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# Rheological properties of Mg based feedstocks with micro or nano $Al_2O_3$ powder for injection molding

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**In powder injection molding process, the rheological properties of feedstocks significantly influences the steady flow and the uniform filling into the mold. In this study, we investigated the effect of micro and nano size particles of $Al_2O_3$ on the rheological properties of Mg-$Al_2O_3$ feedstocks. A binder system containing Paraffin wax, Bees wax, and Stearic acid was synthesized. This binder was mixed with pure Mg and $Al_2O_3$ powders in various proportions. The $Al_2O_3$ powders contained both nano- and micro-$Al_2O_3$ differing in concentration from one sample to another. Flow characteristics of the samples were then investigated under different circumstances of shear rate and temperature by means of a rotary rheometer. Viscosity of the feedstocks was found to be decreased with micro size $Al_2O_3$ content whereas increased via nano size $Al_2O_3$.**

**Key words: Injection moulding, Micro-$Al_2O_3$, Nano-$Al_2O_3$, Rheological properties, Mg-$Al_2O_3$.**

## Introduction

Development of new structural materials with higher strength-to-weight ratios is one of the main challenges in transportation industry to reduce fuel consumption and greenhouse gas emissions [1]. Discontinuously reinforced magnesium matrix composites (DRMMCs) have been receiving great attention in weight critical structure applications such as automotive and aerospace equipment because of their high specific properties, good damping capacities, high wear-resistance, and relative ease of fabrication [2]. As the lightest structural metal, magnesium is considered for many other structural applications such as bicycle frames, computer hardware and portable electronic equipments [3, 4]. In medical science, magnesium alloys are very promising candidates for degradable implants [5].

Compared to traditional powder metallurgy, powder injection molding (PIM) process allows for producing high density products, more intricate shape, higher mechanical properties, and better surface finish than that of traditional powder metallurgy products [6]. This process involves mixing either metal or ceramic powder with a binder to produce a feedstock. During molding, pressure is applied to the feedstock which then flows into and fills a mold to form a green part with the desired shape. The resulting part is then debinded and sintered to full or near full density. The molding stage is a critical step for the fabrication of sound parts without cracks and distortions. It requires specific rheological behavior, so that the rheological characteristics of feed stocks are of crucial importance [6].

Non-homogenous flow and powder-binder separation can produce defects during molding, which result in crack formation during debinding and sintering, and ultimately poor physical and mechanical properties of the final PIM product. Amongst different parameters, viscosity is the most important predictor of feedstock quality which influences the success of molding stage. It is known that a sound molded part would be obtained when the viscosity is controlled within a narrow range. Therefore, the rheological behavior and stability of PIM feedstock are key features for successful manufacturing [7].

In this study, PIM process is applied to the magnesium based composite. A plethora of investigations have so far been conducted on rheological properties of various feedstocks. Scanty publications deals with the rheological properties of Mg based feedstocks.

In this work the rheological characteristics of Mg-$Al_2O_3$ composite feedstocks and the influence of different parameters such as concentration and particle size of $Al_2O_3$ and temperature are investigated.

## Experimental

### Materials

The magnesium was in commercial grade and the micro- and nano-alumina powders were provided by Martinswerk and Nabond, respectively. The characteristics of the magnesium and alumina powders are summarized in table 1.

The binder composed of paraffin wax (PW) from Behran Oil Industry, refined beeswax (BW) was from a

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**Table 1.** Characteristics of magnesium and alumina powders.

| Powder | $d_{50}$ | Density ($g/cm^3$) | shape | Purity (%) |
|---|---|---|---|---|
| Mg | 53 µm | 1.74 | irregular | 97 |
| micro-$Al_2O_3$ | 0.5-0.7 µm | 3.92 | Spherical | > 99.8 |
| nano-$Al_2O_3$ | 30 nm | 3.98 | Spherical | > 99 |

