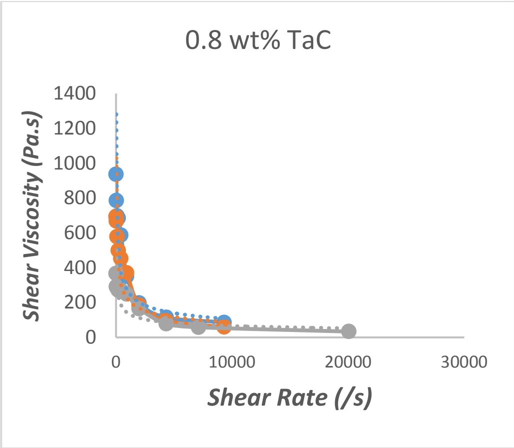
B. Rheological Properties

The rheological properties of the feedstock were evaluated based on the viscosity, shear sensitivity, and temperature sensitivity. The viscosity of the feedstock was significantly influenced by the particle size distribution, particle shape, and density of the powder [10]. Viscosity is also the single most important predictor of feedstock quality as it influences the success of the molding stage [11]. Binder selection is important for achieving a low viscosity, especially for micron-sized powders [12]. All the feedstock exhibited shear thinning or pseudoplastic behavior, which is desirable for MIM. This could be due to particle orientation and ordering with flow as well as breakage of particle agglomerates via release of the fluid binder [9], [13].

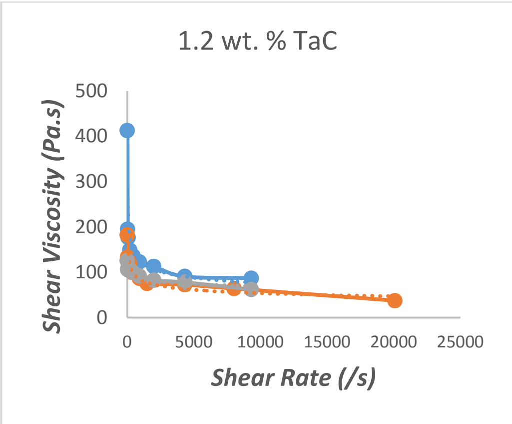
The line graphs plotted in Figure 4(a), (b), and (c) validate the relationship between viscosity and shear rate at 130 ℃, 140 ℃, and 150 ℃. These show that the viscosity of the feedstock decreases with increasing shear rate; this is known as pseudoplastic behavior and is consistent with the power-law equation shown as Equation (2).



(a)



(b)



(c)

Figure 4. Shear Viscosity vs Shear Rate graph for feedstocks with (a) 0.4 wt%, (b) 0.8 wt%, and (c) 1.2 wt% of GGI.

Table III summarizes the important rheological properties of the feedstocks, which are flow behavior index, *n*, activation energy, *E*, and moldability index, α_{stv}. Based on (1), *n* indicates the degree of shear sensitivity and pseudoplasticity. The lower the value of *n*, the quicker the viscosity of the feedstock changes with shear rate and exhibits shear thinning behavior. This higher shear sensitivity is important for producing a complex and delicate product, as this will provide a more stable viscosity during mold filling. Table III clearly shows values of *n* that are relatively high but lower than 1, which are suitable for MIM. However at high shear rates, a pseudoplastic system may act as a dilatant, whereby the powder and binder are separated under high pressure [10]. Defects such as cracks and voids normally occur where the sensitivity of the feedstock to shear is high (small *n*) during injection molding [14]. On average, the lowest value of *n* at 0.4 wt% indicates that the feedstock behavior depends on the shear rate, while other feedstocks show pseudoplastic behavior, as all the *n* values are below 1.

The activation energy, *E*, is another significant parameter used to evaluate the moldability of the feedstock. *E* reflects the dependence of the feedstock on thermal fluctuations that occur during injection from the injector nozzles to the mold cavity. High values of *E* may lead to premature freezing before the melt reaches the bottom of the mold cavity [14]. Based on Table III, 0.8 wt% exhibits a low value of *E*, which indicates that the viscosity is not particularly sensitive to temperature variation; thus, small fluctuations in temperature during molding will not cause sudden viscosity changes. *E* should be as small as possible to avoid abrupt viscosity changes that reduce the flowability of the feedstock and cause stress concentration, cracking, and distortion in the molded section. Large activation energies indicate that viscosity is highly sensitive to temperature. However, E depends on the binder and feedstock compositions. Liu et al. [5], [6] stated that low viscosity is desirable for filling micro-details and ensuring low activation energy [7].

TABLE III. SUMMARY OF RHEOLOGY PARAMETERS FOR THREE DIFFERENT COMPOSITIONS

Feedstock	Temperature, ℃	Flow Behavior Index, (*N*)	Activation Energy, *E*	Moldability Index, α_{stv}
0.4 wt%	130	0.599	23.2	1695.25
	140	0.57	23.2	2918.59
	150	0.577	23.2	3373.09
0.8 wt%	130	0.599	23.1	2194.14
	140	0.606	23.1	3171.11
	150	0.676	23.1	5880.31
1.2 wt%	130	0.792	23.6	2375.81
	140	0.81	23.6	3566.40
	150	0.905	23.6	5181.49

A higher moldability index, α_{stv}, is associated with lower values of *n* and *E*, according to Equation (5), indicating optimum feedstock rheological properties. Specifically, the higher the value of α_{stv}, the better the rheological properties. According to Table III, 0.8 wt% feedstock gives the highest moldability index and is therefore the best candidate from a rheological viewpoint. Furthermore, this is the best powder-binder ratio for ensuring rapid powder repacking and binder molecule orientation during molding. Conversely, 0.4 wt% gives the lowest moldability index and thus could be considered as the least suitable candidate for injection molding in terms of flowability.

IV. CONCLUSION

The main objective is to study the rheological behavior of WC-Co powder with TaC nanopowder as GGI. The feedstock is mixed with PS and PE binder at a powder loading of 43 vol.%, and the rheological properties are verified as shown in Table III. Besides, rheological testing of WC-Co with TaC feedstock was conducted in terms of viscosity, flow behavior index, activation energy, and rheological index at three different temperatures of 130 ℃, 140 ℃, and 150 ℃. Based on the rheological properties, all the feedstocks show pseudoplastic behavior, making them suitable for injection molding, and no dilatant behavior is observed, indicating no powder-binder separation. Conversely, according to the characterization described above, 0.4 wt% would be better than 0.8 wt% and 1.2 wt% based on its having the lowest viscosity for easier flowability and a low flow behavior exponent, *n*, indicating slow viscosity changes with the shear rate. However, the low activation energy at 0.8 wt% is desirable for injection as this lowers the sensitivity of viscosity to temperature variation. Thus, 0.8 wt% with a higher moldability index has better rheological properties compared to 0.4 wt% and 1.2 wt%.

Acknowledgements

The authors would like to thank the Ministry of Higher Education Malaysia and Universiti Tun Hussein Onn Malaysia for a research grant (FRGS-1590) and laboratory apparatus provided at AMMC lab.

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