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Viscosity Analysis of Copper Aluminium Manganese (CuAlMn) Shape Memory Alloy Mixed with Polyethylene Glycol (Peg), Polymethyl Methacrylate Acrylic (Pmma) and Stearic Acid (Sa) Based Binder

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ABSTRACT

Shape memory alloys (SMAs) are a class of smart materials that have the unusual feature of remembering the initial shape after plastic deformation. SMAs differ from traditional elastic/plastic materials in because of reversible hysteresis thermos mechanical behavior. Copper (Cu) based shape memory alloys are the most promising in terms of practical application due to their inexpensive cost and high recovery force. Powder injection molding (PIM) is well known for the creation of complex components (micro parts) and Copper Aluminium Manganese (CuAlMn) materials are studied through this process. The rheological behavior of the feedstock needs to be determined to avoid any non-homogeneous mixture between powder and binder that may result in powder and binder separation during the injection molding process. This work focused on the rheological properties of CuAlMn with a binder system of polyethylene glycol (Peg), polymethyl methacrylate acrylic (Pmma) and stearic acid (Sa). The alloy composition used were 85wt% Cu, 12wt% Al and 3wt% Mn mixed with 73wt% Peg, 25wt% Pmma and 2wt% Sa. Based on such value, the powder loadings used in this work was 58wt% mixed with 73wt% Peg, 12wt% Pmma and 5wt % Sa. A capillary rheometer was employed for the rheological studies where the relationship between shear rate and viscosity was investigated. There were 3 variant temperatures (115℃, 125℃ and 135℃) and 4 loads (40N, 50N, 60N and 70N) applied for the rheology test. The obtained result shows that the overall shear rate and viscosity are within the PIM process recommended range and flow index is below 1. This shows pseudoplastic behavior of the feedstock.

Keywords: Copper; aluminium; manganese; binder system; rheology

INTRODUCTION

Greater thermal conductivity and heat dissipation components are required to allow the merging of new devices as demand for higher capability electronic products grows exponentially. Therefore, developing a material with appropriate thermal properties and the ability to endure the demands of enhanced capabilities electronic gadgets is a difficult task (Kadiman et al. 2018; Pavithra et al. 2014). Shape memory alloys (SMAs) are materials that, when heated to a critical temperature, it will undergo a structural alteration that allows them to regain their original shape after being deformed plastically in the low-temperature phase. (Cava et al. 2015). When exposed to a high temperature or when subjected to a large amount of strain, alloys with the shape memory effect may tolerate extremely high strains and then revert to their original form. In past studies, the Cu-Al-Mn structure is a well-known shape memory alloy with a variety of Cu, Al, and Mn compositions (Aldırmaz et al. 2019).

Copper (Cu) nanocomposite has seen tremendous growth over the last decade, owing to its improved mechanical, electrical, and thermal properties, which have led to a wide range of electronic applications (Pavithra et al. 2014). According to the previous research by Amalina Nordin on solid copper feedstock, every copper feedstock exhibits pseudo-plastic behavior, with viscosities dropping as the shear rate increases (Nordin et al. 2015). Copper is commonly processed with powder metallurgy process because it is more difficult to extrude cast, stamp or machine (Johnson et al. 2005). A few techniques used in powder which is metal injection moulding, powder injection moulding, hot isostatic pressing (HIP) and powder forging (PF) (Omar et al. 2020).

Powder injection moulding is one of the powder metallurgy techniques that suitable to produce small parts with complex shape in high volume process but at low cost (Emeka et al. 2017; Huang et al. 2003; Wei et al. 2014). PIM process also can satisfy the geometry and property requirements (Omar et al. 2020; Poh et al. 2018; Ramli et al. 2019). Usually, PIM starts with a mixing process of powder and binder to form the feedstock. Then, the feedstock will be injected to mould the green parts. The debinding process will take part in order to remove the binder from injected sample using solvent and thermal process. Polyethylene glycol (Peg)/ Polymethyl methacrylate acrylic (Pmma) / stearic acid (SA) are commonly used as binders in previous studies because of their properties which are non-toxicity and commercial availability(Chua et al. 2013; Kadiman et al. 2018; Omar et al. 2020). Due to its good compatibility, Pmma is frequently employed as a secondary binder in binder systems. (Hayat et al. 2015). Stearic acid is commonly used as a surfactant and lubricant to increase\ powder wetting (Ibrahim et al. 2011).

