Rheological study of feed stock for NiTi alloy molded parts

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Abstract. A rheological behaviour of the powder-binder mixture is one of essential analysis upon to success of Metal Injection Moulding (MIM) process. The purpose of this experimental work is to investigate the rheological behavior of feedstock containing mixtures of elemental Ni and Ti powders mixed with composite binder of palm stearin (PS) and polyethylene (PE) binder system. An equiatomic Ni-Ti (50-50) ratio was used in the present work for all formulations owing to excellent shape memory behaviour. The experimental rheological result indicated that all the feedstocks exhibited pseudo plastic flow behaviour; viscosity decreasing with temperature and shear rate. Increasing the powder loading resulted in higher viscosity, particularly at the low-range of shear rate. Owing to pseudo-plastic flow, it was found that the feedstock prepared exhibit promising rheological properties, thus resulting successfully injection moulding at an optimum temperature of 130°C.

1. Introduction
NiTi is categorized as a Shape Memory Alloy (SMA) and has been commercially studied and used in biomedical industry due to two main unique properties, pseudo-elastic (PE) and shape memory effect (SME). Several techniques for producing NiTi alloys by powder metallurgy (PM) have been investigated, emphasizing towards reproducibility and microstructural homogeneity [1]. One of the remarkable PM techniques is metal injection moulding (MIM) which is capable in producing near-net-shape component with a relatively low cost for mass production. However, processing of NiTi by MIM is quite challenging due to restriction in controlling the impurity contents to the lowest level, particularly oxygen and carbon which is mainly originated from inhomegeneity of the powders mixture and residual binder left on particles during debinding stage prior sintering process [1, 2]. Besides that, the powder-binder mixture or generally termed as feedstock should also exhibit good thermal stability and rheological properties to ensure its flowability to fill the mould completely and the shape of moulded part can be retained until the sintering begins [2-4].

The feedstock rheological properties are the key features that affect the steady flow and the uniform filling into the mould. The evaluation of the feedstock rheological properties is based on the viscosity shear and temperature sensitivities, which were used to define a mouldability index [3, 4]. Rheological properties of NiTi alloy feedstock has never been addressed by researchers, since most of them emphasize only the final properties of the SME and PE. It should be borne in mind that the viscosity of MIM feedstock plays a very important role in MIM as it is essential for allowing the particles to flow into the die cavity.
Therefore, specific rheological characteristic is required to establish some insights on the quality of injection moulded samples[5]. The MIM feedstock has often been characterized rheologically by a capillary rheometer especially at low shear rates. Good rheological properties of binder and feedstock are one of the keys to getting green parts with uniform density and defect-free, besides achieving successful debinding and sintering and obtaining high quality products [6].

During injection moulding practice, the feedstock must exhibit pseudo-plastic flow with decreasing viscosity at increased shear rate. This helps to reduce the temperature and pressure required for successful moulding. Generally, during moulding, the shear rate usually ranges between $10^3$ and $10^4 \text{s}^{-1}$, and the maximum useful viscosity for the mixture is 1000 Pa.s or lower at the moulding temperature[7].

The main aim of the present study is to investigate the rheological properties of the feedstock containing elemental Ni-Ti powder blend mixed with palm stearin (PS) based binder. Besides, some experimental on injection moulding was also carried out to demonstrate the feedstock prepared is suitable to be injection moulded.

2. Experimental setup

2.1. Feedstock preparation

Initially, elemental Nickel and Titanium powder were mixed at composition Ti-50.0at% Ni using a stainless steel ball mill for 4 hours at 100 rpm with a ball-to-powder ratio of 2:1 to ensure uniform distribution of the as-mixed powders. Three different powder loadings were studied; 65.5, 67.5 and 69.5 vol% and the binder system consisted of 60 wt% palm stearin (PS) and 40 wt% polyethylene (PE) [8]. The mixing process was carried out using an internal mixer, HAAKE Rheomix at 160°C with a rotational speed of 50 rpm for 2 hrs until homogenous mixtures was observed. The feedstock was then examined using a Hitachi Scanning Electron Microscope (SEM) to observe bonding morphology between the powder and binder.