**Table 2.** Characteristics of binder components.

| Component | Chemical formula | Melting temperature (°C) | Density ($g/cm^3$) |
|---|---|---|---|
| PW | $C_{25}H_{52}$ | 75 | 0.90 |
| BW | $C_{15}H_{31}COOC_{30}H_{61}$ | 66 | 0.96 |
| SA | $CH_3(CH_2)_{16}COOH$ | 71 | 0.94 |

**Table 3.** Mg-micro $Al_2O_3$ mixtures (wt.%).

| Sample code | Powder (33 wt %) | | Binder (67 wt %) | | |
|---|---|---|---|---|---|
| | Mg | Micro-$Al_2O_3$ | SA | BW | PW |
| MA0 | 100 | 0 | 6 | 10 | 84 |
| MAM5 | 95 | 5 | 6 | 10 | 84 |
| MAM10 | 90 | 10 | 6 | 10 | 84 |
| MAM15 | 85 | 15 | 6 | 10 | 84 |
| MAM20 | 80 | 20 | 6 | 10 | 84 |

**Table 4.** Mg-nano $Al_2O_3$ mixtures (wt.%).

| Sample code | Powder (33 wt %) | | Binder (67 wt %) | | |
|---|---|---|---|---|---|
| | Mg | Nano-$Al_2O_3$ | SA | BW | PW |
| MA0 | 100 | 0 | 6 | 10 | 84 |
| MAN1 | 99 | 1 | 6 | 10 | 84 |
| MAN2.5 | 97.5 | 2.5 | 6 | 10 | 84 |
| MAN5 | 95 | 5 | 6 | 10 | 84 |
| MAN10 | 90 | 10 | 6 | 10 | 84 |

locally chemicals vendor and granulated stearic acid (SA) from Merck. The characteristics of the binder components are listed in table 2.

The microstructure of the starting powders was studied by a scanning electron microscopy (Hitachi S-4160) and a transmission electron microscopy (Zeiss em-900). Simultaneous thermal analysis (STA) was conducted on the binders. The examined temperature range was 0 to 600 °C at a heating rate of 5 °C/min in an argon atmosphere with a flow rate of 100 $cm^3$/min.

## Samples

Nine feedstocks were prepared according to tables 3, 4. For all Mg-$Al_2O_3$ bimodal powders, the mixture of powders were prepared by blending pure magnesium and $Al_2O_3$ powder in a RFTSCH PM-400 mechanical alloying machine for 1 h under argon atmosphere with the speed of 200 rpm. Alumina powders were dried before mixing in an oven at 110 °C for 1 h.

# Results and Discussion

## Specifications of binder

During mixing and injection, the temperature should not be less than the highest melting temperature of binder components, nor should it exceed the lowest decomposition temperature of the binder components. Then determination of these temperatures range is important. Fig. 1 shows the STA test result of binder. A small endothermic peak in 75 °C in DTA curve is related to melting point of binder and the weight loss

