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Selection of appropriate polyoxymethylene-based binder for powder injection molding feedstock

Polyoxymethylene (POM) has found applications as a binder material in Powder Injection Moulding (PIM) due to its ability to depolymerize rapidly under acidic conditions. Such ability represents an advantage during the binder removal step of PIM. However, currently available POM has high viscosity that can complicate the injection moulding process of parts with complex geometry. For this reason it is necessary to investigate methods of lowering the viscosity of POM-based binders, but without affecting their solid mechanical properties (i.e. creep compliance). In this investigation, the addition of a low molecular weight polymer, and the reduction of the average molecular weight of POM were investigated as possible ways of decreasing the viscosity of PIM binders.

Auswahl geeigneter Bindemittel auf Polyoxymethylenbasis als Ausgangsmaterial für das Pulverspritzgießen

Polyoxymethylen (POM) wurde als Bindemittel für Anwendungen im Pulverspritzgießen (PIM) aufgrund der Fähigkeit, sich schnell unter sauren Bedingungen zu depolymerisieren, gefunden. Diese Fähigkeit stellt einen Vorteil des Entbinderungsprozesses des PIM dar. Allerdings haben aktuell verfügbare POM eine hohe Viskosität, die das Spritzgießen von Teilen mit komplexer Geometrie erschweren. Aus diesem Grund ist es erforderlich, Methoden zu untersuchen, die die Viskosität von POM-Bindemittel verringern, ohne deren feste mechanische Eigenschaften (d.h. Kriechnachgiebigkeit) zu beeinflussen. In dieser Forschungsarbeit wurde untersucht, ob die Zugabe eines Polymers mit niedrigem Molekulargewicht und die Verringerung des durchschnittlichen Molekulargewichts von POM mögliche Wege zur Verringerung der Viskosität von PIM-Bindemittel sind.

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1   INTRODUCTION

Polyoxymethylene (POM) is an engineering polymer that has also found applications as a binder material in powder injection moulding (PIM), which is a versatile mass production method for small, complex shaped components of metal or ceramic [1-4]. In PIM, POM acts as a carrier medium for metal or ceramic powders during the injection moulding process and it is later removed to obtain a metallic or ceramic piece after sintering. The main advantage of POM in powder injection moulding comes from the instability of acetal linkages, which results in rapid hydrolysis. Since the main chain of POM is composed of $-CH_2-O-$ bonds, the methyl-oxygen bonds are easy to break under heat and oxygen [5]. The process is accelerated in the presence of acid vapours. This breakage results in a continuous depolymerization reaction yielding formaldehyde gas. The released formaldehyde and formic acid formed through oxidation of formaldehyde can accelerate the depolymerization reaction even further; this process is usually called the zipper mechanism [6]. The unzipping process represents a major advantage during the debinding process and it is generally called catalytic debinding [7]. Thus, catalytic debinding occurs at a significantly higher rate than other debinding techniques, such as solvent and thermal debinding, and greatly speeds up the PIM process [8]. Additionally, POM in the solid state has good mechanical properties and thus makes easier handling of moulded parts, which can be fragile or easily deformable in other binder systems. However, POM based-feedstock materials have higher viscosity than other feedstock materials based on polyolefins. Such high viscosity can complicate the injection moulding of parts with complex geometry. Therefore, it is important to reduce the viscosity of POM-based feedstock materials.

In this study, the effect of a low molecular weight additive and reduction of the average molecular weight of POM were investigated as possible ways of decreasing the viscosity of POM-based binders used in PIM. Since it is important to maintain high solid mechanical properties, creep compliance was measured on the modified binder systems.

2   MATERIALS AND METHODS

2.1   Binder preparation

Polyoxymethylene copolymers of different average molecular weight (M_w) were synthesized at BASF (Ludwigshafen, Germany). The nomenclature and average molecular weight of all the POM materials used in this study is shown in Table 1. Molecular weights were measured by the supplier using gel permeation chromatography. For the first part of this investigation POM MW092, which is the POM used in commercially available feedstock materials by BASF, was blended with a low molecular weight polymer, which is named here Additive B or AB for confidentiality reasons. The blend was prepared by extruding together the two components in a twin-screw extrusion machine (PolyLab, Thermo Scientific, Germany) seven times. The details of the process are described elsewhere [8, 9].

