POWDER INJECTION MOLDING OF CU/GRAPHENE COMPOSITE: RHEOLOGICAL PROPERTIES

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ABSTRACT: Powder injection molding (PIM) comes with several benefits, namely, great precision, low cost suitability and high production rate, for metal and ceramics. Mostly compacting and coating process were used for metal composite and only a few studies report the use of an injection process as their processing technique, due to that only few data available related to rheological behavior of Cu/GNp composite. Feedstock rheological behavior needs to be determined in order to avoid any non-homogeneous mixture between powder and binder that may result in powder and binder separation during the injection molding process. This study is focused on rheological properties of Cu/GNp composite produced through PIM. The critical powder loading percentage obtained are 64 % for all 3 compositions; Cu/GNps (0.5, 1.0 and 1.5) vol.%. The optimum powder loading chosen for this study is 62% and within 2-5% below than critical powder loading. For rheological studies Shimadzu Flow Tester CFT-500D capillary rheometer was used. Based on the obtained result, it shows that the overall shear rate and viscosity are within the PIM process recommended range. All tested composition shows pseudoplastic behavior and green part was successfully injected without any physical defect.

KEYWORDS: *Copper; Graphene; Powder Injection Molding; Rheology*

1.0 INTRODUCTION

With an exponential growth in the demand for higher capability electronic products, greater thermal conductivity and heat dissipation components are needed to support the merging of new devices. Therefore, a challenging objective is to develop a material that demonstrates suitable thermal properties and is able to withstand the requirements of today's modern electronic products [1]. Copper (Cu) nanocomposite have shown enormous growth during the past decade, attributable to its enhanced mechanical, electrical and thermal properties, leading to numerous electronic applications [2]. Graphene is considered a perfect reinforcement for MMCs due to its exceptional properties: high thermal conductivity, high young modulus and high tensile stress [3]. Graphene also been used as fillers in numerous application such as electronic devices, sensors and nanocomposites [4-6]. Furthermore, additional of Graphene Nanoplatelets (GNp) in Cu matrix shows better performance at higher temperatures. GNp has showed great thermal conductivity of about 5000 W/mK and tremendous mechanical properties with Young's modulus of 1 TPa [7-8]. Moreover, graphene 2D structure have higher surface area than graphite or CNT [9].

Basically, most of graphene reinforced composited such as Al, Cu or Mg were prepared by using powder metallurgy technique. The process normally has 3 steps; mixing, compacting and sintering. Most of them use compacting method and only some cases use compacting simultaneously with another method compare to powder injection molding (PIM) [3]. PIM also one of powder metallurgy technique that has the potential to produce at low cost and with a high volume process that can satisfy geometry and property requirements [10]. PIM process usually started with a mixing process, combining powder and binder to form feedstock. Next, the feedstock will go through injection molding process to produce green parts. After that, the debinding process consists of solvent and thermal process, used to remove the binder from injected sample. According to previous research, polyethylene glycol (PEG) / polymethyl methacrylate acrylic (PMMA) / stearic acid (SA) binder systems are the most widely used binder systems due to their non-toxicity and commercial availability [10-12]. Finally, the sintering process is used to obtain the final material. However, before the injection molding process, rheological behavior needs to be determined in order to avoid any non-homogeneous mixture of feedstock that may resulting in powder and binder separation during the injection molding process. Furthermore, it can potentially failing the green part, causing in defect such as warpage or cracking during debinding and sintering, and finally will decrease final product mechanical and physical properties [13]. Moreover, current research has demonstrated that viscosity and thermal conductivity are crucial parameters for evaluating heat transfer in a nanofluid system [14].

The lack of data available on Cu/GNp produced through powder injection molding was the motivation to analyze the effect of flow behavior of feedstock with the addition of GNps content. Another aim is to determine the suitability of the feedstock for PIM process, as well as the appropriate temperature required.

2.0 METHODOLOGY

2.1 Materials

The metal powder used in the study is gas atomized copper powder supplied by Sandvik Materials Technology and the fillers employed in this study; is graphene nanoplatelets supplied by XG Sciences, Inc., both material characteristics are presented in Table 1.

