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Улучшенная технология литья порошковых смесей: новые возможности для аэрокосмической отрасли

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Снижение вязкости сырья в ходе литьевого формования порошка имеет важное значение. Это позволяет получать детали геометрически сложной конфигурации. Данное исследование показало, что при средней молекулярной массе вязкость сополимеров полиоксиметилена возрастает по экспоненциальному закону. При наличии таких результатов мы рекомендуем использовать связующее с молекулярной массой приблизительно 24400 г/моль. Сырьевые материалы для промышленности готовилось с рекомендуемым связующим при различных загрузках порошка. При этом было установлено, что его вязкость можно снизить еще и за счет выбора правильного распределения частиц по размерам. В этом исследовании показано, что использование порошка с широким распределением частиц по размерам ведет к росту максимального коэффициента уменьшения массы, что может привести к значительному уменьшению вязкости сырьевых материалов для промышленности. Также было установлено, что из простых моделей, представленных в литературе, модель Zarraga и др. [11] лучше всего подходит к нашим экспериментальным данным. С помощью этой модели можно получить вязкость сырья приблизительно 1000 Па. При этом максимальная загрузка при использовании порошка с самым высоким максимальным коэффициентом уменьшения массы составляет приблизительно 83%vol.

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Improving Powder Injection Molding: an Opportunity for the Aerospace Industry

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This work deals with powder injection molding (PIM) technology of metal and ceramis powders using polyoximethylene (POM) binder. In this study, two ways to decrease the viscosity of PIM feedstock materials with polyoxymethylene were investigated. The first way was to reduce the average molecular weight (AMV) of the binder and the second one to select a polydisperse particle size distribution with high maximum packing fraction. It was shown that binder with AMW equal to 24410 g/mol gives required level of viscosity around 10 Pa/s. It was shown that using the low disperse powder with wide size distribution can lead to volumetric loading of approximately 83 %. Moreover, using such a feedstock has viscosity lower than required by PIM technology 1000 Pa/s.

Keywords: powder-injection-molding (PIM), polyoximethylene (POM), low viscosity feedstock

1. Introduction

Powder injection molding (PIM) is one of the most versatile methods for manufacturing small complex shaped components from metal, ceramic powders for the use in many applications. PIM consists of four stages including: (i) mixing metal or ceramic powder and a polymeric binder, (ii) injecting this mixture in a mold, (iii) debinding to remove polymer from mixture and (iv) sintering to bring together the otherwise loose powder [1]. All these steps are schematically shown in Figure 1.
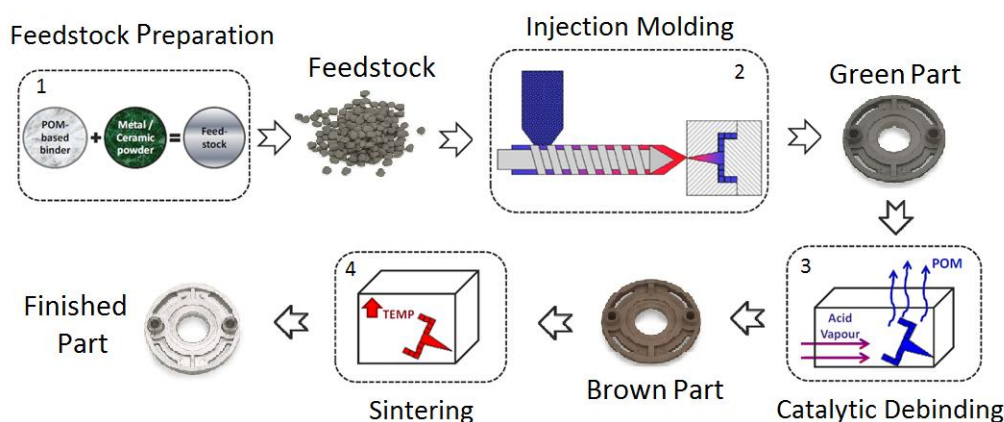
Figure 1. Flow chart illustrating the main stages of PIM process.

