Rheological study of copper and copper grapheme feedstock for powder injection molding

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Abstract. Heatsink is one of the solution to optimize the performance of smart electronic devices. Copper and its composites are helping the electronic industry to solve the heating problem. Copper-graphene heat sink material with enhanced thermal conductivity is the ultimate goal.Powder injection molding (PIM) has advantages of high precision and production rate, complex shape, low cost and suitabality for metal and cremics.PIM consists of four sub sequential steps; feedstock preparation, molding, debinding and sintering. Feedstock preparation is a critical step in PIM process. Any deficiency at this stage cannot be recovered at latter stages. Therefore, this research was carried out to investigate the injectability of copper and copper graphene composite using PIM. PEG based multicomponent binder system was used and the powder loading was upto 7vol.% less than the critical powder loading was used to provide the wettability of the copper powder and graphene nanoplatelets (GNps). Corpper-graphene feedstock contained 0.5vol.% of GNps . To ensure the homogeneity of GNps within feedstock a unique technique was addopted. The microscopic results showed that the feedstock is homogeneous and ready for injection. The viscosity-shear rate relationship was determined and results showed that the addition of 0.5vol.% of GNps in copper has increased the viscosity upto 64.9% at 140°C than that of pure copper feedstock. This attribute may be due to the large surface area of GNps. On the other hand, by increasing the temperature, viscosity of the feedstock was decreased, which was recommended for PIM. The overall viscosity and share rate lies within the range recommended for PIM process. It is clear that both feedstocks showed pseudo plastic behaviour which is suitable for PIM process. In the pseudo plastic behaviour, the viscosity decreases with the shear rate. It may be due to change in the structure of the solid particles or the binder. The molding results showed that both copper feedstocks were successfully molded and free from the physical defects.

1. Introduction

Nowadays, the electronic industry has a serious concern to achieve optimal performance of electronic chips which attain high temperature during operation resulting reduced performance. To overcome this issue, heat sinks are developed with metal composites. These composites are reinforced with highly

conductive reinforced materials results in enhanced the thermal conductivity and these composites are consider more attractive for heat sink applications [1]. These heat sinks are attached to the back of the chips to pull thermal energy away from the chips and transfer it into the surrounding air. PIM is a new technology which modifies the basic molding process of plastics and ceramics and now applicable for metals and ceramic materials. PIM process has emerged as a key technology due to its ability to produce small and complex components at low cost with high production volume [2, 3]. Various materials are used for thermal management and copper is one of the most recommended materials because of its high thermal conductivity. In order to produce the heat sink with complex shape using PIM, a flow able feedstock in molding machine is required[4]. Besides, the fabrication of defects free metal matrix composites using PIM has been reported [5, 6]. In order to achieve a high electrical conductivity in polymeric composites with low cost and easy processing, graphite based materials are getting more research attraction [7]. Apart from that, attempt to incorporate graphene nanoplatelets (GNps) into the feedstock is a new approach to enhance the performance of electronic devices. Graphene is one of the most fascinating materials being studied today, and received world-wide attention due to its potential applications [8, 9]. Graphene is a fast emerging material due to its unique structure and excellent mechanical, thermal and electrical properties [9, 10]. Recent research has shown that the graphene-based materials can have a great impact on electronic and optoelectronic devices, chemical sensors, nanocomposites and energy storage [9]. Graphene has demonstrated excellent mechanical properties with Young's modulus of 1 TPa and high thermal conductivity, about 5000 W/mK for freely suspended samples, which is among the highest of any known material[11-13].

However, in Cu-graphene composite the uniform dispersion of GNps into the feedstock is a challenge for researchers. The developed high performance smart materials for thermal management will provide extensive application of PIM to enhance the performance of electronic chips[14].

This research studied investigates the uniform dispersion of GNps with in copper matrix and their effects on flow behaviour of Cu feedstock by using a lower viscosity binder system. Based on viscosity results suitability of Cu-GNps composite for PIM and appropriate moulding temperature were identified.

