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Critical Powder Loading and the Rheology of Nanosized Cemented Carbide with Titanium Carbide as Grain Growth Inhibitor for Injection Molding

S.N.A. Shahbudin*, Sri Yulis M Amin, M.H. Othman, M.H.I. Ibrahim

Faculty of Mechanical and Manufacturing Engineering, University Tun Hussein Onn Malaysia, 86400 Parit Raja, Johor, MALAYSIA.

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Abstract: The purpose of this paper is to determine the critical powder loading of WC-Co and to study the effect of TiC powder on the rheological behavior of MIM feedstock. WC-TiC-6Co metal powder was taken as raw material. 60% (mass fraction) palm stearin and 40% low density polyethylene were employed as binders to prepare injection feedstock. Three feedstocks were prepared at different TiC % loadings of 0.5, 0.75, and 1.0 (by weight). A homogeneous metal powders is formed by using ball mill mixer and mixed together with binder system by using Brabender mixer. Based on the result obtained, it was concluded that feedstock with 0.75 wt. % TiC powder show a good pseudo-plastic behavior within acceptable ranges in MIM.

Keywords: Injection molding, cemented carbide, grain growth inhibitor, rheological properties

1. Introduction

Although over 70 years old, the WC-Co hardmetals keep on gaining attention for high performance construction and wear parts including cutting, mining and chipless forming tools [1]. However, they can only be made by powder metallurgy forming process. Therefore, with a great technique and cost advantages, powder injection molding (PIM) is the most suitable method to produce complex shapes of cemented carbide components [2]. Basically, PIM was adjusted from metal injection molding process (MIM) [3]. MIM process consists of four main steps: mixing, injection molding, debinding, and sintering. For the first step, powder was mixed with a binder to form a feedstock at a selected volume ratio is molded in order to produce a ‘‘green’’ compact. Some of the green part has to be identified in terms of density, strength, defect, etc [4]. The binder system keeps the particles in place during injection molding. The debinding stage is where the binder system is partially removed from the compact. In the final step, sintering was done aimed at producing the desired mechanical traits [5].

The mechanical properties of these products were depending on their composition and microstructure. Thus, it is important to retain the average grain size of WC during sintering process since the grain size of the product will be reflected toward the final product properties such as hardness, strength, wear resistance and so on [6]. In cemented carbides, there are several parameters that affect the growth rate including inhibitor concentration which is the most frequently studied parameter. However, above a certain concentration no additional grain growth inhibition is achieved [7]. Grain growth inhibitor (GGI) can controlled the growth of metal grain. In the cemented carbide industry, the most commonly used GGI based on the overall effectiveness which has been shown to be VC>Cr3C2>NbC>TaC>TiC>Zr/HfC in order from the most to the least [7, 8].

Table 1: General equations for rheology parameters, associated with their main functions [17]

Parameter	Equation no.	Function
Flow behaviour index, *n*	1) $\eta = K\gamma^{n-1}$	indicates degree of shear sensitivity
Activation energy, *E*	2) $\eta = \eta_o \exp (E / RT)$	Indicates the degree of temperature dependence to the viscosity
Modability index, α	3) $\alpha = \frac{10^9 \lvert (n\text{-}1) \rvert}{\eta_o (E / RT)}$	Indicates the feedstocks ability to be injected

Where η is the viscosity, K is the constant, γ the apparent shear rate, ηo is the apparent viscosity at a reference shear rate, R is the gas constant and T is the temperature.

In PIM, high powder loading can give mixing process some difficulties thus increase the viscosity of the feedstock. But, if the powders volume content is too high, there is not sufficient binder to completely fill the die cavity mold, thus the powder volume loading cannot be increased over than a limited value [9]. Smaller compact volume shrinkage and easier dimension tolerance control

*Corresponding author: snshahmira93@gmail.com

can be obtained by using a high powder loading which is very important during mass process. But too high powder loading is also unsuitable because it will lead to very high feedstock viscosity producing failures of injection moulding [10]. Thus, to prevent undesirable voids during injection molding stage, the determination of an optimal powder volume loading is compulsory [9, 10]. It is very crucial to avoid the defect such as crack and distortions during molding stage where feedstocks are injected into the die cavity [10]. Mold filling by the feedstock is dependent on the viscous flow of the mixture into the mould cavity. Rheological analysis can be used to quantify the stability of the feedstock during the molding process [11].