Table 1: Characteristics of copper powder and graphene nanoplates

Properties	Materials pre-processing	
	Copper powder	Graphene nanoplatets
Product name	Copper Powder	Graphene Nanoplatelets (XGNp – M grade)
Identification	Cu	GNp
Powder source	Sandvik Osprey LTD, UK	XG Sciences, Inc.
Color	Brown	Black
Powder mean diameter (μm)	>22	5 - 25
Density	8.93 g/cm^3	2.2 g/cm^3

The binder system consists of polyethylene glycol (PEG) as the main element, polymethyl methacrylate (PMMA) as the backbone polymer, and stearic acid (SA) as the surface-active agent and lubricant to feedstock in order to improve powder wetting. The binder properties are stated in Table 2.

Table 2: Binder Properties

Material	Polyethylene Glycol (PEG)	Polymethyl metacrylate (PMMA)	Stearic Acid (SA)
Density (g/cm^3)	1.21	1.16	0.96
Melting Point (°C)	61-66	160	67-69
Composition (%)	73	25	2

FESEM micrograph of Cu powder shown in Figure 1, the particles are in spherical shape. Meanwhile, the GNps in Figure 2 shows a flake shape.

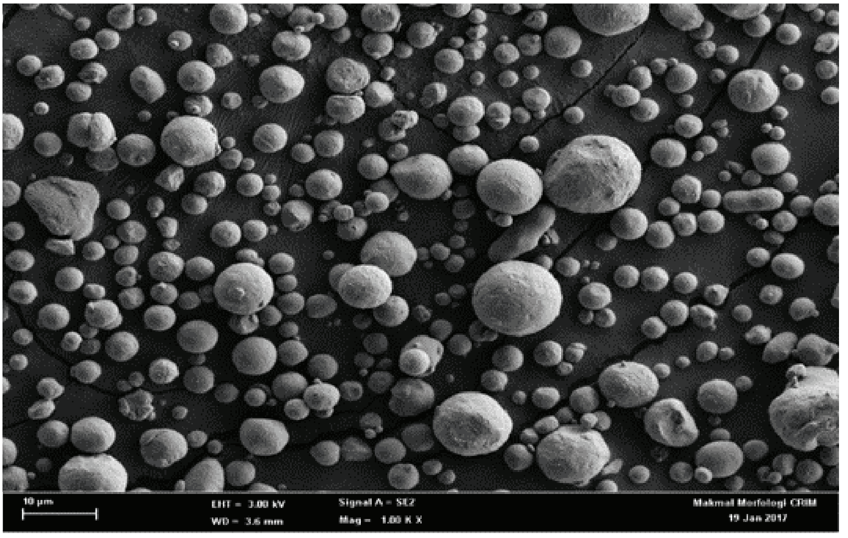

Figure 1: FESEM of Copper powder

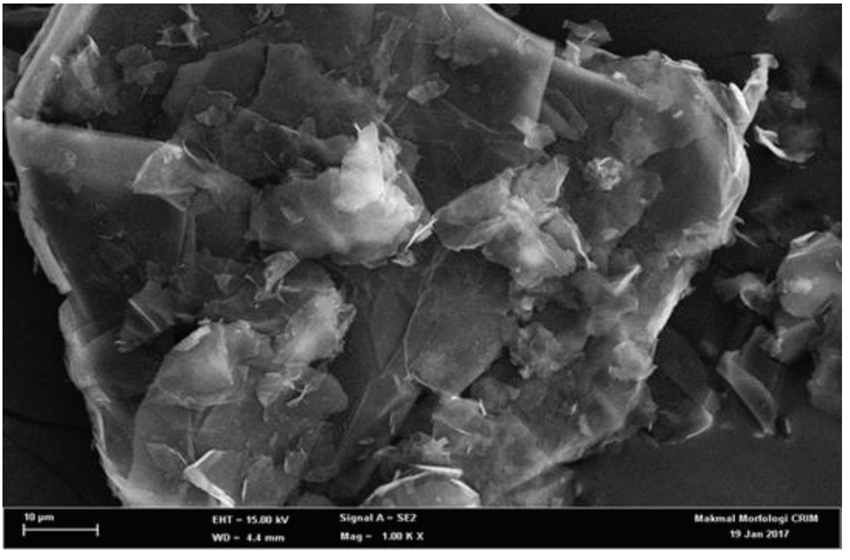

Figure 2: FESEM of Graphene Nanoplatelets

2.2 Critical Powder Loading

Three compositions were used in this study, namely, Cu/GNps 0.5 vol.%, 1.0 vol.% and 1.5 vol.%. The optimum powder to binder ratio can be determine with critical powder loading, it indicates the maximum powder and binder ratio so that the material can mix homogeneously and injected without any problem. The critical powder loading was tested using a Brabender mixer, as presented in Figure 3. The critical powder loading can be determined from critical powder volume percentage (CPVP), it shows the maximum torque evolution curves that state the maximum powder loading percentage for the material. Throughout the process, oleic acid was introduced, and the process was stopped once the graph value started to drop with the addition of oleic acid. The oleic acid acts as binder volume during critical powder loading test. The volume of oleic acid used was 1ml for every 3 minutes.

Figure 3: Brabender mixer

2.3 Feedstock Preparation and Rheology