Material ID	Average Molecular Weight, M_w, [g/mol]	Description
MW010	10240	Virgin POM copolymer, laboratory scale synthesis
MW024	24410	
MW052	52750	
MW081	81100	
MW092	92360	Virgin POM copolymer, industrial scale synthesis
MW109	109000	
MW129	129300	
MW204	204400	
Additive B (AB)	36400	Low molecular weight additive
B-01	N/A	Extruded MW092 + 1 wt% AB
B-02	N/A	Extruded MW092 + 2 wt% AB
B-04	N/A	Extruded MW092 + 4 wt% AB
B-08	N/A	Extruded MW092 + 8 wt% AB
B-16	N/A	Extruded MW092 + 16 wt% AB

Table 1:   Average molecular weight of POM copolymers and description of POM-AB blends.

The Additive B (AB) is a liquid of low viscosity (0.5 Pa s) at 190 °C and has a similar chemical composition to POM; therefore it was expected that a homogenous dispersion of AB could be achieved in POM without the use of compatibilizer agents, thus preventing phase separation. Blends of POM and AB were prepared at different weight percentage of AB content as shown in Table 1. The exact chemical composition and trade name cannot be mentioned due to confidentiality agreements with supplier.

2.2   PIM feedstock preparation

As it will be shown in the results section changing the molecular weight of the POM binder is the most effective way to lower the viscosity of binders compared to adding AB. For this reason, it was decided to prepare 1 feedstock materials in the laboratory with MW024 as the binder in order to compare with the commercially available feedstock material from BASF (Catamold®).

The filler used to prepared feedstock materials was gas atomized stainless steel 316LW supplied by BASF (Ludwigshafen, Germany). The cumulative particle size distribution by volume is shown in Figure 1 as supplied by BASF. The 10th, 50th and 90th percentiles, as well as, the span of the particle size distribution are also shown in Figure 1. Since the span is much larger than 1, it can be said that the distribution is wide.

POM copolymers with M_w = 24400 g/mol were obtained in powder form, thus POM was mixed with the metal powder in solid state. The metal-POM mixture was extruded in a Mixing Extruder (Custom Scientific Instruments, USA) with a fixed temperature of 190°C in both, die and screw. The screw was set at 50% of its maximum speed, which corresponds to 60 rpm. The formulated mixture was fed slowly into the extruder and the output was transported with a conveyer belt and collected in a commercial coffee grinder (Braun, Germany). After the whole mixture was collected at the grinder, the grinder was turned on and its output was extruded again. The extrusion and grinding processes was repeated two times to ensure better mixing.

The prepared feedstock material had a content of powder of 92 wt%, which is slightly higher than the powder content of the commercially available feedstock material with POM binder, which was estimated to be 90 wt%. The binder used in the experimental feedstock was MW024.
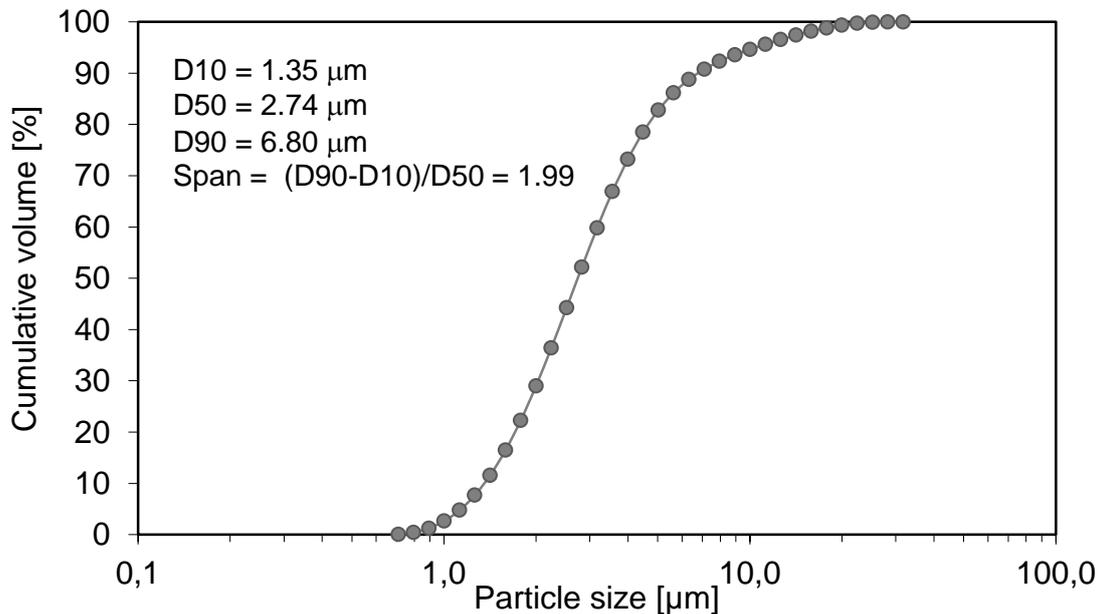
Figure 1: *Cumulative particle size distribution by volume of filler particles used in prepared feedstock materials*