The apparent viscosity is not constant at given temperature and pressure but is dependent on flow condition such as flow geometry and shear rate [12]. When the viscosity behavior is inversely proportional to the shear rate is favorable for the shape forming. Therefore, the rheological behavior and stability of feedstock are the lead factor for successful manufacturing of PIM [13]. In the present work, the critical powder loading concentration were investigating by using brabender plastograph mixer and analyzing the viscosity behavior of the feedstock. Rheology analysis with different loading of TiC was conducted to study the effect of them on the rheological properties and determine the feedstock's pseudoplastic nature and mold reliability.

2. Method

In this study, the powders used to prepare the feedstock were WC-6Co and titanium carbide which act as grain growth inhibitor. For binder formulations, palm stearin (PS) and low density polyethylene (LDPE) were used. Tables 1 and 2 show the characteristics of the starting materials.

Table 2: Powder characteristics

Powder	Particle size (μm)	True density (g/cm^3)	Shape
WC-6Co	40-80	14.7	spherical
TiC	40-60	4.93	spherical

Table 3: The characteristics of the binder component

Type of polymer	Density (g/cm^3)	Melting Temp (C)	Decomposition Temp (C)
PS	0.89	61.4	398.5-598.8
LDPE	0.95	127	389.6-501.6

Table 4: The composition of feedstocks

Feedstock	TiC content (wt %)	Solid loading (vol %)
WC-0.50TiC-6Co	0.5	45
WC-0.75TiC-6Co	0.75	45
WC-1.0TiC-6Co	1.0	45

The feedstocks were prepared by using the same amount of binder system, mixed together with the WC-6Co and TiC powders. Mixing homogeneity is another important feedstock parameter. The WC-6Co and TiC powders was premixed by using milling process for about an hour to achieve a homogeneous feedstock. Then, a mixing process of powder and binder system is conducted by using Brabender mixer at a temperature of 140 °C and a mixing speed of 40 rpm.

2.1 Critical Powder Volume Concentration

The critical powder volume concentration (CPVC) of the WC-Co powder was compulsory to be measured for determine the optimal solids loading for each feedstock. The testing method followed ASTM D-28-31 (American Society for Testing and Materials Oil Absorption Test) by using Brabender measuring mixture (W50 EHT). Oleic acid oil was added until the torque value has passed through the peak value during mixing process before dropped significantly. By using the computerized data acquisitio'n system, the torque value is continuously recorded as a function of time. The CPVC value is calculated according to the following equation corresponding to the peak value of the torque based on the oil content and volume of the binder. The CPVC value is calculated according to the following equation [14].

$$CPVC\% = \frac{Volume\ of\ powder}{Volume\ of\ powder + Volume\ of\ oil} \times 100 \qquad (1)$$

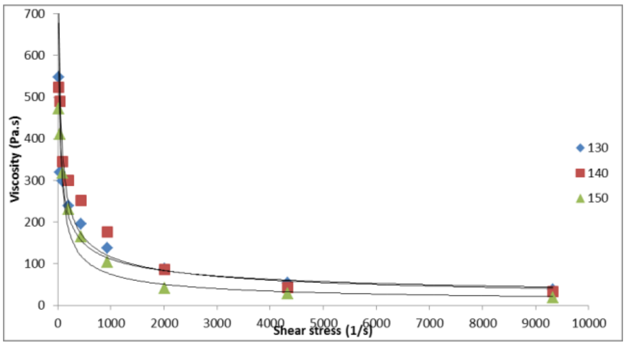
2.2 Rheological Measurement

By using Rosand RH2000 capillary rheometer, the rheological behavior of the feedstock was measured. This is to examine the flow characteristic melted materials pass through an orifice which measures the resistance of viscosity. The test was conducted with different temperature of capillary temperatures (130°C, 140°C and 150°C) at a constant powder loading of 45% with the different TiC wt. %.