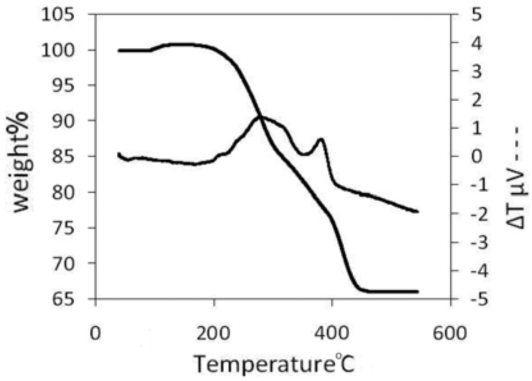


**Fig. 1.** STA of the binder.

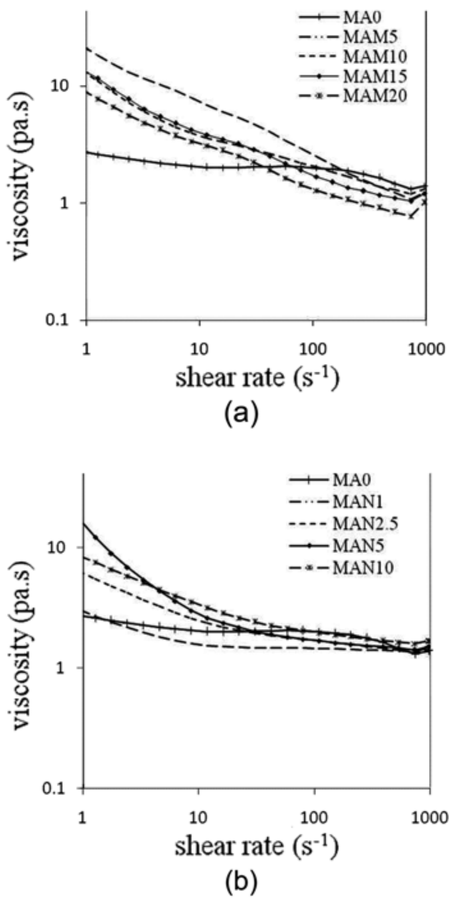


**Fig. 2.** Viscosity versus shear rate at 75 °C of (a) Mg-micro $Al_2O_3$ feedstocks and (b) Mg-nano $Al_2O_3$ feedstocks.

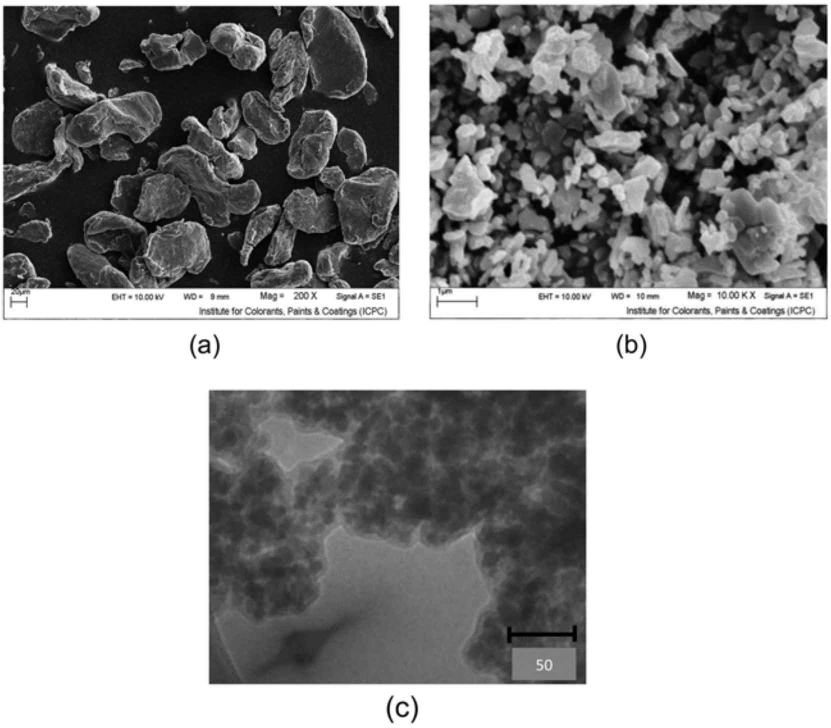


**Fig. 3.** SEM micrographs of (a) magnesium powder (b) micro- $Al_2O_3$ powder and (c) TEM graph of nano- $Al_2O_3$ powder.

which is started at about 200 °C reveals the decomposition of binder.

Mixing operation for all feedstocks was carried out by an internal mixer at a rotating speed of 20 rpm at 75 °C for 15 min. The viscosity of the formulations was measured using a rotary rheometer (Physica MCR 301) after each mixing process. Generally in PIM, the shear rate varies in the range of 100 to 1000 S-1 [8], thus shear rates within this range was applied for all of rheological studies. The test temperature was maintained at 75 °C which is within the above mentioned temperature range.