Three types of binders were utilized in this study; PEG (73 vol.%), PMMA (25 vol.%) and SA (2 vol.%). The powder loading used was 62%, that is, 2-5% lower than the measured CPVP by the Brabender Mixer. Before preparation of the feedstock, in order to achieve a homogeneous dispersion of GNps in Cu matrix, several steps were carried out. Firstly, GNps went through a sonication process. During the process, GNp was submerged in distilled water and placed in a bath sonication machine, the solution was sonicated at 55°C for 1 hour. In order to filter out the distilled water after the sonication process, the solution was dried in a dry oven at 100°C for 18 hours. Next, Cu powder and the dried GNps was mixed using a planetary ball mill Pulverisette 6. The milling speed was set to 100 rpm, and milled for 4 hours, since Chu et al. [15] demonstrates that this was the optimal parameter for Cu/GNps composites. Finally, the milled Cu/GNp powder and binder were mixed together in a Brabender mixer for 1 hour with rotation speed of 40 rpm and the mixing temperature was set at 150°C to form a feedstock. The flow behavior of all three compositions was calculated using a capillary rheometer Shimadzu CFT-500D at several temperatures of 130, 150 and 170°C, where the load was in the range of 30 kg to 100 kg.

3.0 RESULTS AND DISCUSSION

3.1 Critical Powder Loading

Based on the critical powder loading result in Table 2, it shows that the critical powder volume percentage is 64% for all 3 compositions; Cu/GNp 0.5 vol.%, Cu/GNp 1.0 vol.% and Cu/GNp 1.5 vol.%. A greater powder loading is good in term of holding the material, as it can improve sintering and minimizes shrinkage. However, with a high powder loading, the feedstock will be hard to mix and causing an inhomogeneous mixture, so that, the optimum powder loading should be 2~5% lesser than the critical powder loading. As shown in Table 2, the powder loading range for all 3 compositions is 59%, 61% and 62%. The optimum powder loading shows optimum powder to binder ratio so that the materials can mix homogeneously and injected without any problem. The optimum powder selected for this study is 62% due to the value are nearest to the critical powder loading. For all 3 compositions, the powder vol% used is 61.5 vol% Cu and 0.5 vol.% GNp for Cu/GNp 0.5 vol.%, 61.0 vol% Cu and 1.0 vol.% GNp for Cu/GNp 0.5 vol.% and 60.5 vol% Cu and 1.5 vol.% GNp for Cu/GNp 0.5 vol.%.