2.3   Shear viscosity measurements of binder

Viscosity measurements in oscillatory mode were performed in a MARS-II rotational rheometer (Thermo Scientific, Germany). Viscosity tests were performed at 210 °C, which is within the rage of temperatures at which POM is generally processed (180 to 230 °C). A truncated cone-plate measuring-geometry with a 20 mm diameter and angle of 1° was used in all measurements. Two frequency sweeps were performed in each measurement; the first one increasing from 0.01 Hz (0.0628 rad/s) to 100 Hz (628.32 rad/s), and the second one decreasing from 100 to 0.01 Hz. This was done to monitor any possible flow instabilities. All measurements were performed applying a shear stress of 200 Pa, previously determined to be within the linear viscoelastic region of all materials investigated. All viscosity measurements at a given temperature were performed six times per material. In this study, viscosity results are presented as the magnitude of the complex viscosity ($|\eta^*|$), which is related to the constant rotational viscosity (η) through the Cox-Merz rule [10], which has been previously determined to be applicable to POM copolymers and its AB blends [11].

2.4   Shear viscosity measurements of feedstock

Viscosity of experimental and commercial feedstock materials was measured in constant rotational mode, since the Cox-Merz rule does not apply to feedstock materials [12]. Measurements were performed in a MARS-II rotational

rheometer at 180 °C. A plate-plate measuring-geometry with a 20 mm diameter was used and the gap was set to 1 mm. The shear rate was varied from 0.01 to 100 s^{-1}. Measurements were performed in ascending order of shear rate and the shear rate range was divided in 35 steps equally spaced in the logarithmic scale. During each step the material was sheared by 22 seconds in order for stress to stabilize. All viscosity measurements were performed six times per material.

2.5   Shear creep compliance measurements

In order to perform creep compliance measurements cylindrical specimens with diameter D = 5.8 ± 0.1 mm and length l = 29.0 ± 2.0 mm were prepared by gravimetrical casting from materials listed in Table 1. Details on the procedure and schematics of the device used are shown elsewhere [8]. After casting specimens were cut to the required length and glued with acrylate-based glue (F524 black and activator B, Kemis Plus, Slovenia) to custom made metal holders for gripping the cylindrical specimen to the measuring device. Three specimens were prepared for each type of material shown in Table 1.

Creep measurements of binders and feedstock materials in solid state were performed following the methodology developed at the Center for Experimental Mechanics at the University of Ljubljana. Effect of AB addition on creep compliance was performed in the self-developed torsiometer [13], while the effect of molecular weight on binder and feedstock was analyzed using a MARS-II rotational rheometer fitted with solid clamps. Creep compliance was measured in segmental form at various temperatures and shifted to a reference temperature of 110 °C using the principle of time-temperature superposition. Time-temperature superposition was performed using the self-developed Closed Form Shifting Algorithm [14]. The reference temperature of 110 °C was selected because it is one of the temperatures at which catalytic debinding of POM is performed.

3   RESULTS AND DISCUSSION

3.1   Addition of low molecular weight polymer

3.1.1   Shear viscosity measurements

The effect of AB addition on the viscosity of POM is shown in Figure 2. The general trend is that as the AB content increases, the viscosity linearly decreases. Thus, the decrease is not as large as needed. For example, adding 16 wt% of AB reduces the viscosity by approximately 20%, which is not low enough. The needed viscosity should be at least 10 times smaller (90%

reduction) to reach the recommended viscosity for a PIM binder of approximately 10 Pa s [15]. Blends with a higher amount of AB were tried, but they lead to phase separation just after extrusion. It was also observed that the viscosity of the POM-AB blends could be predicted by a simple linear mixing rule of the following form:

$$\eta_{Blend} = x_{POM}\eta_{POM} + (1 - x_{POM})\eta_{AB} \tag{1}$$

where η_{Blend} is the viscosity of the blend (POM + AB), x_{POM} is the mass fraction of component POM present in the blend, η_{POM} is the viscosity of POM and η_{AB} is the viscosity of additive B. The viscosities are of course at the same temperature (210 °C) and angular frequencies (92 rad/s). The viscosity of AB at the selected temperature and angular frequency was measure to be 0.46 Pa s.

