

Time-Dependent Properties of Multimodal Polyoxymethylene based binder for Powder Injection Molding*

Časovno odvisne lastnosti multimodalnih, na polioksimetilenu temelječih veziv praškov za brizganje

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Abstract: Powder injection molding (PIM) is one of the most versatile methods for the manufacturing of small complex shaped components from metal, ceramic or cemented carbide powders for the use in many applications. PIM consists of mixing the powder and a polymeric binder, injecting this mixture in a mold, debinding and then sintering. Catalytic debinding of polyoxymethylene (POM) is attractive since it shows high debinding rates and low risk of cracking. This work examines the possibility of using bimodal POM as the main component of the binding agent by studying its time-dependent and thermal properties and comparing them to monomodal POM. Furthermore, possible optimization of the binder formulation was investigated by the addition of short molecular weight polymeric chains (wax) to bimodal POM, as to create a multimodal material. It was observed that the magnitude of the complex viscosity for the commercial bimodal material was more than 2 times lower than for the chemically identical monomodal POM within the investigated frequency range. Viscosity values were observed to drop as the content of wax was increased, without compromising the binders mechanical properties in solid state. A new formulation of bimodal POM plus 8 wt.% of added wax provided the most appropriate results from investigated combinations. This work has shown how the addition of short polymeric chains in POM influences its time-dependent properties in solid and molten state, which can be an important tool for the optimization of binders designed to be used in PIM technology.

Key words: Polyoxymethylene; Powder; Technology; Binder; Time-dependence

Povzetek: Praškasto brizganje (PIM) je ena najbolj vsestranskih metod za proizvodnjo majhnih kompleksno oblikovanih sestavnih delov iz kovine, keramike ali cementnega karbida v prahu za uporabo v številnih aplikacijah. PIM je sestavljen iz mešanja prahu in polimernega veziva, injiciranja te mešanice v kalup, razvezovanja in nato sintranja. Katalitično razvezovanje od polioksimetilena (POM) je privlačno, ker kaže visoko stopnjo razvezovanja in majhno tveganje za razpoke. To delo obravnava možnost uporabe bimodalne POM kot glavne sestavine veziva s študijem časovne odvisnosti in toplotnih lastnosti in jih primerjati z monomodalnim POM. Raziskana je bila možna optimizacija veziva z dodajanjem kratkih polimernih verig (vosek) bimodalnemu POM za ustvarjanje multimodalnega materiala. Ugotovljeno je bilo, da je obseg kompleksnih viskoznosti za komercialne bimodalne materiale več kot 2-krat nižji kot za kemično enake monomodalne POM znotraj opazovanega frekvenčnega območja. Vrednosti viskoznosti so padale, ko se je vsebnost voska povečala, ne da bi ogrozili mehanske lastnosti veziva v trdnem stanju. Nova oblika bimodalne POM plus 8 ut.% dodanega voska je najbolj ustrezala, glede na raziskane kombinacije.

Ključne besede: polioksimetilen; prašek; tehnologija; vezivo; časovna odvisnost

1. Introduction

Powder injection molding (PIM) is a technology for manufacturing complex, precision, net-shape components from either metal or ceramic powder. The potential of PIM lies in its ability to combine the design flexibility of plastic injection molding and the nearly unlimited choice of material offered by powder metallurgy, making it possible to combine multiple parts into a single one⁽¹⁾. Furthermore, PIM overcomes the dimensional and productivity limits of isostatic pressing and slip casting, the defects and tolerance limitations of investment casting, the mechanical strength of die-cast parts, and the shape limitation of traditional powder compacts⁽²⁾. Finally, the use of finer powder particles in PIM feedstock allows for the densification of parts during sintering, which yields high performance parts made of material systems that are difficult to sinter using conventional methods⁽³⁾. PIM is generally best suited to produce parts less than 6 mm in thickness and weighting less than 100 grams⁽⁴⁾. Therefore, industries that demand miniaturization of complex components can benefit from using PIM in their manufacturing process.