2. Materials and Procedures

Gas atomized copper powder with an average particle size of 22μm with purity 99.9% was supplied by Sandvik Materials Technology, and graphene nanoplatelets (XGnP-M grade) with average thickness of 6 to 8 nm, surface area of 120 to 150 m²/g and average particle diameters of 5, 15 or 25 μm was provided by XG Sciences, Inc.. Binder system contains polyethylene glycol (PEG) as the major component, polymethyl methacrylate (PMMA) as the backbone polymer and stearic acid (SA) as the surface active agent. The physical properties of the binder components are listed in Table 1.

Table 1. Physical properties of binder components used in this study

Binder ingredient	Density (g/cm^3)	Melting Temperature (°C)
PEG	1.21	61-66
PMMA	1.16	160
Stearic acid	0.96	67-69

Fig. 1 shows the FESEM micrograph of Cu copper powder which shows that the particles are spherical in shape.

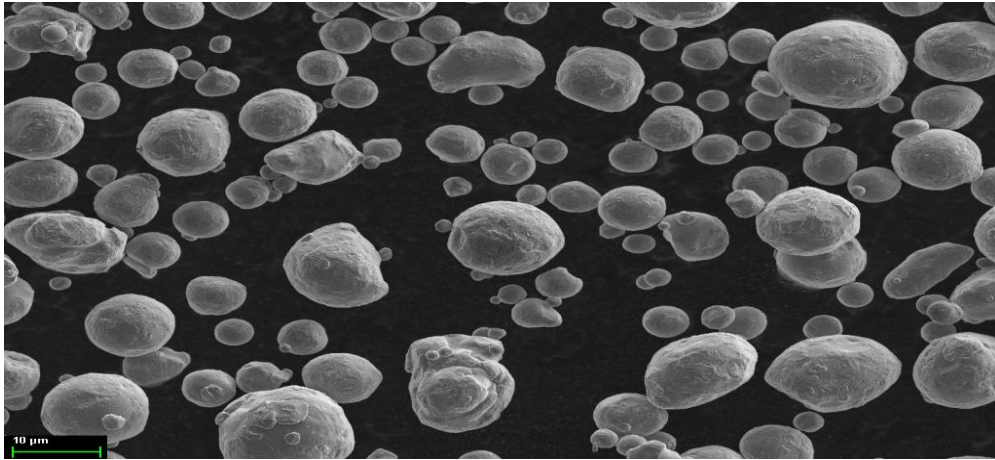On the other hand Fig.2 shows the flake nature of the GNps.

Figure 1. FESEM image of Cu shows spherical nature of the particles
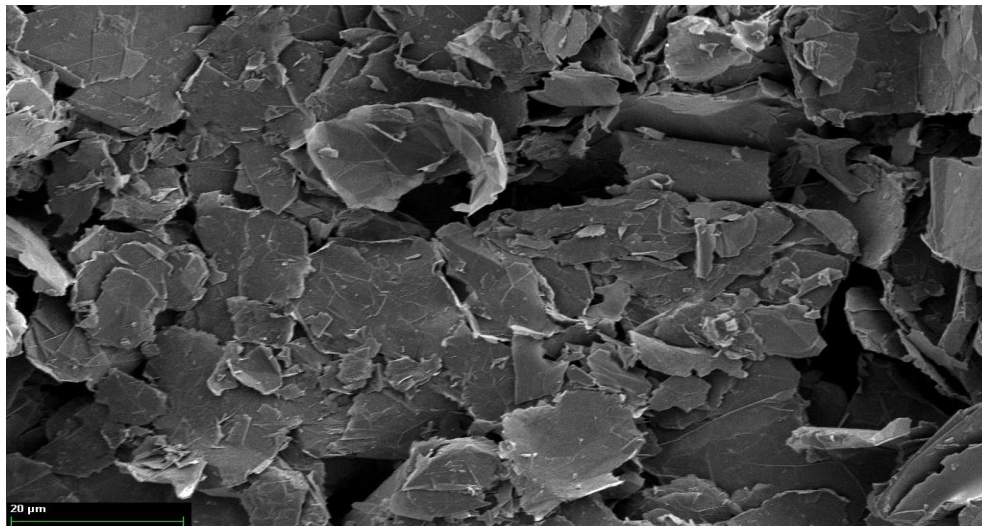