## Viscosity measurement

Viscosity is the most important parameter in determining the rheological behavior of the PIM feedstock. For example, a high viscosity hinders the molding process while a low viscosity separates the binder from the powder [9]. In addition, for PIM, the shear rate can vary from 100 to 1000 $s^{-1}$ and the flow rate requires a viscosity of less than 1000 Pa.s during injection molding [8]. Fig. 2 indicates the rheological behavior of feedstocks at 75 °C.

The viscosity of MA0 sample at shear rate of 1-10 $s^{-1}$ decreases drastically which is due to relatively weak structures in feedstock that is broken with a low shear rate. At shear rates between 10 and 100 $s^{-1}$, it exhibits a shear thickening (dilatant) flow behavior, i.e. the apparent viscosity increases with the shear rate. The mechanism of dilatancy is controlled by factors such as concentration, shape anisotropy, particle size and density, through changing particle interaction [9]. In concentrated systems, applying of shear produces a rearrangement of solids causing a mechanical non-spherical particles process when subjected to shear. This significantly increases the occupied volume and the effective concentration. Large and dense particles possess greater inertia and thus are momentarily retarded, then accelerated when subjected to shear. The energy expenditure required to accomplish this acceleration results in an additional resistance to flow, or a higher apparent viscosity [10]. Fig. 3 shows the morphologies of Mg, micro-$Al_2O_3$ and nano-$Al_2O_3$ particles. It can be seen that magnesium particles are irregular.

The dilatancy behavior can be related to the morphology of these particles. It is clear that alumina particles are relatively spherical. The spherical morphology allows for the reduction of inter particle friction and subsequently yields shear thinning behavior. At shear rates between 100-1000 ($s^{-1}$), all samples exhibited shear thinning (pseudo plastic) behavior and the viscosity decreased as the shear rate increased. The declining of viscosity with increasing shear rate indicates particle (or binder molecule) orientation and ordering with flow, which may improve the homogeneity of the feedstock. It is clear that all samples containing micro- and nano-$Al_2O_3$ yielded only shear thinning behavior. Thus it can be concluded that addition of nano- and micro-$Al_2O_3$ to Mg powder leads to an increase in attraction interaction between particles and this is why shear thinning is the prominent rheological behavior in all shear rates in $Al_2O_3$ containing feedstocks. In order to describe this phenomenon, it can be considered that higher $Al_2O_3$ content can fill the voids within the particles of Mg powder and makes the particle size distribution of the feedstock smoother. This can also affect the powder-binder interaction and prevent its sudden fluctuations due to changes in shear rate.

It can be seen from Fig. 2 that with increasing the amount of nano-$Al_2O_3$, the viscosity of feed stocks containing nano-$Al_2O_3$, initially increases and then decreases, while the viscosity of those with more micro-$Al_2O_3$ content decreases with increasing the amount of micro-$Al_2O_3$. Formation of topical aggregates is probable for nano-$Al_2O_3$ due to their higher specific surface area than micro-$Al_2O_3$ particles. These aggregates can decrease the viscosity of paste in low concentrations via their arrangement within small voids of Mg particles. Higher concentrations of nano-$Al_2O_3$, however, increase their interactions causing an increase in viscosity. For micro-$Al_2O_3$ the interactions of particles are lower than that of nano particles. Moreover, as $Al_2O_3$ particles have spherical shape, an increase in their concentration leads to a decrease in viscosity.

## Effect of shear rate

The Ostwald and De Waele power law [8] was used to study the correlation of viscosity to shear rate at a given temperature:

$$\tau = k\dot{\gamma}^{n} \tag{1}$$

Where $\tau$ is the shear stress, $\dot{\gamma}$ is the shear rate, $k$ is a constant and $n$ is the flow behavior exponent. The value of $n$ indicates the degree of shear sensitivity. Unlike Newtonian fluids, viscosity of non-Newtonian fluids varies as shear rate fluctuates. Dilatant fluids ($n > 1$) exhibit an increase in viscosity at an enhanced shear rate. In pseudoplastic substances ($n < 1$), on the other hand, the viscosity decreases with increasing the shear rate [11].