The fact that a mixing rule can be used to predict the behaviour of a blend is an indication that the components of the blend, in this case POM and AB, are immiscible, which is undesirable since it can leads to phase separation, as it was observed at higher concentrations of AB. Therefore, it can be concluded that addition of AB is not an optimal solution to decrease the viscosity of POM-based binders for PIM feedstock.
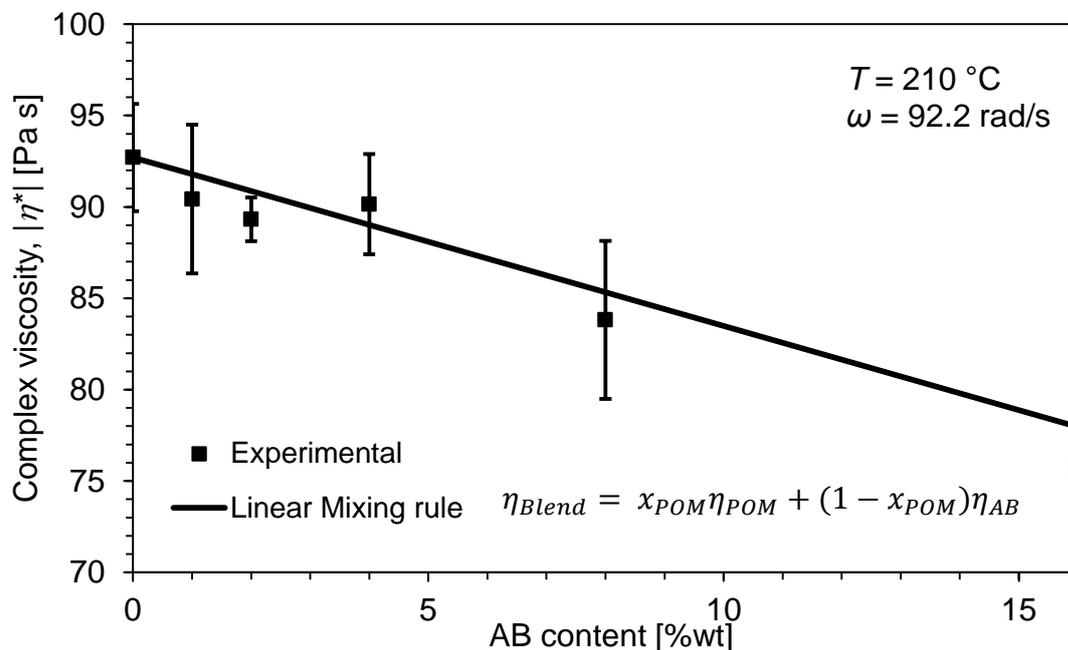

Figure 2:   Viscosity of POM and AB blends at 210 °C and angular frequency of 92 rad/s. The solid line represents a linear mixing rule fitting (Equation 1).

3.1.2   Shear creep compliance measurements

The effect of AB addition on the creep compliance of POM is shown in Figure 3. By adding up to 2 wt% of AB into POM, no significant change in the creep compliance was observed. The horizontal line in Figure 3 represents the average of the three values $J = 7.24 \times 10^{-9}$ Pa^{-1}. After addition of 2 wt% AB, creep compliance linearly increases until it reaches its maximum value at 16 wt%. The straight line in Figure 3 represents a linear fit to the creep compliance data of the last four points, $J = 1.90 \times 10^{-10} + 6.84 \times 10^{-9}$ Pa^{-1}. Adding 16 wt% of AB causes an approximate increase of 16% in creep compliance, which can be considered as acceptable for PIM purposes.