Due to the demand of high performance materials and the miniaturization of complex components in various fields, PIM market has exceeded the USD \$1 billion mark in 2007, becoming approximately six times larger than 15 years before⁽⁵⁾. This impressive growth rate is not expected to slow down in the next few years. As the recent report from Global Industry Analysts announced, a combined world metal and ceramic powder injection molding market is forecasted to reach USD \$3.7 billion by the year 2017⁽⁶⁾. The metal powder injection molding (MIM) is still considered the largest segment of this market, accounting for more than 70% of global output. Although PIM is globally widespread, Europe and Asia-Pacific account for the major share of MIM segment, while USA is still the largest market for Ceramic Injection Molding (CIM)⁽⁶⁾.

The process of Powder Injection Molding (PIM), invariably, consists of four steps: I) Feedstock preparation, II) injection molding, III) debinding and IV) sintering⁽⁷⁾⁽⁸⁾. Figure 1 illustrates the main stages of PIM.

During the feedstock preparation the metal or ceramic powder and an organic multicomponent binder are combined in a variety of compounding equipment, such as extruders and batch mixers. The mixture is then pelletized to an appropriate shape for feeding into the molding machine. The binder is simply a carrying medium for the powder and once a part is molded, the binder is removed in a subsequent step. The powder content usually ranges from 50 to 65% in volume, although there are claims of optimized commercial formulations in which even more than 80 % is used. If the powder content is found to be below 50 vol.%, the sintering ability of the feedstock and the final density of the part are significantly lowered. From another standpoint, it is also important to keep the viscosity of the feedstock as low as possible in order to facilitate the injection molding process. This is the reason why a powder content higher than 65 vol.% should be carefully handled⁽⁹⁾.

The injection molding process is mainly identical to conventional plastic injection molding. Nevertheless, some machine hardware changes are usually required to process a specific feedstock based on its compressibility and viscosity. In addition, injection molding machines for processing of powdery materials are optimized with wear-resistant components and screw geometry adopted to lower the compression rate and extend the compression zone as compared to screws used for thermoplastics⁽¹⁾. Control of the molding process is vital for maintaining tight tolerances in subsequent steps. Most design advantages of PIM technology are captured during molding by relying on the flexibility of incorporating complexities in the tool. A molded part is called a "green part" and is oversized to allow shrinkage during sintering⁽²⁾.

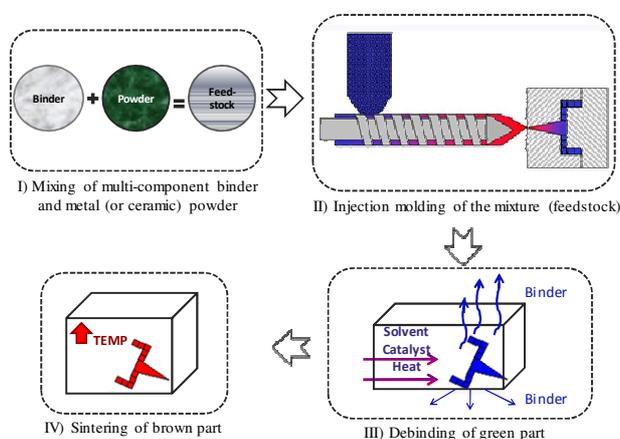


Fig. 1. Flow chart illustrating the main stages of PIM process.

Before sintering, the organic binder must be removed without disrupting the molded powder particles; this process is commonly referred as debinding. Organic polymers have to be removed completely from the “green part”, since carbon residues can influence the sintering process and affect the quality of the final product negatively. Moreover, binder removal is one of the most critical steps in the PIM process since defects can appear due to inadequate debinding, causing problems like bloating, blistering, surface cracking and large internal voids. It has been shown that the rate of binder removal plays a main role in the defect appearance due to structural changes in capillaries inside the green part⁽¹⁰⁾. For these reasons, the debinding is the most expensive and time-consuming stage in the PIM technology. Three main methods can be applied depending on the composition of the binder: thermal, solvent, and catalytic. Catalytic debinding is by far the fastest method of removing the binder from the molded part; it is based on the solid-to-vapor catalytic degradation of polyoxymethylene (POM), which occurs when such polymer is exposed to high enough temperatures (110 to 150 °C) in the presence of nitric or oxalic acid vapor⁽¹¹⁾. It is observed that the debinding rate is proportional to the temperature at which the process is executed. However, this operating parameter is limited by the increasing dimensional distortion as the melting temperature of POM is approached⁽²⁾.

