Selection of appropriate polyoxymethylene based binder for feedstock material used in powder injection moulding

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Abstract. 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. The addition of the low molecular weight additive (WAX) caused a small decrease in the viscosity of the POM-based binder and a small increase in its solid creep compliance. On the other hand, lowering the average molecular weight of POM caused a large decrease in viscosity, but also an acceptable increase in creep compliance. Therefore, by selecting an appropriate molecular weight of POM, it is possible to improve the performance of POM-based binders for PIM.

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 –CH₂-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 dedinding 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. Material 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. 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]. The low molecular weight additive is simply referred as WAX due to confidentiality terms.

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

2.2. Viscosity measurements

Viscosity measurements in oscillatory mode were performed in a MARS-II rotational rheometer (Thermo Scientific, Germany). Rheological tests were performed at 210 °C, which is within the rage of temperatures at which POM is generally processed. 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 (|η*|), 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 WAX blends [11, 12].

2.3. Creep measurements
In order to perform creep compliance measurements cylindrical specimens with diameter $D = 5.8 \pm 0.1$ mm and length $l = 29.0 \pm 2.0$ 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, 9, 13]. 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 in solid state were performed following the methodology developed at the Center for Experimental Mechanics at the University of Ljubljana. Effect of wax addition on creep compliance was performed in the self-developed torsiometer [14], while the effect of molecular weight 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 [15]. The reference temperature of 110 °C was selected because it is one of the temperatures at which debinding is performed.

3. Results and Discussion

3.1 Addition of Low molecular weight polymer (WAX)

3.1.1 Viscosity measurements
The effect of WAX addition on the viscosity of POM is shown in figure 1. The general trend is that as the content of WAX increases, the viscosity linearly decreases. However, the decrease is not as large as needed. For example, adding 16wt% of WAX 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 [16]. Blends with a higher amount of WAX were tried, but they lead to phase separation just after extrusion. Thus, it can be concluded that addition of WAX is not an optimal solution to decrease the viscosity of POM-based binders for PIM.

3.1.2 Creep compliance
The effect of WAX addition on the creep compliance of POM is shown in figure 2. It appears that at the lowest content of wax there is a decrease in viscosity compared to unblended POM. After 1wt% content, creep compliance steadily increases until it reaches the maximum value at 16wt%. Adding 16wt% of WAX causes an increase of 16% in creep compliance, which is acceptable for our purposes. The observed increase in creep compliance could be the result of a decrease in crystallinity, which facilitates movement of polymeric chains when loaded. Such behaviour has also been observed with other polymers, for example LDPE [17]. In terms of binder selection, it appears that the best creep compliance properties could be achieved by adding 1wt% of WAX, but the drop in viscosity is not enough for purposes of PIM. Therefore, WAX addition is not the best solution to optimize the behaviour of binders used in PIM.
3.2. Reduction of average molecular weight

3.2.1. 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 ($\eta_0$) 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 3. 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 [19].

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 [16]. However, in order to make the correct decision, one should consider the results of the solid mechanical properties.

3.2.2. 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 4). As it can be seen in figure 4, the creep compliance has a plateau at the highest molecular weights ($M_w = 81100$ to 204400 g/mol). And as the molecular weight is decreased beyond $M_w = 81100$ g/mol there is a rapid increase in the creep compliance. 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 an acceptable increase in creep compliance, but a very large decrease in viscosity (99% or 240 times) when compared to the current binder (MW092). Since there is a decrease in creep compliance, extra care should be taken when handling the moulded part with the suggested binder.
4. Conclusion
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. This will ensure shape retention and dimensional stability during demoulding and debinding steps of PIM.

In this study, it was observed that addition of 16wt% of WAX 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 goal was to reduce viscosity by at least 10 times. Therefore, addition of WAX 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 24410 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. However, this can be considered a significant improvement, but care should be taken when handling the green part with the selected binder.

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