The observed increase in creep compliance could be the result of a decrease in crystallinity, which facilitates movement of polymeric chains when loaded in shear. Such behaviour has also been observed with other polymers, for example LDPE [16]. In terms of binder selection, it appears that the best creep compliance properties could be achieved by adding 1 wt% of AB, but the drop in viscosity is not enough for PIM purposes even when 16 wt% of AB is added. Therefore, AB addition is not the best solution to optimize the behaviour of POM-based binders used in powder injection moulding.
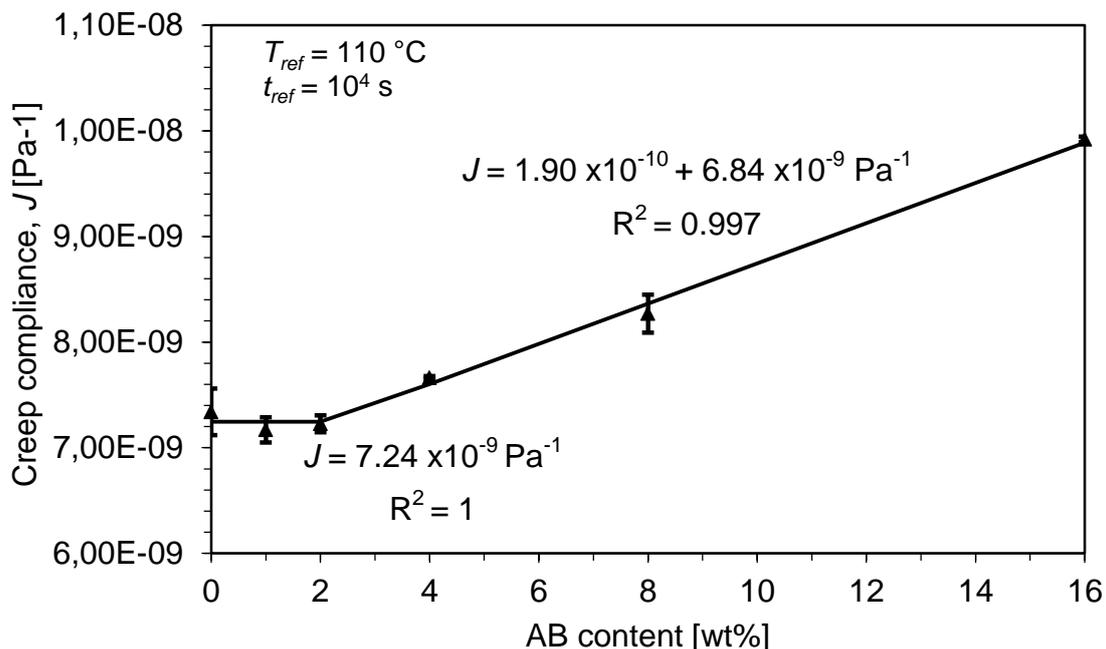

Figure 3: Shear creep compliance of POM and AB blends at reference temperature 110 °C and time of 10000 s. The solid lines represent average and linear fit to the experimental data.

3.2   Reduction of POM's average molecular weight (M_w)

3.2.1   Shear viscosity measurements

The magnitude of the complex viscosity as a function of angular frequency for all POM copolymers was measured at 210 °C. From the measured complex viscosity data ($|\eta^*|$) the Newtonian viscosity (η_0) was estimated from the plateau at frequencies below 10 rad/s. The results are presented as a function of the average molecular weight in Figure 4. As with other polymers, POM copolymers show a rapid decrease in viscosity as the average molecular weight decreases following a power function as proposed by Fox and Flory [17].

With respect to the selection of an appropriate binder for PIM, one could choose between the first three molecular weights (MW010, MW024 and MW052), which are all below the recommended viscosity of 10 Pa s [15]. However, in order to make the correct decision, one should consider the results of the solid mechanical properties described below.
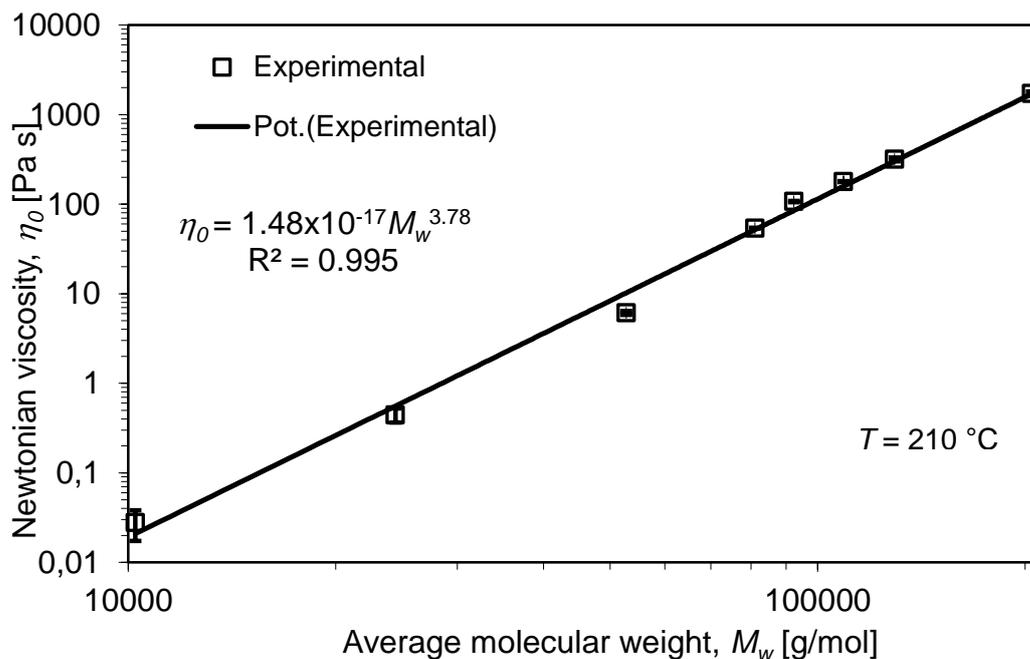

