

## RHEOLOGICAL INVESTIGATION OF A STARCH-BASED BINDER AND FEEDSTOCK FOR METAL INJECTION MOLDING

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### ABSTRACT

This study investigates rheological characteristics of a new binder system based on tapioca starch for metal injection moulding (MIM) process. First in this work, a composition of starch and linear low density polyethylene (LLDPE) as a binder has been provided. Mixture of binder and 316L stainless steel metal powder has been used subsequently to prepare three types of feedstocks with 56, 57 and 58% vol. powder loading. Rheological analysis of the binder and the feedstocks has been accomplished by means of a capillary rheometer. Viscosity values for binders have been measured lower than 10 Pa.s meanwhile this parameter has been obtained less than 1000 Pa.s for feedstocks. It has been observed that binder and feedstocks possess pseudo-plastic flow behaviour which is one of the most crucial requirements in MIM process. Experiments in this study confirm that tapioca starch has the potential to be used as a binder for in MIM process.

**Keywords:** Metal injection moulding, Thermoplastic starch, Binder composition

### 1. INTRODUCTION

Metal injection moulding is one of the effective approaches to produce articles with intricate geometry and high tolerances. This method uses flexibility of plastic injection moulding in producing components with complicated shapes and on the other hand, ability of powder metallurgy in producing components with high mechanical strength. In order to be used in injection moulding, metal powders must be able to flow under pressure. Typically, composition of polymers with different properties known as binder system can provide flowability for metal powders. MIM process consists of mixing metal powders and binder to make feedstock, injection moulding to create green part, debinding to remove binders and sintering to grant enough strength for articles (German and Bose 1997).

Binder composition is the key feature in MIM process due to its effect on all the processing steps. The first concern is miscibility with metal powder in mixing process to make a homogeneous paste. The second issue is binder's viscosity and its flow characteristics during injection moulding. It is desirable for the binder to be easily removed in debinding process and recycled. The next desired property for the binder is to be easily burnt

out with minimum carbon residual at sintering process. In addition to mentioned specifications, a good binder is desired to be environmentally friendly and low cost (German and Bose 1997).

Nowadays, utilizing natural polymers in a wide range of different industries has become an interesting issue because of environmental concerns. Due to their biodegradability, they can be considered as a suitable substitution for synthetic polymers. Starch as an old source of food for human and animals has been known for centuries and its application in textile industries is back to Egyptian times (Kearsley and Dzedzic 1995). Glucose polymerization in starch results in two types of polymers: amylose and amylopectin. Amylose is an essentially linear polymer, whereas the amylopectin molecule is much longer and is branched. The structural differences between these two polymers lead to significant differences in starch properties and functionality. For instance, amylose gives gel properties to starch in aqueous media while isolated amylopectin is easily dispersed in water and does not readily become gel (Thomas and Atwell 1999). Starch is an odourless and tasteless powder, which loses the equilibrium moisture content and decomposes in temperatures higher than 100°C. Then no melting takes place and starch degrades before melting. In other words, starch flow through direct heating is almost impossible (Lin et al. 2007). Mixing starch and water at high temperatures and under shear provides a sticky gel. Hence, an external plasticizer is required to make its behaviour similar to thermoplastic polymers. Plasticizers can form the hydrogen bonds with starch, taking place of the strong reaction between hydroxyl group of starch molecules and make starch plasticized display (Rodriguez-Gonzalez et al. 2004).

In this study, application of tapioca starch as a major constituent of a binder for metal injection moulding process has been investigated.

### 2. EXPERIMENTAL PROCESSES

#### 2.1. Materials

Native tapioca starch was kindly provided from National Starch and Chemicals Sdn. Bhd. Citric acid anhydrous (Batch No. 070215FGKUH and M=192.13 g/mol), stearic acid and glycerol anhydrous (Batch No. 071121KUHUSP and M=92.10 g/mol) were purchased from SYSTERM Co. Linear low density polyethylene

was supplied by TITANEX with melt flow index of 25 g/10min and batch No. LI2516. Table 1 shows ingredients of binder and their properties.