Figure 2. FESEM micrograph showing the flakes of graphene GNps

2.1. Preparation of Copper and Copper-Graphene Feedstock

The binder system used in this study consists of 73vol.% PEG, 25vol.% PMMA and 2vol.% SA. Critical powder loading was determined 67vol.% by using Brabender shown in Fig.3. In order to determine the characteristics and the flow behaviour, two formulation of feedstock have been prepared and shown in Table 2. Formulation C-1 have solid loading 60vol.% while in formulation C-2, powder loading was reduced to 58vol.% due to the presence of 0.5vol.% GNps, having large surface area and caused to raise the viscosity.

Table 2. Feedstock formulations developed for viscosity measurement in this study

Copper mixture	Powder loading (vol. %)	Graphene (vol.%)
C-1	60	0
C-2	58	0.5

Two formulations of copper powder were prepared using a Brabender mixer machine shown in Fig. 3. In order to get homogenous dispersion results of GNps in the Cu matrix, sonication has been applied as the dispersion technique of GNps. Initially, GNps were immersed in distilled water and sonicated for 1 hour at temperature of 50°C follows by the dissolution of PEG in GNps and water solution with

the help of magnetic stirrer. Finally the mix was dried in the oven for 24 hours. The dried GNps-PEG mixture was then mixed with the other components of the binder system (PMMA, SA) and copper powder in Brabender at temperature of 150°C shown in Figure 3. This step allowed GNps to be mixed uniformly within feedstock.

Figure 3. Compounding of Cu-Graphene using Brabender

2.2. Viscosity Measurement
The viscosity of both feedstocks were measured using capillary rheometer Shimadzu CFT-500D at various temperatures from 130 to 150°C and data was acquired to study the effects of temperature and GNps on viscosity of copper.

2.3. Microstructural Analysis
The shape of copper powder, GNps and to ensure the homogeneity of GNps within feedstocks, filed emission electron microscope (FESEM- ZEISS SUPRA 55VP) was used.