2.2. Capillary Rheometer

The flow behavior of the feedstock was characterized using a Rosand RH2000 capillary rheometer manufactured by Malvern Instruments TM. The pelletized feedstock was loaded into a preheated chamber at a temperature range of 110-150°C and increased shear rate from 5–8000 s$^{-1}$. The die orifice used was made of tungsten carbide and having a dimension of 1 mm in diameter and 16 mm in length.

2.3. Injection Mouding

Injection moulding was carried out using a manually operated vertical injection moulding with a tensile shape cavity according to the ASTM 638 type V as shown in figure 1(a) and (b)[6]. The moulding temperature range used was based on the rheological result obtained which in range of 110 to 150°C.

3. Results and discussion

Rheological test is used to determine the viscosity level of feedstock when it passes through a die orifice. Figure 2 shows the rheological results for all the feedstock with different powder loading at different temperatures, clearly shear thinning behaviour or pseudo-plastic curve is observed. The selected temperature was referred to the previous successful study of MIM for NiTi [7].
Figure 1. (a) Schematic diagram of manually operated vertical injection moulding and (b) ASTM D638 Type V specimen. [6]

Figure 2. Viscosity versus shear rate at different temperature for different powder loading; (a) 65.5 vol%, (b) 67.5 vol% and (c) 69.5 vol%.

From figure 2, it shows that increasing powder loading results in increasing viscosity, particularly at lower shear rates with maximum viscosity of 250 Pa.s at the maximum powder loading of 69.5%. The trend of shear thinning is clearly seen with increased shear rate and temperature, thus promoting better fluidity during feedstock flow through mould cavity. The maximum viscosity of 250 Pa.s was achieved for the highest powder loading, which were considerably lower than 1000 Pa.s,[7]. A higher viscosity at low shear rates, particularly lower than 100s$^{-1}$ was attributed from less particle orientation.
and ordering with the flow. As the shear rate increased, the viscosity also decreased, corresponding to improved fluidity and homogeneity.

The relationship between viscosity ($\eta$) and shear rate ($\dot{\gamma}$) for the MIM feedstock can be expressed as equation (1) [7, 8].

$$\eta = K \dot{\gamma}^{n-1}$$  \hspace{1cm} (1)

where 
- $\eta$ is a viscosity
- $K$ is a low yielding stress
- $\dot{\gamma}$ is a shear rate
- $n$ is a consistent flow index

From figure 2, the shear sensitivity ($n$) was determined according to equation (1) and the values are summarized in Table 1. It clearly shows that of the $n$ values calculated are within the range of 0.50 to 0.83, which are slightly higher than the previous research [8-10], owing to different powder characteristics, binder system used and method of mixing. From the MIM point of view, the lowest the $n$ value, the most sensitive viscosity to shear rate changes. However, too high $n$ values will result in instability of the process and difficulties in controlling the quality of the green parts due to greater mixture viscosity [7, 8]. In the present work, the feedstock prepared shows the values of $n$ lower than 1 for all temperature applied, thus suggesting appropriate range of temperature for injection moulding.

**Table 1.** Shear sensitivity value ($n$).

| Feedstock | n   |
|-----------|-----|
|           | 110 | 120 | 130 | 140 | 150 |
| 65.5 vol% | 0.83 | 0.72 | 0.73 | 0.77 | 0.79 |
| 67.5 vol% | 0.50 | 0.56 | 0.58 | 0.52 | 0.60 |
| 69.5 vol% | 0.7  | 0.72 | 0.68 | 0.63 | 0.68 |

Figure 3 shows the effect of temperature on viscosities at different powder loading. According to the Arrhenius equation, the flow activation energy, $E$ can be expressed by equation (2).

$$\eta = \eta_o \exp \left( \frac{E}{RT} \right)$$  \hspace{1cm} (1)

where $\eta_o$ is a relative viscosity and $R$ constant (8.314 kJ/mol).