The rheological behavior must be determined prior to the injection molding process to avoid inhomogeneous feedstock mixtures that can cause separation of powder and binders during the injection process. Besides that, it can cause defects toward the green part such as warpage or cracking during debinding and sintering phase. Therefore, it will reduce the product mechanical and physical properties (Amin et al. 2009; Omar et al. 2003).

In this work, the rheological properties of feedstock containing CuAlMn with binders that consist of Peg, Pmma and Sa were determined in terms of viscosity, shear rate and flow behavior index. Therefore, this study will contribute a great impact to obtain new knowledge and information that related to rheological behavior using composite materials of CuAlMn which plays important role before proceeding the PIM process.

METHODOLOGY

MATERIALS

In this study, copper (Cu) powder containing 99.99% percentage of copper purity, aluminum (Al) powder material and manganese (Mn) material (Figure 1a,1b and 1c) obtained from Vistec Technology Services Sdn Bhd. was used in the production of feedstock. A total of 85 wt.% of Cu, 12 wt% of Al and 3 wt% of Mn were used as the alloy powder mixture material together with binder materials which were blended to produce the feedstock material. Table 1 below shows the characteristics of Cu, Al, and Mn material.

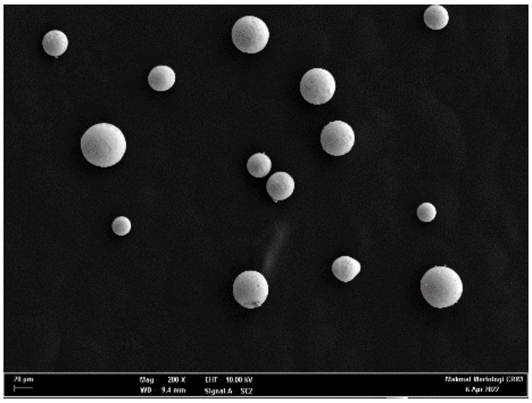
TABLE 1. Characteristics of Copper, Aluminium and Manganese materials

Properties	Type of material		
Product name	Copper	Aluminium	Manganese
Identification	Cu	Al	Mn
Colour	bronze	grey	black
Powder means diameter (µm)	40	105	40
Density (g/cm^3)	8.96	2.7	3.7
Composition (%)	85	12	3

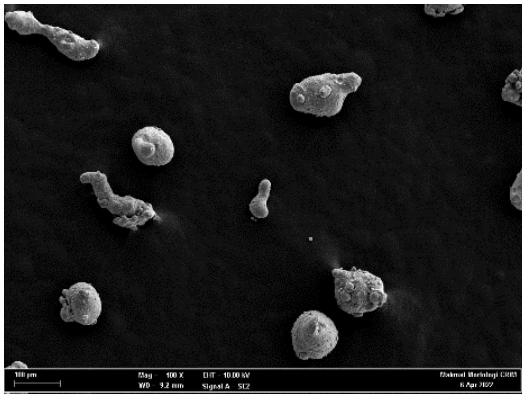
The binder system designed for this experiment consisted of Peg, Pmma and Sa. All these binders were also supplied by the Vistec Technology Services Sdn Bhd. Choosing binder system is important in controlling feedstock homogeneity and injection moulding output quality. There were few past studies have used Peg, Pmma and Sa as their temporary vehicle to transport powder particles into the cavity of an injection mould (Cava et al. 2015; Nor Amalina et al., 2014; Rezvani & Shokuhfar, 2012). However, the research of the binder system consisting of Peg, Pmma and Sa is not yet established. The mixture with a smaller powder loading has a large surface area, which can increase its viscosity. A higher viscosity can lead to a high injection pressure required to push the molten material of the feedstock (Kadiman et al. 2018). Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) were run to determine the melt and degradation temperatures of the binder components. The density of each binder was also obtained from a pycnometer test. Table 2 shows the binder properties for Peg, Pmma and Sa. Field Emission Scanning Electron Microscopy (FESEM) used to capture the microstructure image of the Cu, Al and Mn powder were shown in Figure 1 a,b and c, which show spherical shape, irregular shape and flake shape. The rheological properties of powder-binder combinations are greatly influenced by the particle shape and size of the powder used in PIM. The usage of powders with irregular particle shape increases viscosity, yield stress, and, in general, reduces rheological properties (Schaper et al. 2019).