3. Results and Discussion

3.1. Flow behaviour of Pure Copper and GNps Reinforced Copper composite Feedstocks
Two different volume contents of copper 58 vol. % and 60 vol. % were tested for viscosity over a wide of temperature. The obtained results showed that both formulations exhibit pseudoplastic behaviour which is recommended for PIM [15]. Fig. 4 and Fig. 5 show the relation between viscosity and shear rate for pure copper (C-1) and graphene reinforced copper composite (C-2) feedstock respectively. Formulation C-2 showed higher viscosity as compared to C-1 even at low solid loading. It may be due to the presence of GNps which create hurdles and resist against the movement of copper powder particles. At lower temperature 130°C the addition of GNps, the viscosity of C-1 is 90.39 Pa.s – 231.6 Pa.s while the viscosity of C-2 is 81.4 Pa.s – 308 Pa.s. At this temperature, the viscosity of composite mixture Cu/Graphene is higher up to 32.76% than that without graphene. The increasing factor in viscosity was assumed due to large surface area of graphene nanoplatelets. On the other hand, the interstitial type of packing within the powder particles attributed to the increase of viscosity of the mixture. At the temperature of 140°C, the viscosity value of C-1 was measured to be 77.5 Pa.s – 141.3 Pa.s while the value of C-2 is 56.5 Pa.s – 233 Pa.s. For this temperature, the difference in viscosity is up to 64.9%. At higher temperature (150°C), the viscosity values for both feedstocks are apparently low. For C-1 feedstock, the viscosity value is 69 Pa.s – 150 Pa.s while for C-2, the viscosity value is 33.7 Pa.s – 152 Pa.s. This is occurred because at higher temperature, the binder particles begin to soften and entering the spaces between the metal powder thus facilitating the outflow when pressure is applied. From this rheology test, it was found that the viscosity of the feedstock was decreased as the temperature was increased, which is a good criteria required in PIM.
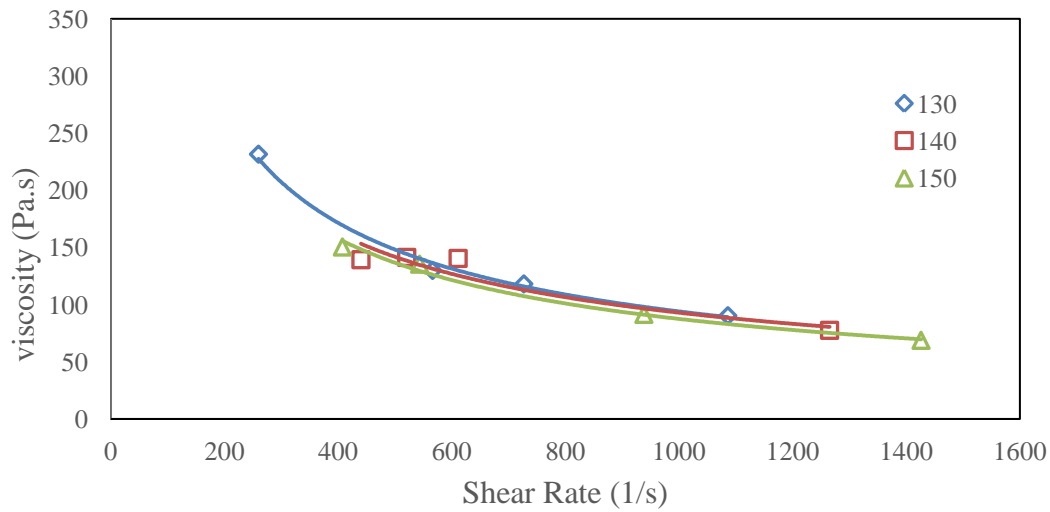
Figure 4. Viscosity vs. shear rate of copper powder (C-1) feedstock showing pseudo plastic behaviour
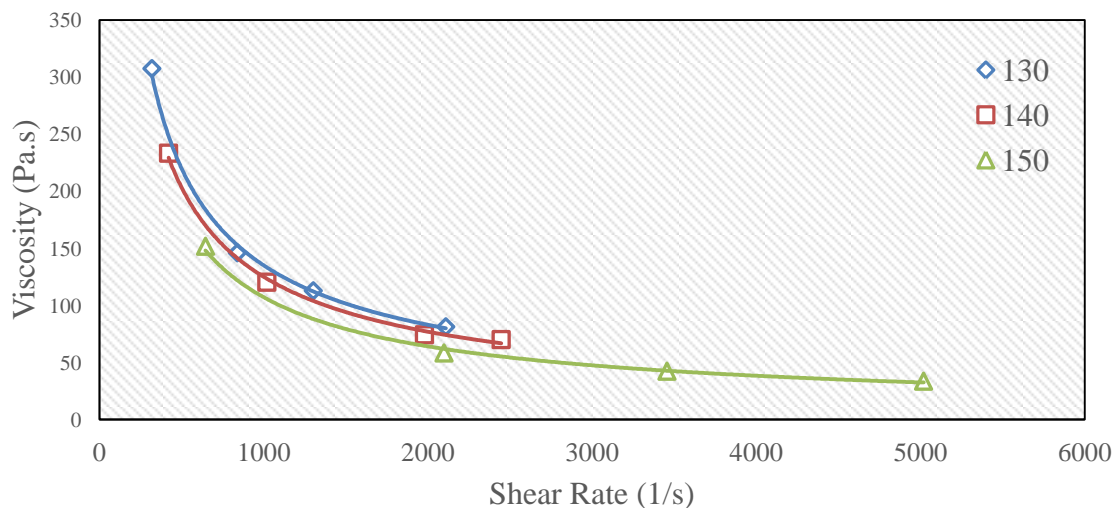