Table 1 Binder components and their characteristics (Mark, 1999)

Component	Chemical structure	$\rho$ (g/cm <sup>3</sup> )	Melting point (°C)
Starch	(C <sub>6</sub> H <sub>10</sub> O <sub>5</sub> ) <sub>n</sub>	-	-
Glycerol	C <sub>3</sub> H <sub>5</sub> (OH) <sub>3</sub>	1.261	18
LLDPE	(C <sub>2</sub> H <sub>4</sub> ) <sub>n</sub>	0.918	130
Citric acid	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	1.665	153
Stearic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	0.847	69.6

The metal powder used for preparation of feedstocks in these experiments was water atomized 316L stainless steel which was purchased from EPSON ATMIX Corporation, with the average particles size of 20  $\mu$ m.

## 2.2. Binder Preparation

In this study, a composition of ingredients in Table 1 are used in binder formulation. As mentioned before direct melting process for starch is almost impossible. Therefore, other approaches should be taken to make starch flowable. Starch attribute in water has been recognized for long time in its commercial applications. Starch granules uptake water at temperatures higher than 50°C (depend on botanical source) and swell and make a large molecular network. This process is known as gelatinization which provides flowable property for starch (Rutenberg 1980). Before mixing starch with other major binder components including LLDPE as the backbone and stearic acid as the surfactant, starch behaviour must be made similar to thermoplastic polymers by plasticization process. At the first stage, a blend of starch, distilled water and glycerol was heated in a sigma-blade mixer to make a yellow transparent fluid, which could be considered thermoplastic starch (TPS). The mixing temperature was set at 130°C. As it was anticipated, the excess water content in thermoplastic starch evaporated due to the working point temperature (Rodriguez-Gonzalez et al. 2003).

The next step was mixing thermoplastic starch and the backbone agent. In order to facilitate mixing of TPS and LLDPE, a compatibiliser was required. One of the most readily applicable agents is citric acid (Wang et al. 2007). Citric acid and LLDPE were added to thermoplastic starch simultaneously that produced a white homogeneous paste after 30 minute of mixing. Finally, stearic acid was added to the mixture as surfactant to bridge between binder and metal powder. Table 2 shows the proportion of binder components. It was observed that the stiffness of the binder at room temperature was reasonably acceptable which means backbone content has been adequate to ensure green part strength. Typically, backbone components in MIM involve approximately 30% of binder composition (Loh et al. 2001).

Table 2 The binder's composition

Component	Content (wt.%)
Starch	41.3
Glycerol	23.3
LLDPE	28.5
Citric acid	1.9
Stearic acid	5

## 2.3. Feedstock Preparation

After preparation of binder, blends of metal powder and binder with different solid contents were provided as feedstock samples. This process was conducted by a sigma blade mixer. The mixer rotational frequency was set at 48 rpm. The mixing temperature was set at 140°C to obtain homogeneous pastes. In order to find suitable solid loading, three types feedstocks were prepared with 56, 57 and 58% vol. powder loading. Hereafter, these feedstocks are identified by F1, F2 and F3 respectively.

## 2.4. Samples Characterization

Rheological behaviour of prepared samples including TPS, binder and feedstocks was assessed using a CTF-500D Shimadzu Capillary Rheometer. The samples were extruded through a die with 1 mm diameter and 10 mm length. Depending on density of samples, different amount of materials can be loaded. Here, 1 gram for TPS and binder and 4 grams for feedstocks were taken to carry out the measurements. In order to reach thermal balance after charging the cylinder, the preheating time was set 5 min for TPS and binder. Since, thermal conductivity of feedstocks due to presence of metal powders is normally higher than binders, thermal balance phase was decreased to 3 min for feedstocks. In these series of experiments, measured viscosity and shear rate were in Pa.s and s<sup>-1</sup> units respectively. In order to increase reliability of experiments, for binder and feedstocks, the tests were repeated for each point. In case of TPS, the aim of rheological analysis has been just observation of flow characteristics, thus the tests were conducted for each point once only. Flow behaviour of TPS was investigated at three sets of temperature including 70, 90 and 105°C. Temperatures points of 70 and 105°C were selected to assess TPS's fluidic behaviour below gelatinization point and after losing water content, respectively.