Sintering is the last stage of the PIM process; it is a thermal treatment that transforms metallic or ceramic powder into bulk material with improved mechanical strength that in the majority of cases has residual porosity. Sintering is performed at temperatures below the melting temperature of the major constituent in the metal or ceramic powder, generally within 70 to 90% of the melting point⁽¹²⁾. The temperature inside the sintering furnace is high enough to start the recrystallization process of the metal or ceramic particles, but low enough so that the particles remain unmelted. At such temperatures, the particles recrystallize into each other causing them to fuse together⁽⁴⁾. Depending on the material, debound parts are sintered at temperatures ranging from 1200 to 1600°C under a controlled atmosphere⁽¹³⁾.

Low viscosity at the molding temperature and a high drop in viscosity at high shear rate are very important properties of the binder for mold filling with less energy. This is particularly important when dealing with complicated geometries⁽¹⁴⁾. When cooled, the binder should be strong and rigid to prevent distortion of the molded part. Finally, high thermal conductivity, low thermal expansion coefficient, good adhesion with powder, no orientation, and be chemical inertness with respect to the powder are also desirable properties that should be taken into account when selecting a binder⁽¹⁵⁾.

As previously mentioned, catalytic debinding is the fastest debinding method available. However, POM has a higher viscosity compared to other binder systems and in some instances this can complicate the injection molding process. On the other hand, POM is a polymer with a high degree of crystallinity in solid state and as such the molded part with this binder has very good mechanical properties and dimensional stability, which are very desirable to ensure a final part with the correct geometry. Therefore, it is important to find a way to decrease the viscosity of the molten binder without deteriorating its mechanical properties in solid state. A common method of lowering the viscosity of polymers is to decrease their molecular weight, but this in turn causes a drop in their solid mechanical properties. Thus other methods need to be investigated.

One particular method is to modify the polymer molecular mass distribution by changing its modality, in other words to have more than a single peak in the molecular mass distribution of the polymeric material. Figure 2 shows a schematic representation of a bimodal and monomodal molecular mass distribution.

The effects of bimodality have been previously studied in some polymers. For example, Emri & von Bernstorff⁽¹⁶⁾ reported that bimodal Polyamide 6 (PA6) showed a significant improvement on the relaxation modulus as compared to conventional monomodal PA6; a difference of almost two decades in time dependency between the monomodal and bimodal PA6 materials. Similar results were observed for the same materials in terms of creep compliance by Kubyshkina *et al.*⁽¹⁷⁾.

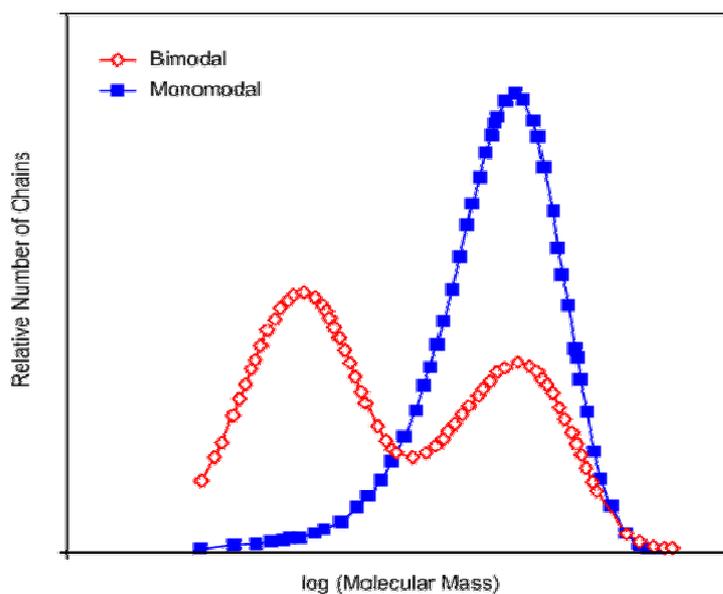


Fig. 2. Schematic representation for monomodal and bimodal molecular mass distribution in polymeric materials.