Figure 5. Viscosity vs. shear rate of graphene reinforced copper (C-2) feedstock shows pseudo plastic behaviour

Formulation C-1 has powder loading 60vol.% that is 2 vol.% higher than C-2 (58vol.%). In formulation C-2, lower powder loading was used due to the presence of GNps. The lower powder loading caused to reduce the friction among the powder particles and GNps due to the excessive binder [16]. However, in this case, the addition of graphene nanoplatelets to the C-2 feedstock contribute to the increase of viscosity even though it has lower powder loading because of large surface area of the graphene nanoplatelets.

3.2. Effects of GNps on flow index (n) and activation energy (E)
The value of flow index 'n' at various temperatures is given in Table 3. The results revealed that the value of 'n' is less than 1 which means feedstock has pseudo plastic behaviour as clear from Fig.4 and Fig.5. On bases of these results both feedstocks are considered suitable for injection molding. Table 3 shows the values of flow behaviour index 'n' at a range of temperatures. The values of flow index 'n'

is not uniform it may be due to the orientation of GNpsand low viscosity of binder at higher temperature.

Table 3. n-values of feedstock at different temperatures

Feedstock	Temperature (°C)	N
C-1	130	0.344
	140	0.391
	150	0.357
C-2	130	0.3192
	140	0.3233
	150	0.2922

Temperature dependency of viscosity is very important to judge the flow of feedstock. Fig. 6. showed that formulation C-2 has a higher value of activation energy which is 17.71 kJ/mol, compared to feedstock C-2 which is 4.96 kJ/mol. Higher value of E means, feedstock has a strong temperature dependency to viscosity [17]. Therefore, feedstock C-2 required a more accurate temperature control during injection molding compared to feedstock C-2. But for this case, even the value of C-2 is higher as compared to C-1, but it is still in acceptable range.
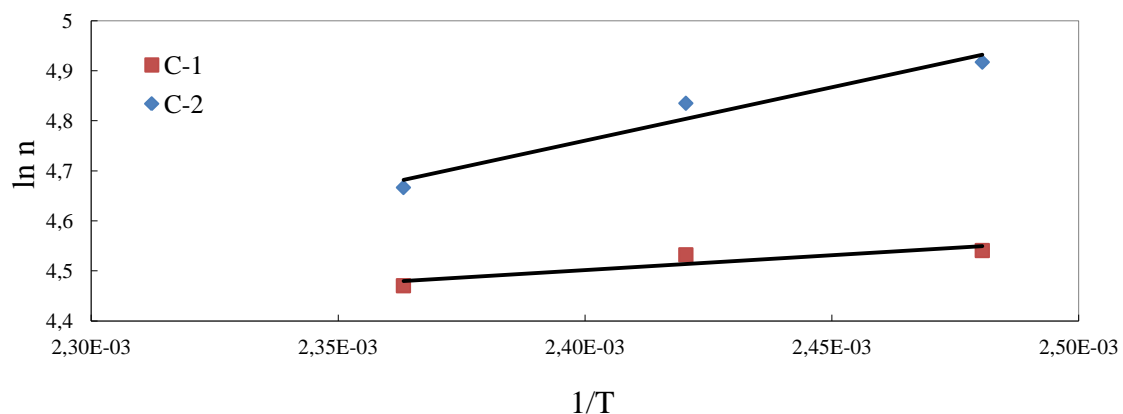

Figure 6. Relationship between viscosity and temperature at shear rate of 1000 s^{-1}

3.3. Molding analysis of feedstock
The feedstocks were successfully molded andmolded parts are free from the physical defectsas shown in and Fig. 7.