Table 2: Critical powder loading for the compositions

Composition	Graphene (vol. %)	Critical Powder loading (vol.%)	Powder Loading Range (vol.%)
Cu/GNp 0.5 vol.%	0.5	64	59, 61, 62
Cu/GNp 1.0 vol.%	1.0	64	59, 61, 62
Cu/GNp 1.5 vol.%	1.5	64	59, 61, 62

3.2 Rheology

In order to reduce segregation during the injection process and to obtain an isotropic shrinkage after sintering, it is crucial to have a homogenous scattering of the powder particles and binder in feedstock [16]. All 3 feedstocks with different GNps content (0.5 vol.%, 1.0 vol.% and 1.5 vol.%) used the same powder loading (62%) for the test. The results show that all 3 feedstocks display a shear thinning or pseudoplastic behavior, which is a good criteria in PIM. Figures 4, 5 and 6 illustrate the variation of viscosity as the shear rate increases at Cu/GNp 0.5 vol.%, 1.0 vol.% and 1.5 vol.% for temperatures of 130°C, 150°C and 170°C.

At 130°C, the viscosity for Cu/GNp 0.5 vol.% is 155 – 380 Pa.s; for 1.0 vol%, the viscosity is 150 – 350 Pa.s, and for 1.5 vol.%, the viscosity is 170 – 400 Pa.s. This indicates that at this temperature the viscosity of all 3 feedstocks is nearly the same. At 150°C, the viscosity for Cu/GNp 0.5 vol.% is 60 – 160 Pa.s; for 1.0 vol.% the viscosity is 90 – 194 Pa.s; and for 1.5 vol.% the viscosity is 98 – 211 Pa.s. This shows that at this temperature, the viscosity of each feedstock increased with the addition of GNp content. The viscosity for 1.0 vol.% increased 21 %; and that for 1.5 vol.% increased 32%, compared to 0.5 vol.%. This may be effect of GNp large surface area. Lastly, at 170°C, the viscosity for 0.5 vol.% is 29 – 92 Pa.s; for 1.0 vol.% the viscosity is 38– 130 Pa.s; and for 1.5 vol.% the viscosity is 46 – 163 Pa.s. At this temperature, the viscosity values are higher than those at previous temperatures: for 1.0 vol.% is 41%, and for 1.5 vol.% is 77 %, higher than GNp 0.5 vol.%.