Figure 4:   Newtonian viscosity of POM copolymers at 210 °C. The solid line represents a power law fit to the experimental data.

3.2.2   Shear creep compliance measurements

After the creep compliance segments were shifted to a reference temperature of 110 °C, isochronal curves at 10000 s (~3 h) were estimated and plotted as a function of the average molecular weight, Figure 5. As it can be seen in Figure 5, the creep compliance has a plateau at the highest molecular weights (M_w = 81100 to 204400 g/mol). The horizontal line represents the average of the

last five data points, $J = 7.13 \times 10^{-9}$ Pa^{-1}. And as the molecular weight is decreased beyond $M_w = 81100$ g/mol there is a rapid increase in the creep compliance that follows a power law dependence. Since it is desirable not to have a drastic increase in creep compliance in the PIM binder, it is not recommended to choose the lowest molecular weight (MW010) available, but the second lowest (MW024). This will ensure a non-drastic increase in creep compliance, but a very large decrease in viscosity (99% or 240 times) when compared to the current binder (MW092). Since the recommended POM copolymer has reduced creep compliance, extra care should be taken when handling the moulded part. Therefore, it can be said that this is not an optimal solution, but still can be considered a significant improvement.
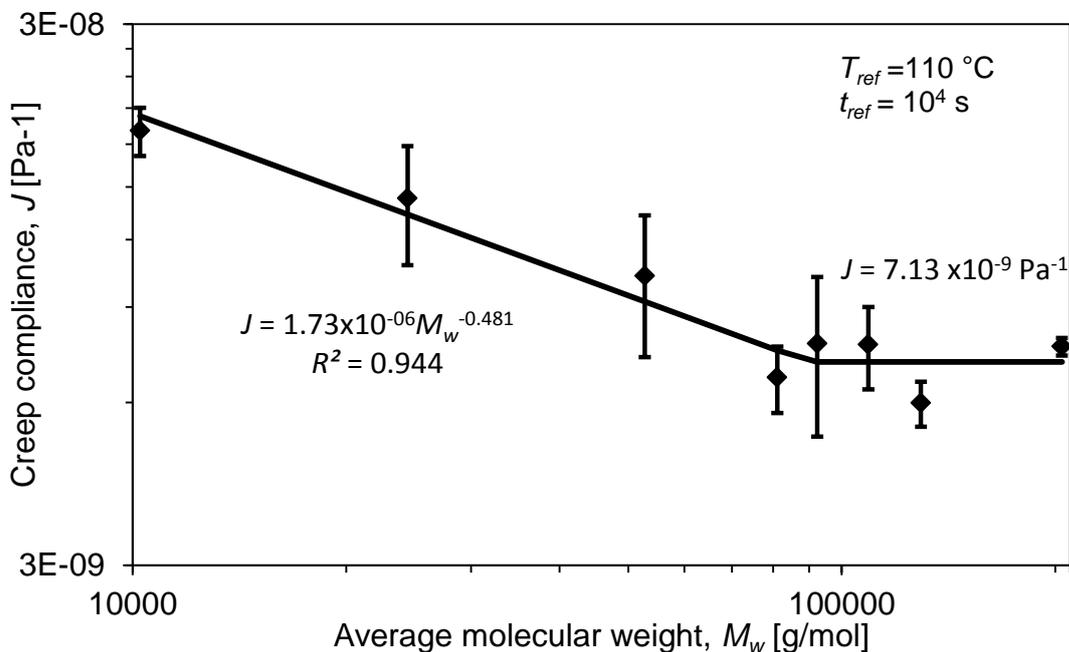

Figure 5: Shear creep compliance of POM copolymers at reference temperature 110 °C and time of 10000 s. The straight solid line corresponds to the power law fit first, followed by the average of the last 5 data points.