One of the interesting applications of PIM is the aerospace industry because PIM can be used to combine multiple parts into a single part with complex geometry, and parts are lighter since porosity remains in the final part while the fatigue resistance increases. Fatigue resistance increases since the small parts act as crack stoppers therefore preventing crack propagation and failure of a part loaded cyclically. Therefore, it can be said that PIM can help reduce the weight of aerospace vehicles, which is a major concern from the environmental and economic point of view in this industry.

Ceramic injection molding has been around since 1940's [2] and metal injection molding since the 1970's [3], in fact, some of the first applications of metal injection molding was for the aerospace industry. Some examples include flat screw seals and rocket burning system, which were produced at the end of the 1970's [4]. there is still room for improving the process and materials utilized in PIM. One of the main limitations of current PIM is the long debinding time, which has been partially solved by introducing binder systems that undergo catalytic sublimation (polyoxymethylene-based binders); thus the molded part is debound in the solid state without meting or dissolving the polymeric binder in a much shorter time. However, current catalytic binders have the main problem of high viscosity. In this study, two ways to decrease the viscosity of PIM feedstock materials with polyoxymethylene were investigated. The first way was to reduce the average molecular weight of the binder [5] and the second one to select a polydisperse particle size distribution with high maximum packing fraction.

## 2. Materials and methods

2.1. POM-based binders

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.

Table 1. Average molecular weight of POM copolymers

Material ID	Average Molecular Weight, M_w, [g/mol]	Description
MW010	10240	Virgin POM copolymer, laboratory scale synthesis
MW024	24410	Virgin POM copolymer, laboratory scale synthesis
MW052	52750	Virgin POM copolymer, laboratory scale synthesis
MW081	81100	Virgin POM copolymer, laboratory scale synthesis
MW092	92360	Virgin POM copolymer, industrial scale synthesis
MW109	109000	Virgin POM copolymer, industrial scale synthesis
MW129	129300	Virgin POM copolymer, industrial scale synthesis
MW204	204400	Virgin POM copolymer, industrial scale synthesis

2.2. Metal powders and feedstock materials

316LW stainless steel metal particles were supplied by BASF (Germany). The powder was produced via gas atomization and separated into five fractions with different particle size distribution (Figure 2) using a centrifuge. Particle size distribution was measured by laser scattering. The matrix used in the suspension was polyoxymethylene (POM) copolymer with an average molecular weight of approximately 24400 g/mol. The POM copolymer was also produced by BASF (Germany).
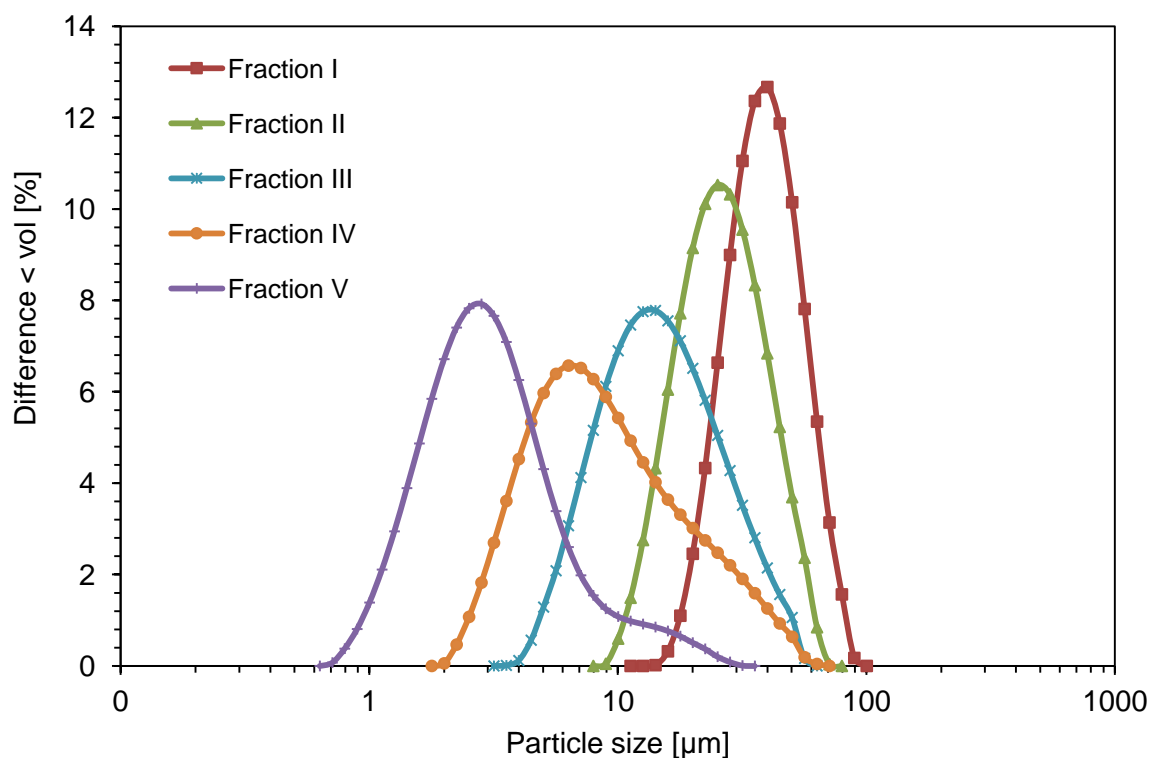
Figure 2. Differential volumetric particle size distribution for steel powder fractions.