Fluidic characterization of binder system was investigated near to its melting temperature (120, 130 and 140°C). Normally, by mixing metal powders and binder, the inter-particle friction increases. Thus, for the purpose of increasing flowability, one of the most effective approaches is increasing temperature. Therefore, rheological analyses of feedstocks were performed at higher temperatures (160, 170 and 180°C) rather than binder.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Effect of Shear Rate

Typically in MIM process, shear rate varies between 100 and 100000 s<sup>-1</sup>. In this range of shear rate, viscosity of a desirable feedstock at moulding temperature must be lower than 1000 Pa.s. In order to achieve this viscosity, maximum viscosity of used binder should be 10 Pa.s (German and Bose 1997). For non-Newtonian fluids, relationship between viscosity and shear rate could be described by following equation:

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

where  $K$  is a constant and  $n$  is flow behaviour index. This parameter ( $n$ ) determines shear dependency of viscosity. Unlike Newtonian fluids, viscosity of non-Newtonian fluids varies with increase or decrease of shear rate. Dilatant fluids ( $n > 1$ ) exhibit an increase on meeting ascended shear rate. Meanwhile, in pseudo-plastic substances ( $n < 1$ ), the viscosity decreases with increased shear rates.

Flow characteristics of TPS as the major component of binder was investigated at three sets of temperature including 70, 90 and 105°C. The results of these measurements are given in Figure 1.

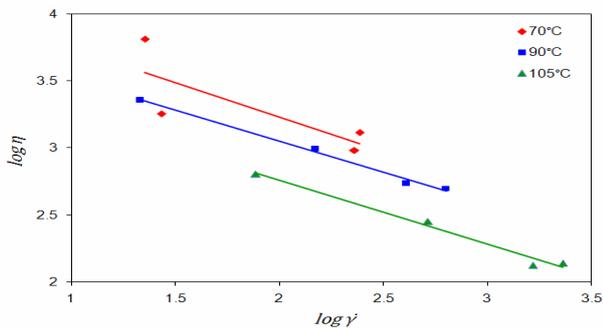


Figure 1 Relationship between viscosity and shear rate of thermoplastic starch

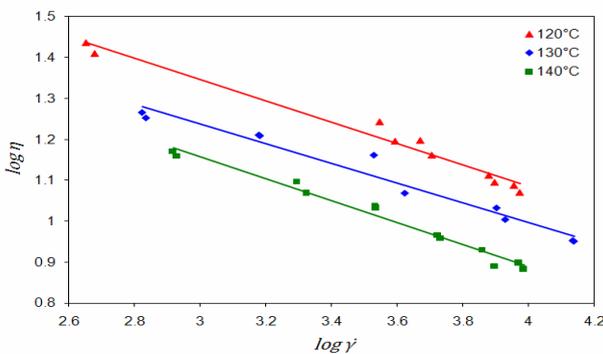


Figure 2 Relationship between viscosity and shear rate of binder

Decreasing viscosity by increasing shear rate implies pseudo-plastic behaviour of TPS which satisfies the preliminary requirement of a binder component for MIM.

In other words, the base component in terms of flow behaviour is eligible for injection moulding.

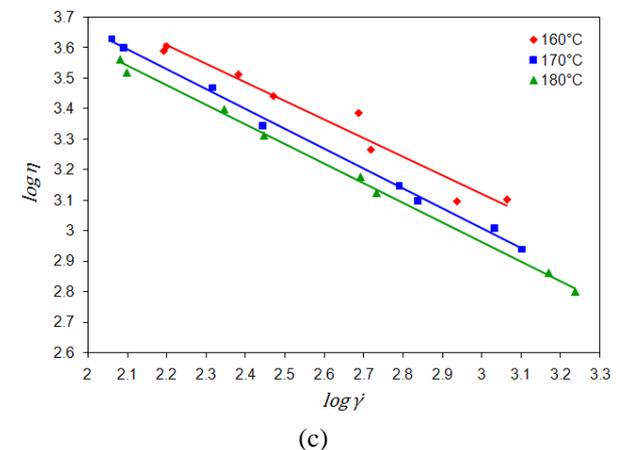
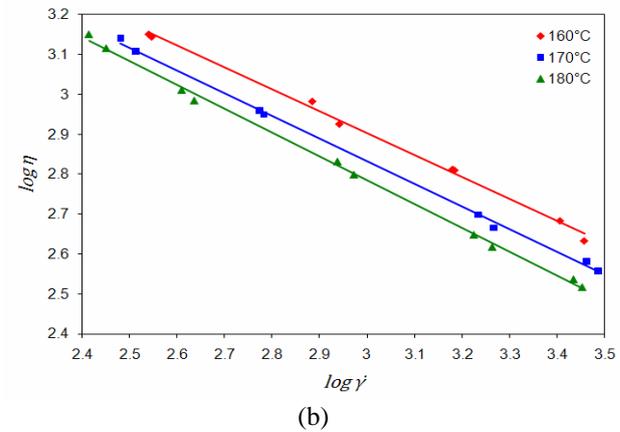
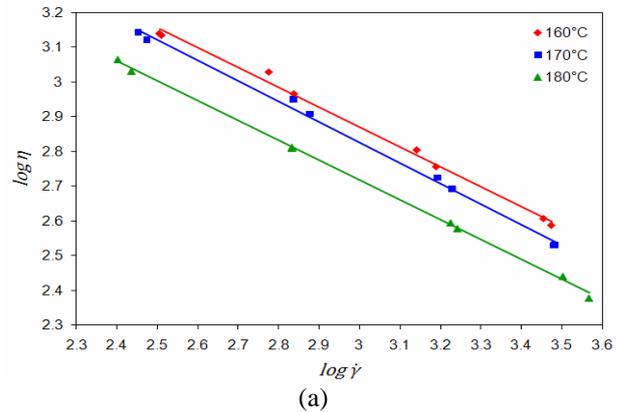