3.3 Comparison of commercial and experimental feedstock

3.3.1   Shear viscosity measurements

The viscosity of the prepared feedstock and the commercial feedstock is shown in Figure 6. Even though the viscosity was measured from 0.1 to 100 s^{-1}, the flow curve shown in Figure 6 starts at approximately 0.3 and ends at approximately at 17 s^{-1}. The first three points on the curve were omitted since

the stress did not reach a constant value in the specified shearing time, while at higher shear rates than 20 s^{-1} there was sample expulsion and shear banding that caused the viscosity to decrease abruptly.

By looking at Figure 6, it can be seen that feedstock prepared using POM copolymer with 24000 g/mol has significantly lower viscosity than the commercially available feedstock at all the shear rates measured. For example at 10 s^{-1}, the prepared feedstock has a viscosity approximately 7 times lower than the commercial feedstock, even though the metal content by mass is higher. The big error bars in the vertical direction could be attributed to the method used to prepare the feedstock materials which is not the most efficient way to prepare a homogeneous dispersion of powder in the polymeric matrix, but it was the only method available. The error bars in the horizontal direction suggest that the flow in the rheometer is not as stable as the flow behaviour of the commercial feedstock material and probably due to slip.

The measured data was also fitted with a power law and it can be seen that the shear thinning is more pronounced for the experimental feedstock compared to the commercial one; this can be seen by the slightly bigger exponent for the experimental material (1.1 vs. 1.3). Therefore, it is expected that the viscosity at higher shear rates will still be lower for the experimental feedstock.
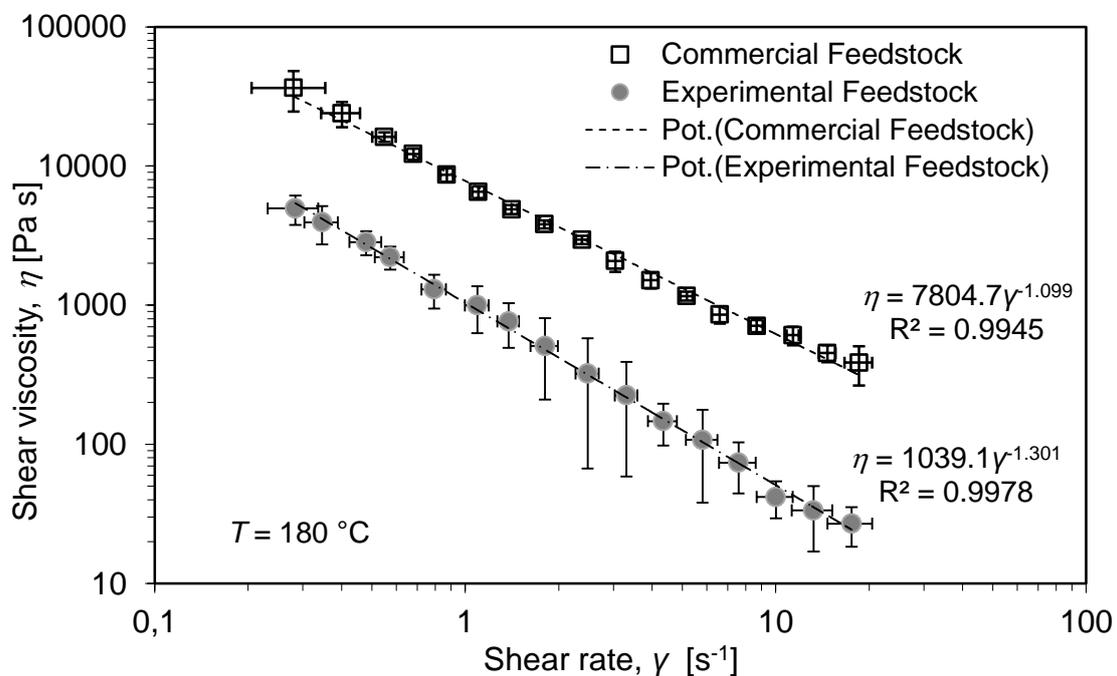

Figure 6: Comparison of viscosity at 180 °C between commercially available POM-based feedstock and experimental feedstock material

3.3.2   Shear creep compliance measurements

The creep results at a reference temperature of 110 °C for the commercial feedstock material and the prepared feedstock material are shown in Figure 7. As a reference, also the creep compliance of neat POM MW024 at the same reference temperature is shown.