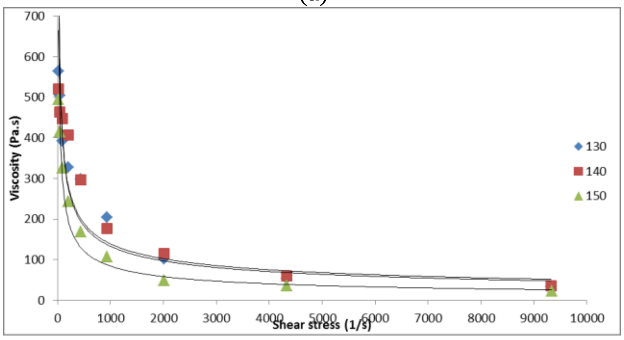
3. Results and Discussion

In PIM, determination of the critical powder loading was a key factor where the powder particle is perfectly packed and all spaces between particles are filled with binder. Fig. 1 shows the torque evolution of the critical solid loading for the WC-Co powder during testing. While using oleic acid to serve as a binder, torque value increase with addition of powder. The excess powder is no longer part of the powder-binder mixture shows when the torque value gradually decreased when the critical solid loading was reached, which leads to reduced cohesion mixture [15]. In preparing feedstock with optimal powder loading, the powder content should be less than the critical value (i.e. 2 to 5% lower than the critical value) where the feedstock in mold cavity are easy to flow with the excess binder [16]. Based on the result, optimal solid loading was at 42, 43, 44 and 45%. Since the powder used was not milled beforehand, the value obtained is similar by previous study [17], who stated that 46 vol. % of critical solid loading is obtained due to unmill metal powder. This is because; milling process enhances the maximum powder loading of the feedstock.

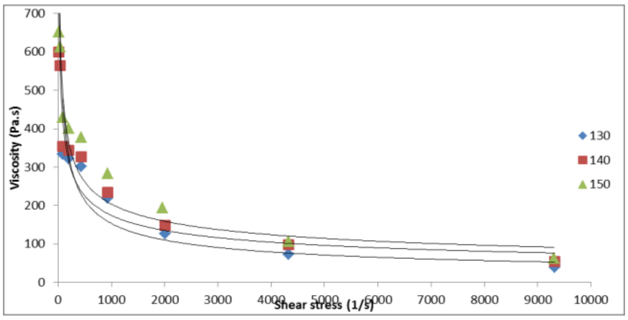
Determination of rheological behaviour of feedstocks was a crucial step before a prepared mixture is injected. This characterization is currently the prime approach to predict the flow ability of feedstocks during injection molding. Viscosity variation with shear rate for three feedstocks prepared with different amount of TiC wt. % added at a powder loading of 45 vol.% with a different temperature used are shown in Figure 2(a), 2(b), and 2(c). All the feedstocks exhibit a shear thinning or pseudo-plastic behavior as seen in the figure below, which is common for PIM feedstocks. This might cause by a breakage of particle agglomerates with release of fluid binder and ordering with flow as well [18]. In a non-Newtonian fluid, viscosity generally varies depending on shear rate.



(a)



(b)



(c)

Fig. 1 Relation between viscosity and shear rate in different wt% of TiC: (a) 0.5wt%, (b) 0.75wt%, and (c) 1.0wt%.

Figure 2(a), 2(b), and 2(c) shows the viscosity of 0.5wt%, 0.75wt% and 1.0wt% of TiC powder added in feedstock respectively. As observed in all Figure 2 above, as expected. The temperature affects the viscosity. The viscosity at high temperatures are tend to be lower than at low temperatures. Feedstock viscosity decreases as shear rate increases at 150°C. During heating, viscosity is decreased with higher temperature as powder volume reduced from the release of the molecular chain and larger binder expansion [19]. Powder and binder segregation potential during injection is high at high temperature and high shear rate with a low powder loading of feedstock. Additional of TiC powder into the mixture exhibited higher viscosity in the composite feedstocks, particularly at lower shear rates. A non-linear flow behavior of the composite feedstocks, i.e. a sudden drop in viscosity as the shear rate increases, is also noticeable.