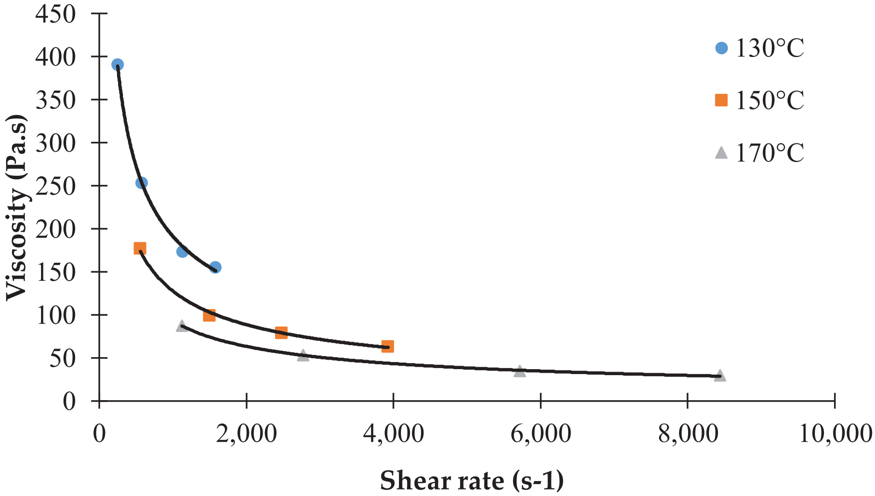

Figure 4: Viscosity vs. shear rate of Cu/GNp 0.5 vol.%

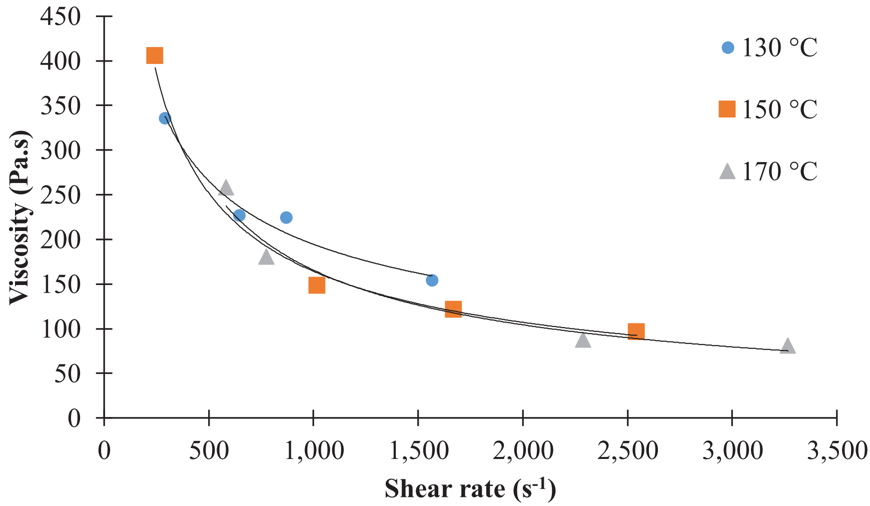

Figure 5: Viscosity vs. shear rate of Cu/GNp 1.0 vol.%

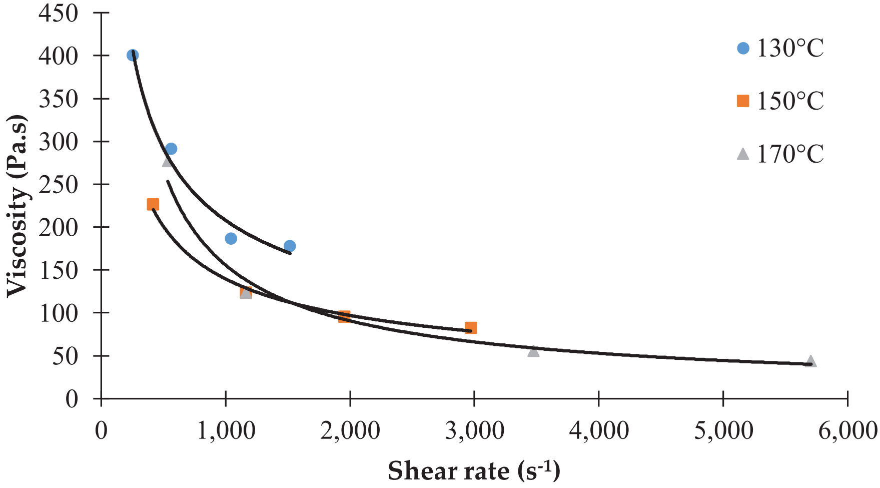

Figure 6: Viscosity vs. shear rate of Cu/GNp 1.5 vol.%

The higher the viscosity, the harder for the feedstock to flow. In other words, the flowability are related to the viscosity of feedstock [17]. Moreover, the flowability of the feedstock not only depend on the viscosity of the binder, but also on the powder loading. The flowability of the feedstock can be determined by the flow behavior index, n, which shows the degree of shear sensitivity. Power of law as shown in Equation (1) is used to identify flow behavior index, where η is the viscosity, K is constant and γ is shear rate. So the lower the value of n, the better flowability of the feedstock.

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

Based on the value of flow behavior index in Table 3, the values of n for feedstocks Cu/GNp 0.5 vol.%, Cu/GNp 1.0 vol.% and Cu/GNp 1.5 vol.%, based on the flow behavior index data, are less than 1, which indicates pseudo-plastic behavior. This shows that the optimum powder loading used for this study can be used for injection processes. At temperatures of 170°C, all feedstock show the lowest n value, indicating that this temperature is the optimal compared to the other two temperatures used in the injection process.