Feedstock materials with different solid content (20 to 45 vol%) were produced by extruding the steel powder with the POM copolymer at 190 °C. In order to determine the final content of solids (φ), the binder was removed by heating up the feedstock material up to 300 °C for two hours, and the remaining mass was used to estimate (φ).

2.3. Shear viscosity measurements

Viscosity measurements in oscillatory mode were performed in a MARS-II rotational rheometer (Thermo Scientific, Germany). Viscosity tests were performed at 190 °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. 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. 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 [6].

Constant rotational shear viscosity of the resulting feedstock materials was measured in a rotational rheometer fitted with parallel plates of 20 mm diameter at 180 °C (MARS II, Thermo-Scientific, Germany). All measurements were performed in triplicate. Shear rate was varied from 0.1 to 100 s^{-1}.

3. Results and discussion

3.1. Shear viscosity measurements of binder

The magnitude of the complex viscosity as a function of angular frequency for all POM copolymers was measured at 190 °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 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 [7]. The propose equation for POM copolymers is shown inside Figure 3.
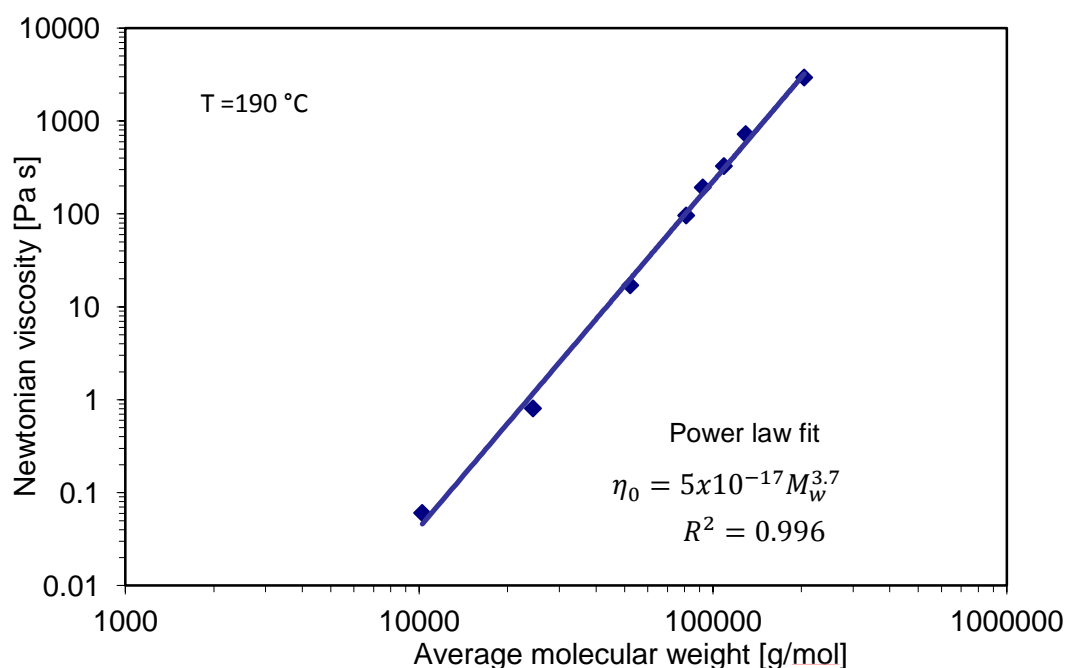