The lower the value of $n$, the more quickly the viscosity of feedstock changes with shear rate. Injection molding of PIM feedstock is conducted under pressure and temperature. It is desirable that the viscosity of the feedstock should decrease quickly with increasing shear rate during molding. This high shear sensitivity is especially important in producing complex and delicate parts [12]. Fig. 4 indicates the shear rate against shear stress at 75 ºC.

The power law equations were extracted for each sample from this figure and the values of n were obtained (Fig. 5). Expectedly n in micro-$Al_2O_3$ containing samples is smaller than that of nano-$Al_2O_3$ containing ones because samples with nano-$Al_2O_3$ yield more pseudoplastic behavior than micro-$Al_2O_3$ containing ones. In other words, the attractive interactions between particles are stronger for nano particles than micro particles.

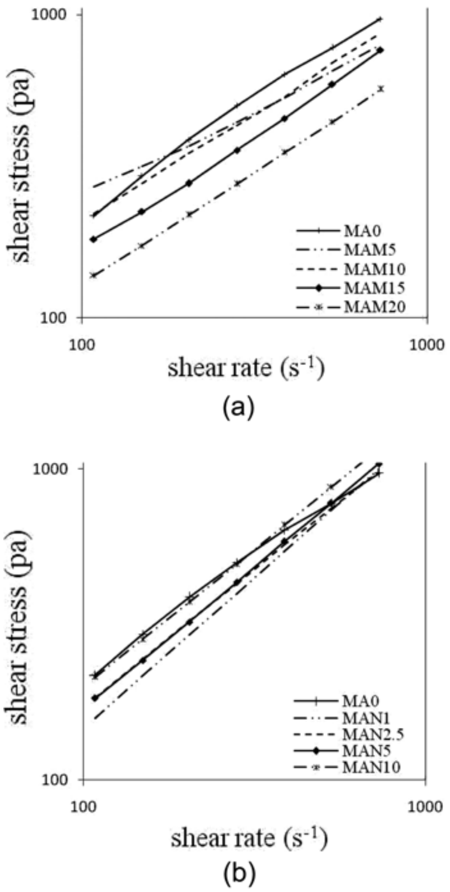


**Fig. 4.** Shear stress versus shear rate of feed stocks at 75 ºC of (a) Mg-micro $Al_2O_3$ feedstocks and (b) Mg-nano $Al_2O_3$ feedstocks.

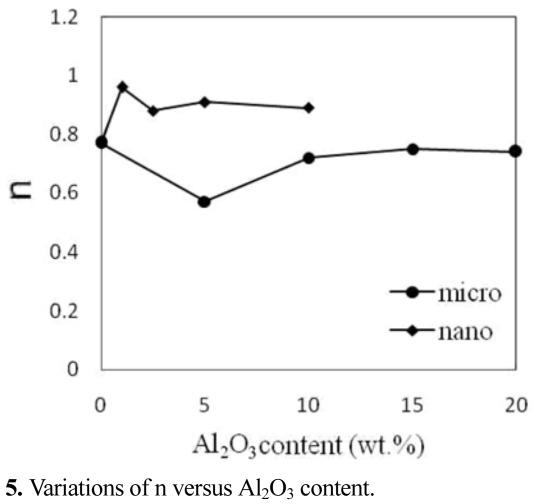


**Fig. 5.** Variations of n versus $Al_2O_3$ content.

It is clear that the feedstock with larger amount of micro-$Al_2O_3$ powder shows more pseudoplastic flow behavior than other feedstocks and is more suitable for injection molding. Whilst, feedstocks with a higher contents of nano-$Al_2O_3$ powder is more difficult for injection. Overall, unlike nano-$Al_2O_3$ powder, addition of micro-$Al_2O_3$ powder makes molding easier and is more favorable from this point of view.