Figure 3 Relationship between viscosity and shear rate of feedstocks a) F1 b) F2 c) F3.

By estimation of test results to straight lines and according to general shear rate dependency of viscosity equation (Equation 1), the values of  $n$  could be easily calculated (Huang et al. 2003). The flow behaviour index at 70, 90 and 105°C was derived from slope of graphs as 0.49, 0.54 and 0.52 respectively. It can be observed that, TPS does not show uniform flow behaviour at 70°C. A possible explanation for this might be that starch gelatinization occurs at 76°C and at 70°C starch is still in suspension form but at higher temperatures, it exhibits a

linear correlation between viscosity and shear rate. As expected, TPS shows more shear thinning attribute at higher temperatures which can be observed from descending trend of flow behaviour index from 0.54 to 0.52. The rheological measurements of the binder were carried out at three different temperatures including 120, 130 and 140°C. Figure 2 shows the correlation of viscosity and shear rate for the binder.

As illustrated in Figure 2, the viscosity generally decreases with an increase in shear rate. As mentioned before this attribute is called pseudo-plastic behaviour which satisfies initial requirement of a good binder. It can be observed that, the viscosity values, especially at 140°C were obtained less than 10 Pa.s. The rheological measurements show that the shear rate values (up to 10000 s<sup>-1</sup>) fulfil the requirement of shear rate ranges of MIM as well. Slope of above graph is equal to values of  $n-1$  at Equation 1 which can be readily derived. Consequently, the values of  $n$  for temperatures 120, 130 and 140°C were obtained 0.74, 0.76 and 0.73 respectively.

Rheological characteristics of feedstocks were evaluated at 160, 170 and 180°C. The effects of solid loading on flow characteristics of feedstocks were investigated. Results of these measurements have been represented in Figure 3. Decreasing viscosity with increasing shear rate implies pseudo-plastic behaviour of all provided feedstocks. This property avoids powder-binder separation during injection moulding (German and Bose 1997). Apparently, the feedstock which consists of 56% vol. powder loading shows lower viscosity.

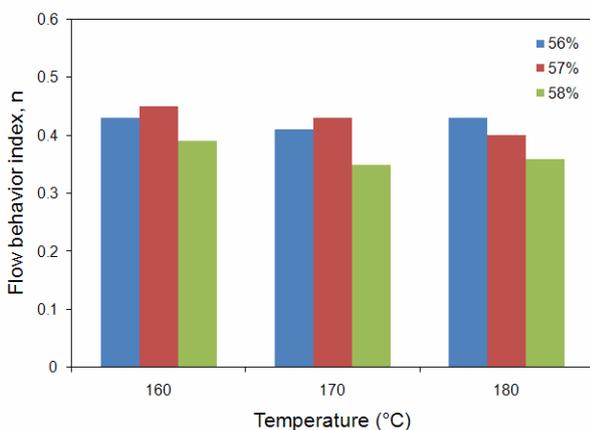


Figure 4 Flow behaviour indexes of feedstocks at different temperatures.