Figure 7. Physically defects free Cu-GNpscomposite parts produced via PIM

3.4. Microstructural analysis of Feedstock

FESEM analysis was performed to ensure the coating of PEG on GNps. Fig. 8 showed that the GNps were evenly coated with PEG after stirring. The SEM results in Fig.9 revealed that the binder was uniformly distributed within the matrix and it covered the metal and GNps. With the addition of GNps no evidence of clustering was observed.
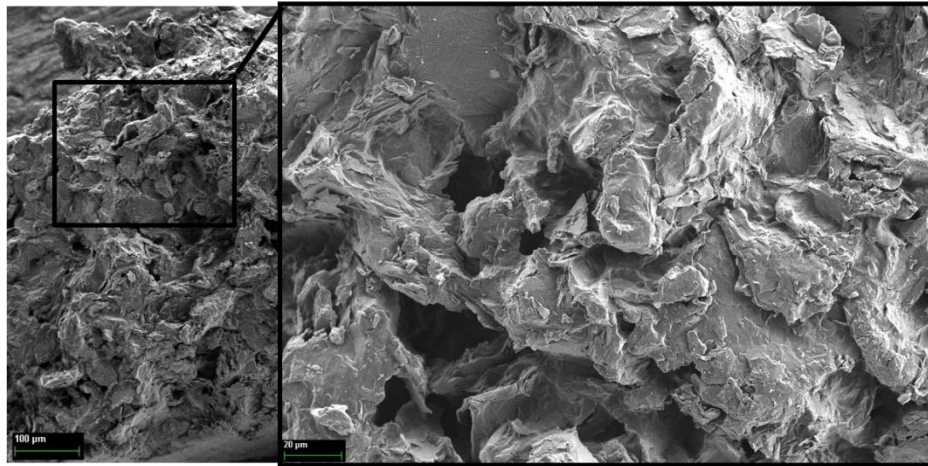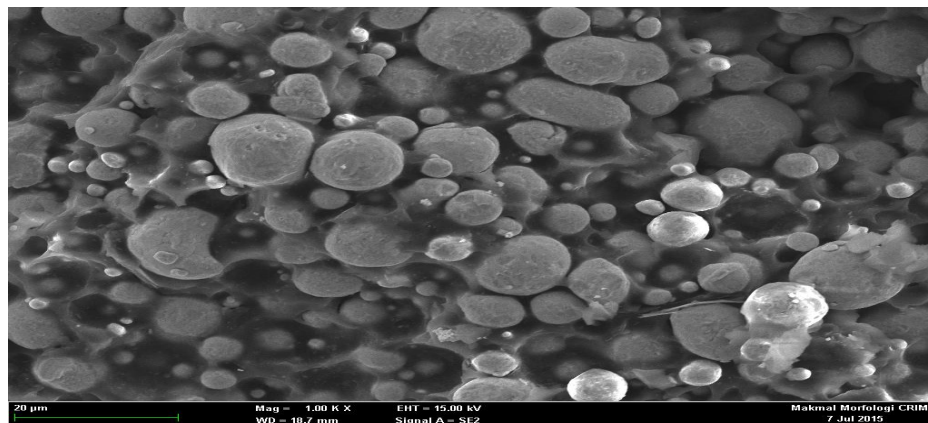

Figure 8. FESEM of shows the coating of PEG on GNps

Figure 9. Scanning electronic microscopy image of Cu-Graphene feedstock showing uniform dispersion and spherical particles of Cu

4. Conclusions

The adopted procedure to disperse GNps within the Cu matrix is suitable to achieve uniform dispersion and recommended for PIM. It is found that both formulations exhibit pseudo plastic behaviour and can be injected successfully through injection molding process. The results of rheological studies showed that small amount of GNps increased the viscosity of the composite it is recommended that for Cu-GNps composites the solid loading should be more than 5% less that of critical powder loading.

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