Flow Behavior of Cu/CNTs Feedstocks for Powder Injection Molding

Ali Samer Muhsan, Faiz Ahmad, Norani Muti Mohamed, and M. Rafi Raza

***Abstract*—In this study, the flow behavior of multi-walled carbon nanotubes (CNTs) reinforced copper matrix feedstocks is presented. The solid loadings in the copper feedstock were investigated in the ranges of 55-61 Vol. % using binder. Pure copper (Cu) and Cu/CNTs feedstocks were compounded using internal mixer machine for homogenous dispersion of solids in the binder. The flow behavior was measured using a capillary rheometer in the shear rate range expected to occur during powder injection molding. An acceptable increasing trend in viscosity of the copper feedstock with powder loading was recorded. Cu/CNTs composite feedstocks showed viscosity more than 1000 Pa.s which is most probably due to the addition of CNTs and increasing trend in viscosity of Cu/CNTs was noted as well. The results also identified that the feedstock containing 59 vol. % copper was most suitable for substitution of CNTs in Cu feedstock.**

***Index Terms*—Powder injection molding; Compounding; Feedstock, Binder; Viscosity; Carbon Nanotubes; PIM.**

I. Introduction

An improvement in technologies is encouraging to extend the application in new directions. Powder injection molding (PIM) of non-ferrous materials is new and complex due to the nature of materials investigated [1]-[3]. PIM of copper has been attempted for electrical applications [4], [5] and in electronic industry as heat sink [6], [7]. Hi-tech electronic industry has a serious concern to achieve optimum performance of smart electronic chips which attain high temperature during operation results their reduced performance [8], [9]. PIM is a state of art technology and can produce heat sink according to the geometry of the electronic devices [10], [11]. The production of complex shape heat sink using PIM requires a flow able feedstock in the molding machine. The viscosity of the molding feedstock is dependent on the filler loading [12], [13]. PIM has been tested for molding and rheology of metal composite feedstock [14], [15]. Attempts have been made to fabricate defects free metal matrix composites using PIM [16]. However, incorporating carbon nanotubes into the feedstock is a novel approach and the development of high performance heat sinks for electronic industry will provide an extensive application of PIM to enhance the performance of electronic chips.

This research studied the binder formulations to select a lower viscosity binder system for incorporation of copper powder to optimize copper feedstock. Based on viscosity of copper mixture, a suitable copper mixture was identified for subsititution of carbon nanotubes (CNTs) in preparing composite feedstock. Composite feedstocks were developed for measurement of viscosity and determine the suitability of composite mixtures for metal injection molding.

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II. Materials and Procedures

The copper powder (99.95% purity) of spherical in shape was used in this study. The copper powder produced by gas atomization was supplied by Sandvik Osprey LTD, UK. Particle size distribution of copper powder was >22 µm particle size. Analysis was performed using CILAS 1190 DRY and the results are shown in the Table I.

TABLE I: Results from Particle Size Analyzer

Copper powder	D_{10}	D_{50}	D_{90}
Size (µm)	3.31	8.96	17.19

In Fig. 1, a micrograph which has been taken by scanning electron microscope (SEM) to Cu/CNTs feedstock shows a spherical shape of particles, and a wide particle size distribution is considered suitable to achieve higher volume loading during PIM and densification in the sintered parts. The multi-walled CNTs used for this research was supplied by Shenzhen Nano-Technologies Port Co., Ltd., China. The dimensions of CNTs were: diameter 10-20nm, length 5-15 µm. The purity is 95-98% and ash ≤0.2 wt % and it is also shown in Fig. 1.