The next observation in feedstocks rheology has been on viscosity values. This parameter has been less than 1000 Pa.s for F1 and F2 meanwhile F3 principally shows higher viscosity values. It means that flow behaviour of F3 does not satisfy injection moulding requirements, although a higher solid loading feedstock is more suitable to produce compacts with minimum dimensional shrinkage. Through gradient of above graphs, flow behaviour indexes can be easily calculated using Equation 1. Figure 4 illustrates flow behaviour indexes of

feedstocks at different temperatures. Despite of high viscosity values of F3, it shows more sensitivity to shear or greater pseudo-plasticity compared to two other feedstocks. A comparison between F1 and F2 represents that the feedstock including 56% vol. powder loading has lower  $n$  values rather than F2 except at 180°C, though these values are very close together for these two feedstocks.

### 3.2. Effect of Temperature

Temperature dependency of viscosity is the next significant factor which is very valuable in determination of the fluid characteristics. With a good approximation, Arrhenius equation can be utilized to describe correlation of viscosity and temperature:

$$\eta = \eta_0 \exp\left(\frac{E}{RT}\right) \quad (2)$$

where  $\eta_0$  is viscosity at reference temperature,  $E$  is activation energy,  $R$  the universal gas constant and  $T$  is the temperature. Flow activation energy can be derived through correlation between viscosity and temperature. Slope of  $\ln \eta$  versus  $\frac{1}{T} \times 10^3$  graph is equal to flow

activation energy in Arrhenius equation. The relationship between temperature and viscosity for the examined binder is given in Figure 5. Knowing that such an illustration is common for the feedstock not the binder, the given graph is presented just as a base for comparison with the graphs following this part.

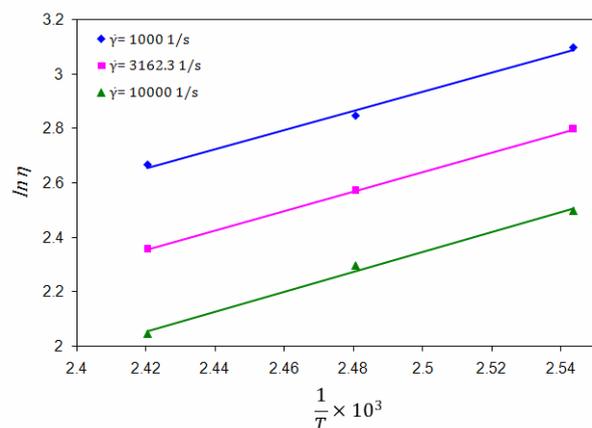


Figure 5 Correlation of viscosity and temperature for binder

The derived flow activation energy values for binder are equal to 29.2, 29.8 and 30.5 kJ/mol at shear rates of 1000, 3162.3 and 10000 s<sup>-1</sup>, respectively. Similarly, temperature dependency of two acceptable feedstocks, F1 and F2 has been drafted at three sets of shear rates including 398.1, 1000 and 2511.9 s<sup>-1</sup> in Figure 6. Temperature dependency of viscosity for F2 in these graphs could be fitted to straight line showing better agreement of its behaviour with Equation 2. Flow

activation energies of feedstocks derived in different shear rates are tabulated in Table 3.

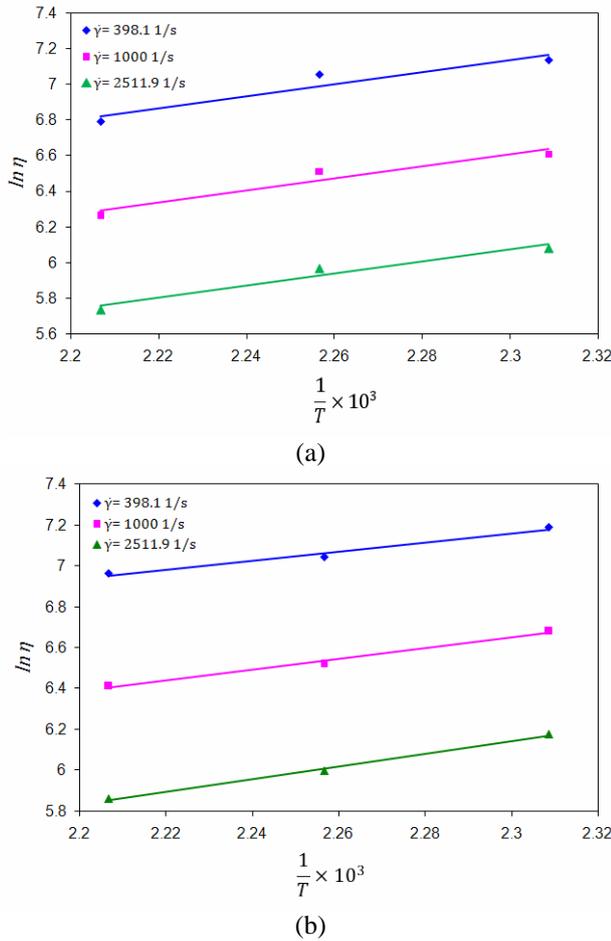


Figure 6 Correlation of viscosity and temperature for feedstocks a) F1 b) F2

Table 3 The flow activation energy of feedstocks (kJ/mol)