TABLE 2. Properties of binders

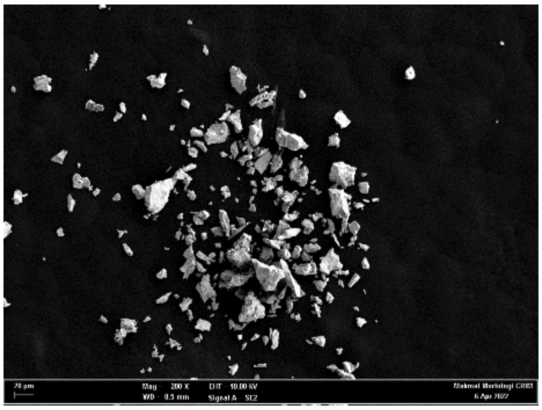
Material	Polyethylene Glycol (Peg)	Polymethyl Metacrylate (Pmma)	Stearic Acid (Sa)
Density (g/cm^3)	1.21	1.16	0.96
Melting point (C)	62.2	125	63.3
Composition (wt%)	73	25	2



(a)



(b)



(c)

FIGURE 1. Microstructure image of (a) Cu powder (b) Al powder (c) Mn powder

FEEDSTOCK PREPARATION

The brabender mixer machine was used to obtain critical power loading. The critical powder volume percentage (CPVP) needs to be obtained to get the critical powder loading. It shows the highest torque evolution curves, which indicate the maximum percentage of powder loading. Oleic acid was used during the process and stopped once the value dropped shown in graph with the addition of oleic acid. During the critical powder loading, the oleic acid acts as a binder and the oleic acid drops every 5 minutes. The Peg (73 wt%), Pmma (25 wt%) and Sa (2 wt%) were three types of binders that have been utilized in this study. The powder loading used was obtained by using calculation in equation 1 as shown below. The solid loading Φ is the volumetric ratio of the volume of solid powder to the combined volume of powder and binder. Powder and binder weight fractions are represented by the letters W_p and W_B, respectively, while their densities are indicated by the ρ_p and ρ_B (Gonzlez et al. 2012).

$$\Phi = \frac{\frac{w_p}{\rho_p}}{\frac{w_p}{\rho_p} + \frac{w_B}{\rho_B}} \quad (1)$$

Several steps were carried out in order to obtain homogenous dispersion binders in composite of Cu, Al and Mn. Firstly, Pmma binder was diluted using Acetone with ratio 1:2 ml acetone. The initial temperature to mix the Cu, Al and Mn was 70°C for first 5 minutes and followed by adding the diluted Pmma for another 15 minutes. Peg was added for another 15 minutes. Next, the mixture was continued to blend in brabender mixer for 60 minutes at 125°C with rotation speed 25rpm. A crused of CuAlMn feedstock using stone mortar as shown in Figure 2 was used to run the rheology test.