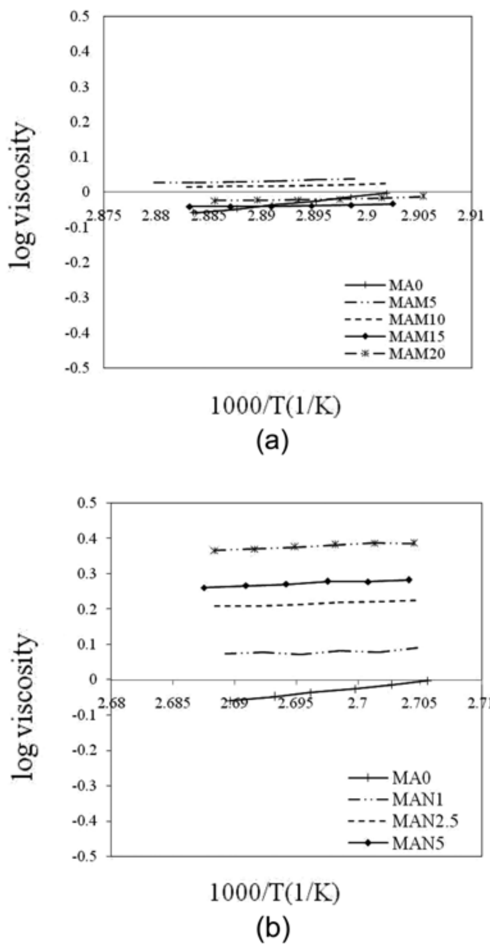


**Fig. 6.** log viscosity versus $\frac{1000}{T}$ at 75 ºC of (a) Mg-micro $Al_2O_3$ feedstocks and (b) Mg-nano $Al_2O_3$ feedstocks.

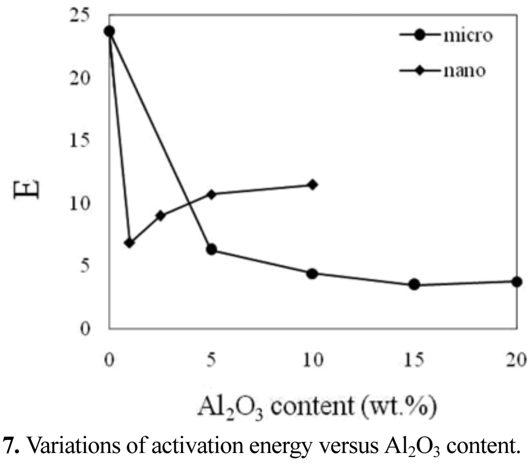


**Fig. 7.** Variations of activation energy versus $Al_2O_3$ content.

## Effect of temperature

Temperature dependency of viscosity is another prime factor to determine fluid characteristics. With a good approximation, Arrhenius equation can be utilized to describe correlation of viscosity and temperature [13]:

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

Where $\eta_0$ is the reference viscosity, $E$ is the flow activation energy, $R$ is the gas constant and $T$ is the absolute temperature. The value of $E$ expresses the effect of temperature on the viscosity of the feedstock.

Fig. 6 reveals the log viscosity versus 1000/T.

The slopes of the graphs indicate the temperature-dependency of viscosity, which should be minimized as much as possible to avoid sharp viscosity changes that reduce the flowability of the feedstocks and causes stress concentrations, cracking and distortion in the molded parts. In addition, a weak temperature-dependence of viscosity allows for greater pressure transmission to the cavity and helps to prevent shrinkage-related defects [13]. As it can be seen from Fig. 6, the slopes of curves are lower for all $Al_2O_3$ containing samples than that for MA0 sample.