Figure 3. Newtonian viscosity of POM copolymers at 190 °C; the solid line represents a power law fit to the experimental data.

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 [2]. For the purpose of this investigation we selected the middle one (MW024) for preparing feedstock materials.

3.2. Shear viscosity measurements of feedstock

Viscosity results for feedstock materials as a function of volumetric solid content (φ) are shown in Figure 4. Please notice that relative viscosity (η_r) is used in the vertical axis, which is the ratio of the viscosity of the suspension over the viscosity of the polymeric matrix, both viscosities measured under the same shear rate (100 s^{-1}) and temperature (180 °C). As expected, as φ increases so does the relative viscosity η_r, but the increase is significantly different depending on the fraction used in the feedstock material, since each fraction has different particle size distribution (Figure 2). Using Fraction V, the highest φ was achieved without increasing much η_r.
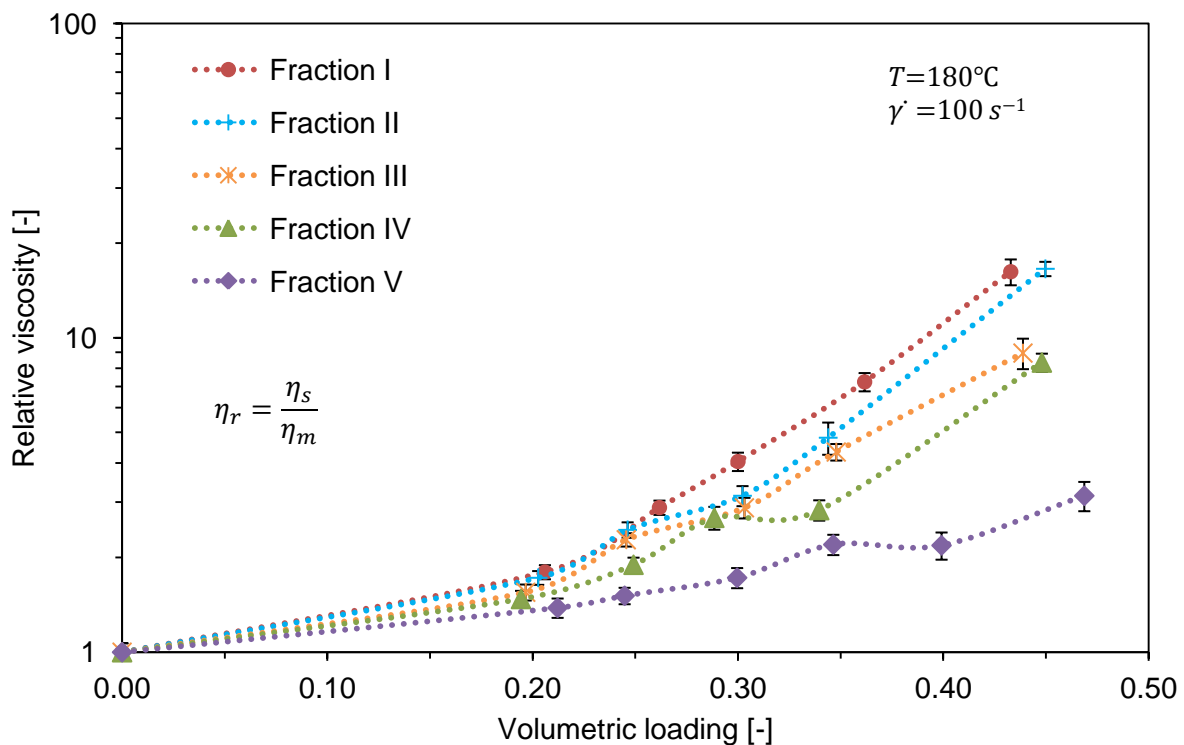
Figure 4. Relative shear viscosity η_r at 100 s^{-1} and 180 °C as a function of particle load φ for prepared feedstock materials containing powder fractions I-V