As it can be seen in Figure 7, both feedstock materials (commercial and experimental) have a significant lower creep compliance compared to the unfilled POM MW024. Therefore, as mentioned in the literature addition of particles to POM decreases the magnitude and rate of creep [18]. When comparing the commercial feedstock to the experimental feedstock, it can be seen that at short times (t < 0.01 s at 110 °C), the commercial feedstock and the experimental feedstock creep the same amount and at the same rate. At longer times (t > 1.0 s), the experimental feedstock actually creeps less than the commercial feedstock. The creep behaviour of the feedstock material is mostly dependent on the creep behaviour of the binder. The commercial material has PE and POM, it is known that POM has a higher degree of crystallinity than PE [8, 16] and that crystallinity greatly influence the creep behaviour of polymers [16]; therefore it is expected that the commercial feedstock would creep more compared to the experimental feedstock.
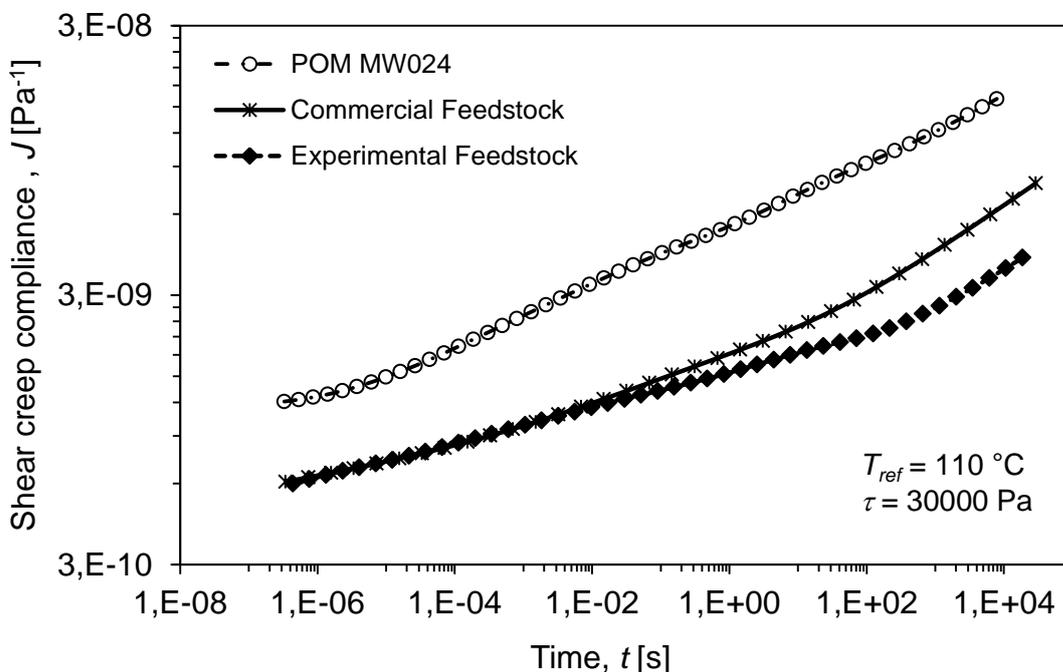

Figure 7:   Long-term creep behavior of commercially available PIM feedstock, experimental feedstock and neat POM MW024

4   CONCLUSIONS

Reduction of viscosity of PIM feedstock is very important, since it will facilitate the injection moulding of parts with complex geometry. However, it is important to maintain the solid mechanical properties in the moulded part. Having good mechanical properties in the solid state will ensure shape retention and dimensional stability while removing the green part from the mould and up to the beginning of the binder removal step of PIM.

In this study, it was observed that addition of 16 wt% of AB to POM copolymer reduces viscosity of the binder by approximately 20% and increases its shear creep compliance by 16%. The increase in creep compliance can be considered acceptable, but the reduction of viscosity can be considered insufficient, since the recommended viscosity of a PIM binder is at least 10 times smaller than the currently used POM binder and its AB blends. Therefore, addition of AB is not recommended to solve flowability problems of POM-based binder systems for PIM.

Furthermore, it was observed that viscosity of POM copolymers increases with average molecular weight following a power law relationship. On the other hand, shear creep compliance of POM copolymers decreases with average molecular weight reaching a plateau at molecular weights larger than 81100 g/mol. With these results on hand, one can recommend to use a POM-based binder with a molecular weight around 24400 g/mol. Using POM MW024 represents a reduction of 200 times in viscosity and an increase in creep compliance of 85% with respect to the current POM-based binder system.

When the selected binder was mixed with powder at 92 wt% and compared to commercially available POM-based feedstock a decrease of approximately 1 order of magnitude was observed at all the frequencies measured. For the creep compliance it was observed that the experimental feedstock had lower creep compliance than the commercial feedstock. This represents a significant improvement in the performance of POM-based feedstock materials for PIM.

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Stichworte:

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