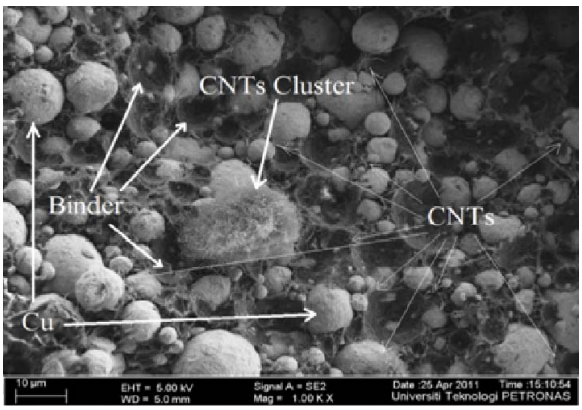

Fig. 1. Scaning electronic microscopy image of Cu/CNTs feedstock.

A. Preparation of Binder Systems

In order to study the flow behavior and to select a suitable binder system with lower viscosity to achieve optimum volume loading of copper and CNTs, three binder systems have been formulated and extrusion compounded. The binder system consists of three ingredients. Paraffin wax is a major binder component supplied by Merck Sdn Bhd, Malaysia. High density polyethylene (HDPE) was supplied by Titan Pet chem.(M) Sdn Bhd, Johor, Malaysia as a minor binder component and stearic acid was supplied by ACROS organics as a surface active agent or flow promoter. The physical properties of the binder components provided by the supplier are listed in Table II-A and binder formulations prepared for viscosity measurements are shown in Table II-B. Binder formulations were named as B1, B2 and B3 and were extrusion compounded using co rotating twin screw extruder. The barrel temperature profile was maintained at 140-150-160°C. A die of 2.5 mm diameter was used to produce extruded binder. The extruded binder was cooled in a water tank and chopped using an automated chopper to granule size of 3~4 mm for measurement of viscosity of binder.

TABLE II-A: PHYSICAL PROPERTIES OF BINDER COMPONENTS USED IN THIS STUDY

Binder ingredient	Density (g/cm3)	Melting Temperature (°C)
Paraffin wax	0.90	60-65
HDPE	0.95	130
Stearic acid	0.96	67-69

TABLE II-B: BINDER FORMULATIONS DEVELOPED FOR VISCOSITY MEASUREMENT IN THIS STUDY

Binder ingredient	B1	B2	B3
Paraffin wax	55	65	70
HDPE	40	30	25
Stearic acid	5	5	5

TABLE III-A: FORMULATIONS OF COPPER/ BINDER MIXTURES FEEDSTOCK PREPARED IN THIS STUDY

Copper mixture	Copper loading (vol. %)	Binder, B3 (vol. %)
C-1	55	45
C-2	57	43
C-3	59	41
C-4	61	39

TABLE III-B: FORMULATIONS OF COPPER- CNTS/ BINDER MIXTURES FEEDSTOCK PREPARED IN THIS STUDY

Composites mixture	Cu (vol. %)	CNTs (vol. %)	Binder, B3 (vol. %)
C/MWCNT1	56.50	2.5	41
C/MWCNT2	54.0	5.0	41
C/MWCNT3	51.50	7.50	41
C/MWCNT4	49.0	10.0	41

B. Preparation of Copper Feedstock and Cu/ CNTs Feedstock

Four formulations of copper powder with binder, B3 were prepared using an internal mixer machine as shown in Fig. 2. All mixtures of copper/binder were prepared at a temperature of 140°C and Z-blade rotation speed of 50 rpm for 40 minutes. The details of copper mixtures and copper/ CNTS are given in Tables III-A and III-B respectively. For preparation of copper/ MWCTNs feedstock , copper and CNTs were dry blended in a ball mill for 20-30 minutes followed by compounding in the internal mixture at 140°C [13]. Ensuring uniform dispersion of CNTs and copper powder in binder, mixtures were solidified and granulated to > 5 mm for powder injection molding.