Five models were selected from the literature (Table 2) that predict the viscosity of concentrated macroscopic suspensions just by knowing the particle loading (φ) and the maximum packing fraction (φ_m), which represents the particle loading at which the viscosity goes to infinity. Other models were available in the literature, but they were ignored since they depend on other empirical parameters or are not applicable for concentrated suspensions.

Table 2. Models to predict the relative viscosity of concentrated suspensions

Authors	Year	Equation
Frankel & Acrivos [8]	1967	$\eta_r = \dfrac{9}{8}\dfrac{\left(\frac{\phi}{\phi_m}\right)^{1/3}}{1-\left(\frac{\phi}{\phi_m}\right)^{1/3}}$
Chong *et al.* [9]	1971	$\eta_r = \left[1 + 0.75\left(\dfrac{\frac{\phi}{\phi_m}}{1-\frac{\phi}{\phi_m}}\right)\right]^2$
Quemada [10]	1976	$\eta_r = \left(1 - \dfrac{\phi}{\phi_m}\right)^{-2}$
Zarraga *et al.* [11]	2000	$\eta_r = e^{-2.34\phi}\left(1 - \dfrac{\phi}{\phi_m}\right)^{-3}$
Mendoza & Santamaria-Holek [12]	2008	$\eta_r = \left(1 - \dfrac{\phi}{1-c\phi}\right)^{-2.5} \quad c = \dfrac{1-\phi_m}{\phi_m}$

Data shown in Figure 4 was fitted with the five models selected and (φ_m) for each powder fraction was estimated. The coefficient of determination (R^2) was used to determine which model fits the data better overall. The results for the best (Zarraga *et al*) model are shown in Table 3.

Table 3. Maximum packing fraction (φ_m) and coefficient of determination (R^2) obtained by fitting at 100 s^{-1} and 180 °C by Zarraga *et al* model [11].

Powder Fraction	Maximum packing fraction, φ_m	Coefficient of determination, R^2	Maximum loading φ before η_r reaching 1000 Pa s
I	0.602	0.997	0.554
II	0.622	0.998	0.573
III	0.666	0.996	0.615
IV	0.689	0.985	0.637
V	0.889	0.971	0.832

Using the model proposed by Zarraga et al, one can estimate the maximum loading needed to achieve a viscosity close to 1000 Pa s at the selected conditions for each fraction. Table 3 shows that Fraction V has the highest (φ_m) and therefore it can be loaded the most without increasing the viscosity beyond 1000 Pa s, approximately to up to 83 %vol.

4. Conclusions

Reduction of viscosity of PIM feedstock is very important, since it will facilitate the injection molding of parts with complex geometry. In this study it was observed that viscosity of POM copolymers increases with average molecular weight following a power law relationship. With these results on hand, we recommend to use a POM-based binder with a molecular weight around 24400 g/mol. Feedstock materials were prepared with the recommended binder at different powder loadings. It was observed that viscosity of feedstock materials for PIM can be further

reduced by selecting the appropriate particle size distribution. In this study it was shown that using powder with a wide particle size distribution leads to higher maximum packing fraction that can reduce significantly the viscosity of feedstock materials. It was also observed that from the simple models available in the literature the model of Zarraga *et al* [11] best fits our experimental data. Using this model the maximum loading for the feedstock to reach a viscosity of approximately 1000 Pa s using the powder with the highest maximum packing fraction is approximately 83 %vol.

5. Acknowledgements

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