![Figure 3. Arrhenius plots of different powder loading feedstock.](image)

The activation energy $E$ was obtained from the slope of the curve as shown in Figure 3; $E_{65.5} = 15.8$ kJ/mol, $E_{67.5} = 20.9$ kJ/mol and $E_{69.5} = 45.2$kJ/mol, clearly the $E$ increases as the powder loading
increases. From the standpoint of MIM flow during injection, the lower \( E \) value is required to ensure viscosity stability as a result of changes in temperature and shear rate\[10\]. This is particularly important when the part geometries consist of sharp edges and significant changes in cross sectional areas, thus, defects-free moulded parts can be minimized\[7\]. It means the viscosity is not so sensitive to temperature variation and will not result in sudden viscosity which may cause cracking and distortion. The activation energy of feedstock \( E_{65.5} \) is the lowest which implies the best from the standpoint of temperature sensitivity. Compare to the previous research, the current study achieved considerably lower \( E \) for NiTi feedstock with the same powder loading employed. This is probably due to the binder system used, in which the one used by Ismail \[11\] was based on PEG-PMMA system.

Figure 4 shows the morphologies of the feedstock observed under SEM with different powder loadings. It shows that increasing powder loading resulted in greater particles packing with less fraction of binder network observed resulting greater viscosity of the feedstock. The use of palm stearin and polyethylene as a binder in the present work is believed could reduce the feedstock viscosity significantly; when comparing the same powder loading of 69% conducted by Ismail\[11]\, with maximum viscosity observed at 10s\(^{-1}\) was approximately 500 Pas. Therefore, less friction between feedstock and die wall could be expected during injection moulding and parts' surface defects could be minimized considerably. It also attributed a deviation viscosity with increasing temperatures. Similar results were reported by several researchers, claiming the same trend of viscosity\[7,8\].

![Figure 4. SEM micrograph of different powder loading; (a) 65.5 vol%, (b) 67.5 vol% and (c) 69.5 vol%.

The rheological behaviour explicitly shows how important the development of optimized feedstock composition is. Even though rheological test has been carried out, it is difficult when translating the data during injection moulding practice. This is because the arbitrary value must depend on machine pressure and sprue, gate and mould design, to make it possible for higher viscosity to be tolerated. However, the data would give some insights on the scope of the parameter condition to be applied.
during injection moulding practice. Initial experiments of rheological behaviour showed that the choice of a suitable binder system is a major challenge.

During injection moulding process, it was observed that the samples were successfully injection moulded at the barrel temperature of 120°C to 150°C. Figure 5 shows the image of the defect free moulded samples. The total cycle time for each sample was approximately 5 minutes owing to manually operated process, taken into account the time to place the mould underneath the nozzle, injection moulding (~ 1-2 seconds), cooling stage, mould removal and removal of samples. It was observed that the green parts exhibited adequate strength to be handled after they were removed from the mould cavity.

![Image of moulded samples](image.png)

**Figure 5.** Defect free moulded samples.

### 4. Conclusions

All the prepared NiTi feedstocks containing PS/PE binder indicated pseudo-plastic behaviour that facilitated the moulding process. It was found that the viscosity increased as the powder loading increased owing to greater amount of powder in the feedstock. Increasing the powder loading resulted in increased flow activation energy instead of flow behaviour gives fluctuate value.

### Acknowledgement

The authors would like to be obliged to Ministry of Education (MOE) and UniversitiTeknologi MARA for providing laboratory facilities and financial assistance under project no 600-RMI/RACE 16/6/2 (5/2012) and RMI/FRGS 5/3 (38/2012).

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