Table 3: Feedstock n-values at different temperatures

Feedstock	Temperature	N
Cu/GNp 0.5 vol.%	130	0.487
	150	0.472
	170	0.450
Cu/GNp 1.0 vol.%	130	0.510
	150	0.474
	170	0.220
Cu/GNp 1.5 vol.%	130	0.552
	150	0.384
	170	0.334

Figure 7 shows the feedstock viscosity dependence on temperature, which measures activation energy, E. The activation energy calculated using Arrhenius's equation as shown in Equation (2). From Equation (2), R is the gas constant, T is the temperature, η is the viscosity and η_° is the viscosity at a reference temperature. The activation energy, E for Cu/GNp 0.5 vol.% was 29.97 kJ/mol, for Cu/GNp 1.0 vol.% was 10.8 kJ/mol and for Cu/GNp 1.5 vol.% was 6 kJ/mol. This shows that a feedstock of Cu/GNp 0.5 vol.% has a higher activation energy compared to 1.0% and 1.5%. The higher value of E means that the feedstock has a stronger dependence on viscosity. Meanwhile, a low E value exhibits low sensitivity toward temperature and pressure changes that can minimize defects during the injection process [18]. However, the E value for Cu/GNp 0.5 vol.% was still in an acceptable range, but it required more precise temperature and pressure control throughout the injection process compared to 1.0% and 1.5%.

$$\eta = \eta_{\circ} \exp\left[\frac{E}{RT}\right] \quad (2)$$

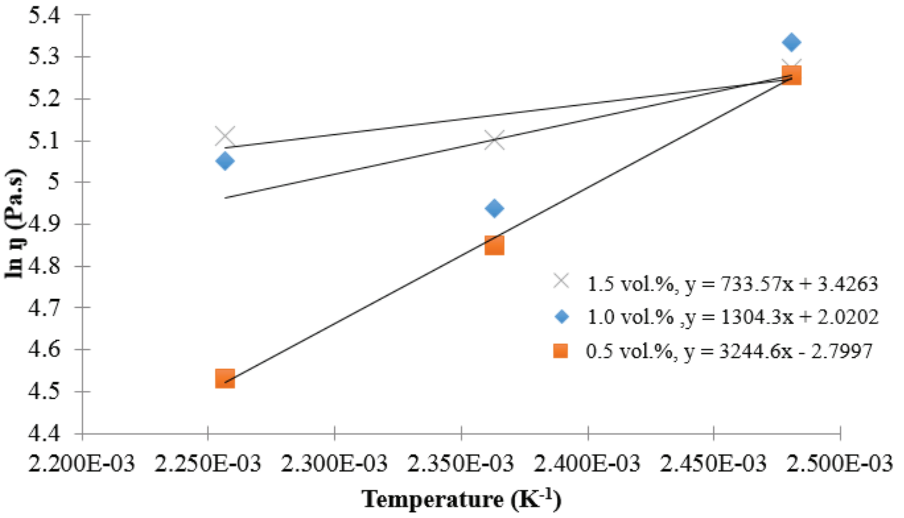

Figure 7: Relationship between viscosity and temperature at shear rate of 1000 s-1

The feedstock with Cu/GNp 0.5 vol.% was successfully injection-molded. Figure 8 shows the tensile shape of the injection-molded parts. The part was injected using a Boy 22A with a single gate at one end. As shown in the picture, the part is defects free and can continue to next processes such as debinding and sintering.

Figure 8: Injection-molded part (green part)

4.0 CONCLUSION

Based on the critical powder volume percentage (CPVP), the optimal loading was established. The optimal powder loading used for this study is 62% since all 3 feedstocks had the same result in critical powder loading. Furthermore, this study has successfully demonstrated that all 3 feedstocks, Cu/GNp 0.5 vol.%, Cu/GNp 1.0 vol.% and Cu/GNp 1.5

vol.%, with 3 different temperatures of 130°C, 150°C and 170°C, show pseudoplastic behaviour that is suitable to be injection molded, and during 170°C, all feedstock show the lowest n value, indicating that this temperature is the optimal compared to the other 2 temperatures used in the injection process.

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