The flow behavior index, *n*, indicates the degree of sensitivity of viscosity against shear rate. We determined *n* values from the slope of logarithmic plots of shear stress versus shear rate. The lower the value of *n*, the more sensitive is the viscosity versus shear rate [20]. This characteristic or a pseudoplastic behaviour is desirable in PIM because it can help fill the mold without creating defects [21]. The average results of *n* value are presented in Table 4. The flow behavior index decreases with addition of TiC particles, particularly at the higher temperature. Nevertheless, at higher shear rate, the effect of TiC addition was found to be only marginal. When the TiC loading increased to 1.0 wt. %, the influence of TiC is noticeable, somehow similar to that of the low shear rate results. When TiC% increases, the n value decreases. This similar behaviour is described by other authors with different metal feedstocks [22]. However, a very low *n* value can cause molding defects. In this case, the feedstock at 150°C showed the best properties because it has the highest value of *n* or the lowest sensitivity to shear thinning behavior for 0.5wt.% and 0.75 wt.%.

The activation energy, *E* is another important characteristic of PIM feedstock which indicates the degree of the dependence of temperature to viscosity. Thus, a strong temperature- dependence of the molding is shows high values of *E* resulting in a sudden viscosity change causing defects in the molded parts. In contrast, feedstock with less activation energy (less sensitivity to temperature) will minimize stress concentration, cracks and distortion in the molded part, thus suitable for injection molding. Based on Table 5, feedstock with 1.0 wt. % of TiC is the best rheological properties in term of flow. Sudden viscosity change will happen with any small fluctuation of temperature during molding if the viscosity is very sensitive to the temperature variation. The sensitivity of shear viscosity to temperature has implication on the choice of processing conditions as well as on the quality of the final product [23].

Besides that, modability index, α indicates the best powder binder ratio to get quick powder repacking and binder molecule orientation during molding thus feedstock with low α values will be prone to powder-binder separation. The higher value of α, the better the rheological properties. As shown, all the feedstock used showed high α, indicating that minimal compact defects will be produced. According to the Table 5, 0.5wt% feedstock using 150ºC gives the highest α and therefore it would be the best candidate from a rheological point of view. It is known that a feedstock viscosity with low temperature sensitivity is desire. In the present work, the influence of TiC addition on the rheological behavior of WC-6Co feedstock was evaluated. The feedstock with a higher value of α with low n values is prone to powder-binder separation. Generally, the influence of shear rate on enhancement of the defined index is noticeable.

Table 5: Summary of the rheology properties of feedstock at shear rate 1000 s^{-1}.

Feedstock (% of TiC)	Temp (ºC)	Flow behaviour index, *n*	Activation energy *E* (kJ/mol)	Modability index α
0.5	130	0.42	39.48	789.14
	140	0.47	39.48	852.67
	150	0.56	39.48	1591.92
0.75	130	0.46	37.68	764.10
	140	0.45	37.68	708.18
	150	0.53	37.68	1386.13
1.0	130	0.48	23.40	1103.75
	140	0.37	23.40	756.13
	150	0.36	23.40	627.38

4. Summary

This paper summarizes experimental investigations carried out on early stage of PIM process on WC-6Co metal powder. From the torque analysis, the critical powder loading spotted for the WC-6Co powder is 47%. Thus, the optimal powder loading used is 45% for powder–binder mixture. The rheological behavior of feedstock composed of WC-6Co and TiC powder were investigated at different processing temperature. Based on the rheological properties, it was concluded that under different temperatures and amount of TiC added, the feedstocks possess different rheological characteristics. All feedstock exhibits shear thinning behavior or pseudo plastic which is suitable for injected molding. The addition of TiC powder increase viscosity of WC-Co feedstock at lower shear rate show good pseudoplastic behavior. However, the best feedstock obtained is at 0.75wt % TiC powder since it has desirable properties such as moderately high *n*, low E and high modability index.

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