FIGURE 2. Crushed of CuAlMn feedstock

RHEOLOGY

The capillary rheometer Shimadzu CFT-500D was used to test the feedstock behaviors which is used to measure the viscosity resistance of feedstock when melted material passed the die orifice. The flow behavior was calculated at several temperatures of 115°C, 125°C and 135°C, where the loads were in the range 40N, 50N, 60N and 70N. There are three types of flow that can be shown by the feed material during the rheological properties test which are newtonian, pseudoplastic and dilatant. The value of n for Newtonian, pseudoplastic and dilatant flow is 1, <1 and >1 respectively. Most previous studies have shown that feedstock has pseudoplastic flow properties which are said to be most suitable for the injection molding process. In addition, the dilatant flow is said to tend to the phenomenon of separation of powder-binding materials that will produce green parts that have physical defects. The difference between pseudoplastic and dilatant is viscosity, where viscosity (Pa.s) decreases with shear rate (s^{-1}) for pseudoplastic but viscosity increases for dilatant flow types.

RESULTS AND DISCUSSION

MIXING TORQUE ANALYSIS

The additional of oleic acid were stopped because the graph value started to drop after 21ml were added as shown in Figure 3. Then, the CPVP was calculated, and the value obtained was 63 wt%. The critical powder loading choosed was 58 wt% which was 5% less than CPVP. In addition, powder loading had been chosen based on previous studies in Azaman et al (2016) and Kadiman (2018) which were 58 wt% powder and 42 wt% of binder. A constant increase in the first 20 minutes shown in Fig 4 shows a good mixing process between metal composite of CuAlMn with binder of stearic acid. The first spike line shown in graph indicates the high torque occur during the mixing of composite with diluted Pmma with acetone which is in high viscosity that led to a high resistance in rotor blade. The second spike graph shows the mixing of PEG which has less torque compared to Pmma. This is due to the Peg have low melt temperature and can be easily melt during mixing compared to Pmma.

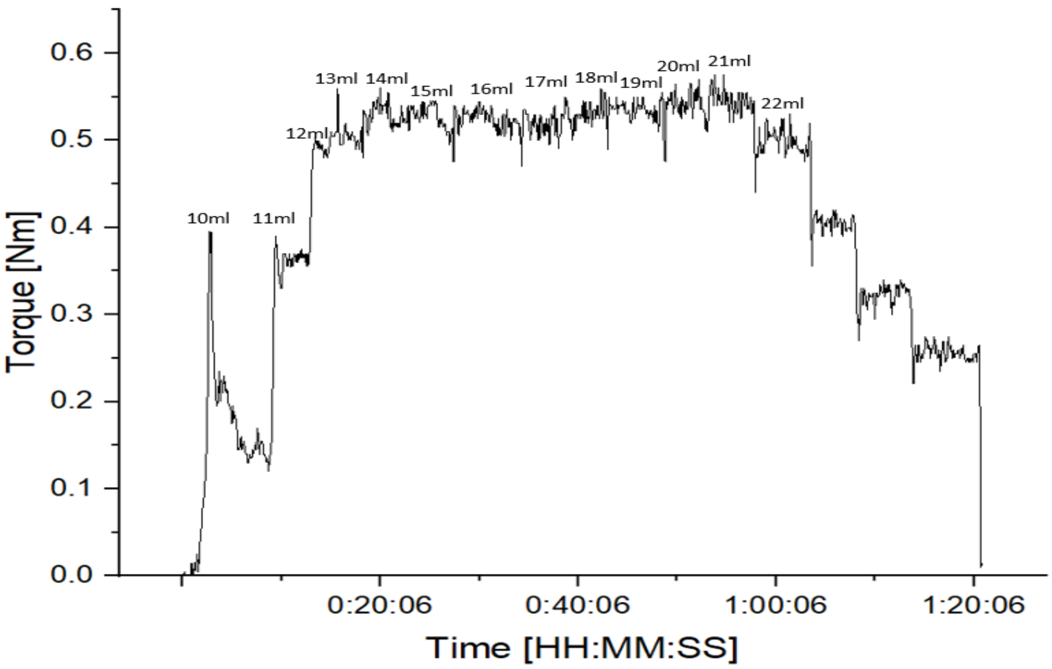


FIGURE 3. Graph for critical powder volume percentage (CPVP)