C. Viscosity Measurement

1) Binder Systems

A capillary Rheometer (Shimodzu flow tester CFT-500D), using a capillary die of 1 mm diameter and length of 10 mm was used to measure the viscosity of binder systems to identify a suitable binder with minimum viscosity to achieve higher loading of solids. Binder granules were filled into rheometer barrel heated to 160 °C and slight pressure was applied using rheometer ram and allowed for 5-10 minutes to attain equilibrium temperature throughout the materials. The materials were extruded through the capillary die and time taken was recorded. Volumetric flow of melt was calculated for shear rate and corresponding shear stress was calculated to determine the viscosity of the binder. The viscosity of binder was measured over a shear rate of approximately 2000 s^{-1}.

2) Copper mixtures and CNTs/Copper feedstock

Four formulations of Cu/binder system, B3 were prepared using internal mixture. Binder B3 was selected due to its lower viscosity and with an objective to achieve higher solid loadings. The viscosity of copper mixtures was measured using capillary rheometer and data was acquired for four mixtures to study the effects of increasing copper contents on the viscosity. Based on the data, one copper mixture was identified for substitution of CNTs and the selection was based on the process ability of the mixtures. The viscosity of Cu/CNTs feedstocks and effects of increasing CNTs in copper were also measured at 160 °C copper/ CNTs feedstock [11].

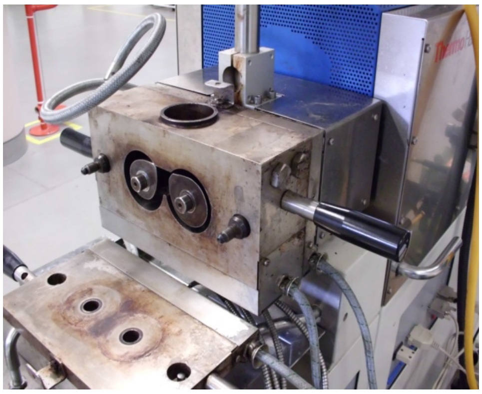

Fig. 2. Internal mixer used for compounding of CNTs/Cu feedstock.

III. RESULTS AND DISCUSSION

A. Viscosity of Binder Systems and Selection of Binder

Three types of binder systems consisting of paraffin wax 55, 65 and 70 weight percent were tested for viscosity measurement and results are shown in Fig. 3. Results showed that increasing paraffin content in the binder system reduced viscosity of the binder system. Binder B1 containing 55 wt% wax has viscosity approximately 80 Pa.s at shear rate of 200 s^{-1}. An increase of 10 wt% wax in the binder, B2 and reducing the percentage of HDPE in B2. The viscosity of this binder system was reduced to 30 Pa.s which is approximately 67 percent less compared to B1. Further addition of 5 wt% paraffin wax to binder B3 and further reduction of HDPE in binder system B3 reduced viscosity level to approximately, 17 Pa.s. Based on the viscosity, this binder formulation was considered suitable in further investigation for incorporation of copper powder and CNTs [11].

B. Viscosity of Copper Powder Feedstock

Based on the viscosity data of binder sytems, B3 was selected to study the effects of introducing copper powder into this binder. Four different volume contents of copper, 55, 57, 59 and 61 vol. % were tested for viscosity over a wide shear rate range expected to occur in PIM. Results are illustrated in Fig. 4 and viscosity of mixture C1, containing 55 % copper showed viscosity of 529 Pa.s at lower shear rate, 93 s^{-1}. A further addition of 2 vol% of copper, mixture, C2 (57 vol. %) showed viscosity of 641 Pa.s at the same shear rate which is approximately 18% higher compared to viscosity of formulation C1 [13, 14].

The viscosity-shear data for mixture containg, 59 vol.% copper, C3 is also illustrated in Figure 4. The viscosity of this formulation was 775 Pa.s which is 17% higher when compared to C2. A further increase of copper powder to 61 vol. % in formulation, C4 showed viscosity of 981 Pa.s at lower shear rate. This viscosity value was 21 percent higher compared that measured for C3 [11], [12]. This value of viscosity is still within range required for powder injection molding. Injection molding experiments revealed that formulation C3 containing 59 vol. % copper was considered suitable for substitution of CNTs due to ease in processing during injection molding.