The value of E was determined from Fig. 6 and was not constant at various measured temperatures. At initial studied temperatures E has almost a constant value but at higher temperatures it subsides to zero. It means that the interactions of particles in feedstock depend weakly on temperature. In other words, an increase in the $Al_2O_3$ content increased the amount of small particles of the system and the specific surface area of solid content. Thus, a higher temperature is necessary to reduce the activation energy of this sample down to zero.

Fig. 7 shows the variations of E versus $Al_2O_3$ wt %. The addition of $Al_2O_3$ powder in micro and nano size effectively decreases the value of E. This reduction is larger in micro-$Al_2O_3$ than nano-$Al_2O_3$. Therefore, it seems that particle size distribution of $Al_2O_3$ influences temperature dependency of viscosity more than its dependency on shear rate [14]. This is also worth mentioning that with increasing the amount of micro-$Al_2O_3$ powder, E decreases while with increasing the amount of nano-$Al_2O_3$ powder, it increases. In fact this is another reason for this claim that nanoparticles of $Al_2O_3$ increases the interactions of particles due to their active surfaces while micro size $Al_2O_3$ particles diminishes the friction between particles just due to their spherical morphology.

## General rheological behavior

For most applications of feedstocks, viscosity depends negligibly on shear rate or temperature. In order to establish a general molding index, the model Weir proposed for polymers can be used [7]. The influence of $Al_2O_3$ addition on the rheological behavior of Mg feedstock was evaluated according to the following equation:

$$\alpha = \frac{n}{E\eta} \tag{3}$$

Where α is the general molding index and η is the viscosity at 100 $s^{-1}$. In the absence of problems such as jetting or high residual stresses, the higher value of $\alpha$ is

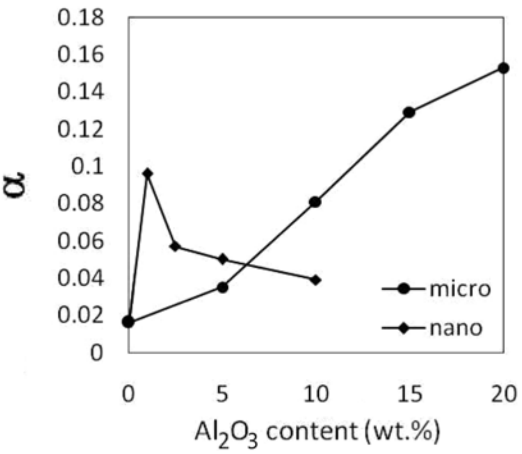


**Fig. 8.** Variations of a for feedstocks.

desirable since feedstocks with low *n* values are prone to powder-binder separation [7]. The relative $\alpha$ values for examined feedstocks at 75 °C and shear rate of 100 $s^{-1}$ can be seen in Fig. 8.

It can be seen that with increasing the amount of micro-$Al_2O_3$, α continuously increases and improves the condition for injection compared to the feedstock without micro-$Al_2O_3$. On the other hand, addition of nano-$Al_2O_3$ up to 1 wt% increases α and further increment of nano-$Al_2O_3$ decreases it. It reveals that feedstocks with high contents of nano-$Al_2O_3$ are not suitable for injection molding.

## Conclusions

Effects of addition of micro and nano $Al_2O_3$ powders on rheological properties of Mg based feedstocks were studied. It was found that the addition of $Al_2O_3$ can modify the rheological properties of such feedstocks. The results revealed that the rheological properties tangibly differ from micro to nano $Al_2O_3$ containing samples. Rheological properties were also found to depend on the concentration of $Al_2O_3$ in either size. All compounds exhibit the pseudo plastic flow behavior after the addition of $Al_2O_3$. For rheological properties, the power law index (n), was more sensitive to binder than powder characterization. It was found that the micro size $Al_2O_3$ decreases the viscosity and activation energy of feedstock due to its friction reduction effect. Reversely, nano size $Al_2O_3$ resulted in an increase in the viscosity and activation energy of the studied feedstock mainly due to the active surfaces of nanoparticles.

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