$\dot{\gamma}$ (s <sup>-1</sup> )	F1	F2
398.1	28.06	18.51
1000	28.08	22.01
2511.9	28.10	25.51

Basically, the flow activation energy values are in a range which previously have obtained by Huang et al. 2003, Li. et al. 1999 and Li et al. 2007 for MIM process. Generally, the results represent that F2 needs lower energy to flow in comparison with F1.

A comparison between binder and feedstock from the viewpoint of temperature dependency of viscosity shows that binder needs more energy to flow due to the different temperature set ups. Rheological behaviour of binder was tested at 120-140°C while these experiments conducted for feedstocks at 160-180°C. These results reconfirm the dependency of viscosity to temperature.

### 3.3. General Rheological Behaviour

There are several factors which contribute to a successful injection moulding process such as viscosity and its dependency to shear rate, temperature and powder loading. A feedstock with low viscosity, low flow behaviour index and low activation energy exhibits better rheological properties for injection moulding. However, sometimes there is a contradiction among these parameters. Hence, another parameter is introduced to assess general rheological properties of MIM feedstock (Khakbiz et al. 2005; Ibrahim et al. 2009). The mouldability index ( $\alpha_{STV}$ ) has been established to integrate the effect of all above mentioned factors:

$$\alpha_{STV} = \frac{1}{\eta_0} \frac{\left| \frac{\partial \log \eta}{\partial \log \dot{\gamma}} \right|}{\left| \frac{\partial \log \eta}{\partial \left( \frac{1}{T} \right)} \right|} \quad (3)$$

The subscriptions *S*, *T* and *V* of  $\alpha_{STV}$  predicate the influence of shear, temperature and viscosity respectively. Practically, this equation is used in a simplified form:

$$\alpha_{STV} = \frac{1}{\eta_0} \frac{|n-1|}{\frac{E}{R}} \quad (4)$$

It has been stated by Li. et al. 1999 that the higher values of  $\alpha_{STV}$  show the better general rheological properties. Table 4 shows the mouldability index of examined feedstocks at 1000 s<sup>-1</sup> as a function of temperature.

Table 4 General moldability index of feedstocks at different shear rates

Temperature (°C)	F1	F2
160	2.3	2.6
170	2.6	3.2
180	3.2	3.8

As can be observed, mouldability of feedstock generally improves at higher temperatures. Feedstock with 57% powder loading (F2) shows higher general rheological index compared to the feedstock with 56% powder loading (F1), which confirms F2 as an acceptable composition for injection moulding.

### 4. CONCLUSIONS

Gelatinisation process was chosen as the best approach providing fluidic behaviour for starch. The result of this stage was a viscous colloidal fluid, which satisfied flowability necessities for starch. Combination of tapioca starch and other binder system ingredients after cooling to room temperature, demonstrated a rigid bulk which

satisfied the stiffness requirement of the binder system. The result of mixing binder and metal powders showed that homogenous pastes of binder and powder can be prepared as feedstocks. Rheological analysis of TPS showed decrease in viscosity of TPS by increasing shear rate which implied pseudo-plastic behaviour of TPS. This aspect satisfied the preliminary requirement of a binder component for MIM process. In other word, in terms of flow behaviour the prepared sample is eligible for injection moulding.

Investigation of rheological characteristics of binder verified eligibility of this starch based binder system for metal injection moulding since, during flow characterization of binder system, viscosity values were less than 10 Pa.s and flow behaviour of binder followed pseudo-plastic attribute. Shear thickening characteristics of feedstocks support application of this binder formulation for MIM process as well. Among three provided feedstocks, F2 with 57% vol. powder loading was distinguished as the best composition due to its low viscosity values (less than 1000 Pa.s), the lower flow activation energy and foremost among them higher mouldability index. Results of this study represent that tapioca starch can be a promising alternative for synthetic polymers in MIM process.

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