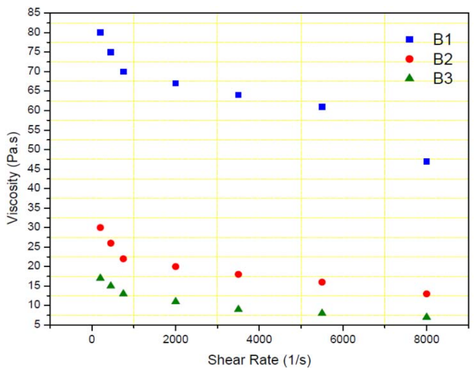

Fig. 3. Viscosity vs. shear rate of binder systems tested at 160°C.

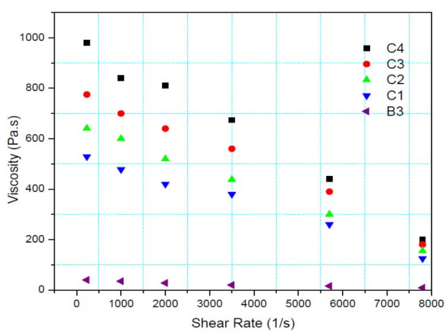

Fig. 4. Viscosity vs.shear rate of copper powder feedstocks at 160 °C.

C. Viscosity of CNTs Reinforced Copper Feedstocks

The viscosity-shear rate relationship measured for volume loading was maintained to 59 vol. %, however, volume contents of CNTs were varied from 2.5 to 10 percent. To study the effect of increasing contents of CNTs on viscosity was measured and compared. The viscosity of composite mixture CuCNT-1 at a shear rate 220 s^{-1} was measured 905 Pa.s which is 27 percent higher than that without CNTs [11], [12]. This higher increase in viscosity was considered due to large surface area of CNTs and interstitial type of packing within the powder particles which tends to increase the viscosity of the mixture. An increase on CNTs contents to 5 vol. %, mixture CuCNT-2, the viscosity was increased to 1080 Pa.s which is approximately 16 percent higher compared to CuCNT-1, Composite mixture, CuCNT-3 containing 7.5 vol. % CNTs showed only 7.5 higher viscosity compared to earlier mixture and this may be due alignment of CNTs in capillary die. The viscosity measured for composite mixture, CuCNT-4 containing 10 vol. % CNTs, was 1350 Pa.s and showed 14 percent high viscosity. Interestingly, mixtures with viscosity higher than 1000 Pa.s have been injection molded successfully except one where the injection pressure was increased and molded samples produced were free from defect [16].

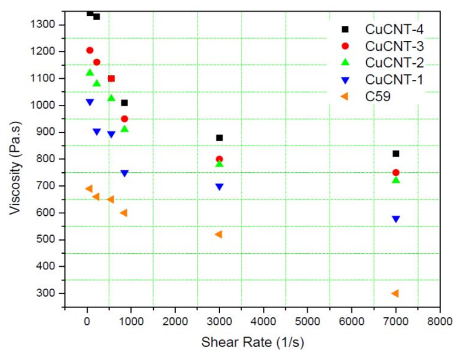

Fig. 5. Viscosity vs. shear rate of Cu/ CNTs systems tested at 160°C.

IV. CONCLUSION

The viscosity results detrmined from the binder systems suggested that the binder system B3 with lower viscosity, was the most suitable binder for incorporating copper powder. Reasonably acceptable solid contents of copper were achieved in the binder, B3. The viscosity of the feedstocks was low enough to be injected through PIM machine and thus Cu/CNTs feedstocks can be molded successfully. The CNTs based mixtures experienced slightly high viscosity and was more than 1000 Pa.S. However, increase in injection pressure managed to produce the test samples with free defects.

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