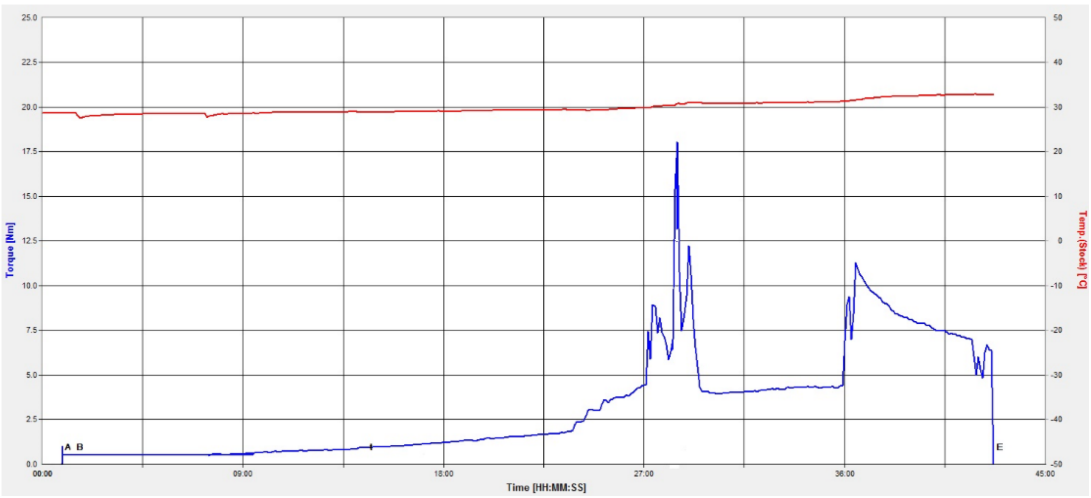


FIGURE 4. Graph for binder mixing (Sa, Pmma and Peg)

RHEOLOGY (VISCOSITY)

The comparison of different loads applied towards the same powder loading of 58% at temperatures of 115 ℃, 125 ℃ and 135 ℃ were presents in Figure 5. The temperatures chosen were above the melt temperature of the binders. This is to ensure the performance of the feedstock viscosity is great at a temperature range of the melting temperature of the binder. The homogeneity and moldability of the prepared feedstock were indicated by the results from the rheology analysis. This show the characteristics of the pseudoplastic behavior and the result was inline as reported by previous researchers (Basir et al. 2020; Nordin et al. 2015; Omar et al. 2020). This behavior complies with one of the fundamental characteristics of a good binder system and is in good correlation with pseudoplastic behavior due to flowability index is lower than 1.

The feedstock's pseudoplastic behavior shows that the fluid binder produced during processing aids in breaking up particle agglomerates, which causes particle reorientation and ordering as the feedstock flows inside the die. According to the previous study, it is preferable for the injection moulding process to have a shear rate value between 1000 s^{-1} and 100000 s^{-1}. The graph result of viscosity versus shear rate which can be seen in Figure 5 shows the value of the viscosity reduce with the increases value of shear rate at a constant load applied when the temperature increases. Viscosity value is seen to decrease with increasing shear rate due to reduced frictional force of powder and binder. At high temperatures, the binder material begins to melt and enter the gap of the materials which makes the flow smooth when pressure is applied (Kadiman et al. 2018).

At a constant temperature, an increasing load will cause a higher viscosity and shear rate. The increasing viscosity value is due to the friction that occurs between the particles because of the high powder loading (Murtadhahadi et al. 2007). Therefore, a high load is required to break up the clumps that form in the feedstock as a result of the high shear rate (Liu & Tseng 2000).

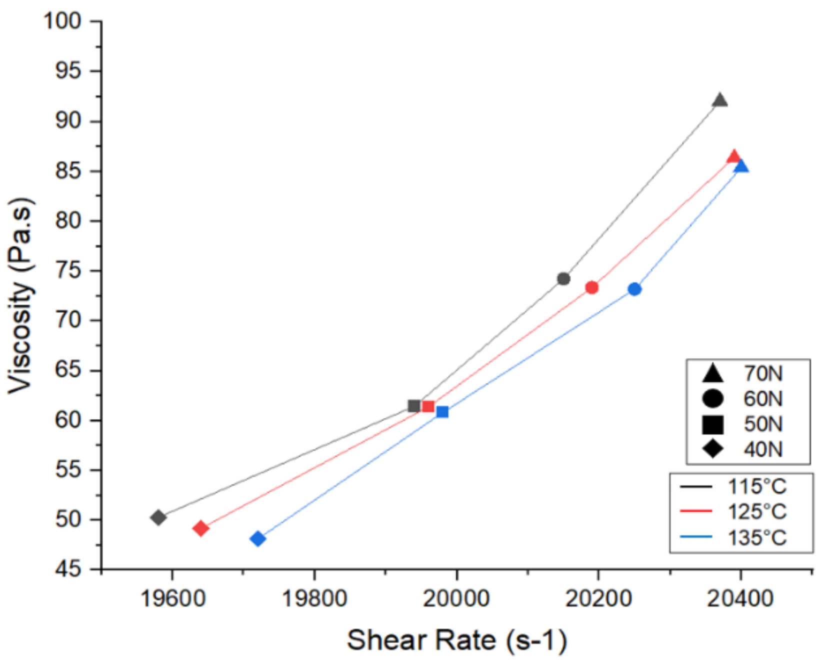


FIGURE 5. Graph for viscosity versus shear rate.

FLOW BEHAVIOR INDEX (η)

The feedstock will be hard to flow when the viscosity is high. In other words, the viscosity of the feedstock is really affecting the flowability and it is not only dependent on the binder but also on the powder loading. The flow behavior index, n, which indicates the level of shear sensitivity, may be used to determine the feedstock's flowability. Equation 2 shows power of law which is to identify the flow behavior, where K is constant, η is the viscosity and γ is shear rate. The lower value of n implies a good flowability of the feedstock.

The values of η based on the flow behavior index data shown in Table 3 indicates that the feedstock have a pseudoplastic behavior because of the values less than 1(Donald et al. 2019; Mohamad et al. 2020). As can be seen from the flow behavior index result, the lowest η values were at 135°C which indicate that this is the optimal temperature compared to 115°C and 125°C that can be used in injection process.

$$\eta = K\,\gamma^{\eta-1} \tag{2}$$

TABLE 3. Flow behavior index values at temperatures 115°C, 125°C and 135°C

Weight (Kgf)	Temperature (°C)	Flow Behavior Index (n)
40	115	0.396
	125	0.394
	135	0.392
50	115	0.416
	125	0.416
	135	0.415
60	115	0.435
	125	0.433
	135	0.433
70	115	0.456
	125	0.449
	135	0.448

CONCLUSION

Based on the critical powder volume percentage (CPVP), the feedstock with powder loading 58 wt% was selected for rheological measurements. In addition, this study has successfully demonstrated using 3 different temperatures of 115°C, 125°C and 135°C and 4 different loads applied. The most suitable temperature that can be referred in injection moulding process can be 135°C because of the lowest value for flow behavior index compared to 115°C and 125°C. Furthermore, the finding of the study also shows that the viscosity of the feedstock reduced with the increasing temperature. An increasing temperature also led to an increasing shear rate at a constant applied load. All results show a pseudoplastic behavior and this powder loading feedstock is suitable for powder injection moulding process.

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DECLARATION OF COMPETING INTEREST

None

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