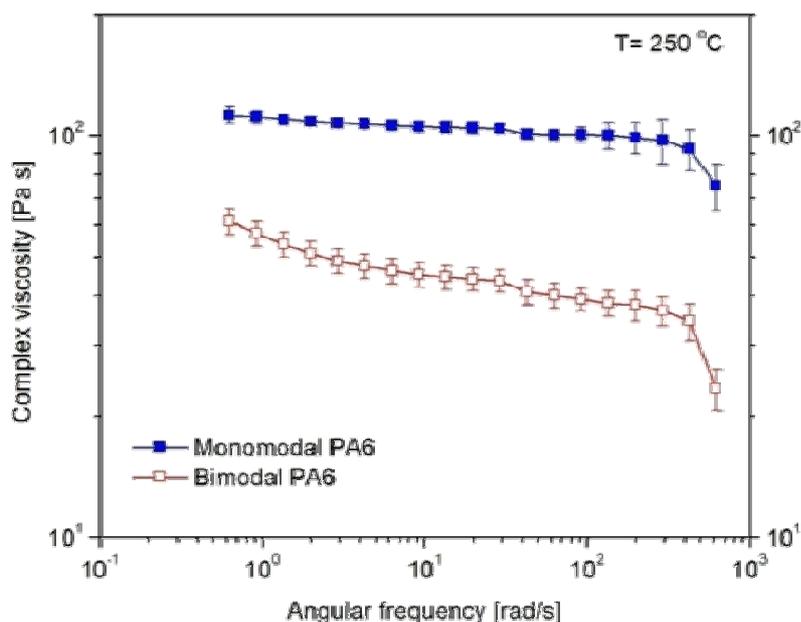


Fig. 3. Complex viscosity of mono- and bimodal PA6 as function of frequency.

Viscosity measurements have been recently performed by our group on monomodal and bimodal PA6 and are shown in Fig. 3. As can be appreciated, the viscosity of bimodal PA6 is significantly lower than its monomodal counterpart in all the range of frequencies studied. Therefore, one can conclude that bimodality has brought the required properties to PA6, i.e., lower viscosity in the molten state and high mechanical properties in the solid state. Unfortunately, PA6 does not exhibit catalytic decomposition and could not be used in catalytic PIM. For this reason, it was decided to investigate if a similar

behavior could be achieved in POM through multimodality in its molecular mass distribution.

The present work focuses on the characterization of the time-dependent properties of monomodal POM and different formulations of bimodal POM-based materials. The aim is to understand how the addition of short polymeric chains influences the macroscopic properties of POM and thus design a binder more suitable to the requirements of PIM technology.

Nomenclature

- D*: diameter
- l*: length
- I*: moment of inertia
- J*: creep compliance
- M*: shearing torque
- T*: Temperature
- t*: time
- η^* : complex viscosity
- φ : rotational angle

Subscripts

max: maximum

- min*: minimum
- p*: polar
- ω : angular frequency

2. Materials and Methods

2.1 Materials

Monomodal (MO-0) and bimodal (BI-0) POM were supplied by BASF (Germany). Their notation used in this study and corresponding thermal properties are specified in Table 1. As it can be seen in Table 1, thermal properties of the two types of POM have no significant difference.

Table 1. Notation and thermal properties of monomodal and bimodal POM⁽¹⁸⁾.

Notation	Supplier	Molecular Mass Distribution	Melting Temperature (°C)	Crystallization Temperature (°C)
MO-0	BASF	Monomodal	165.8± 0.7	134.0± 1.1
BI-0	BASF	Bimodal	164.3± 3.2	134.9± 2.8

In the second step of our investigation the bimodal POM was further modified by adding different concentrations of a polymer with low molecular weight to obtain material with multimodal molecular weight distribution. Bimodal POM was modified by adding different concentrations (1, 2, 4, 8 and 16 wt.%) of a compatible polymer with low molecular weight (referred as ‘wax’ due to confidential terms). The blends of bimodal POM and wax were prepared by mixing the two

components in a twin-screw extruder at the maximum concentration (16 wt.%). This master batch was subsequently diluted with previously extruded bimodal POM until the remaining concentrations were achieved. All the materials were extruded seven times in total to ensure a homogeneous distribution of the short chains among the long ones. Neat bimodal POM was also extruded (BI-00E) and characterized in order to investigate the effects of extrusion (Fig. 4).

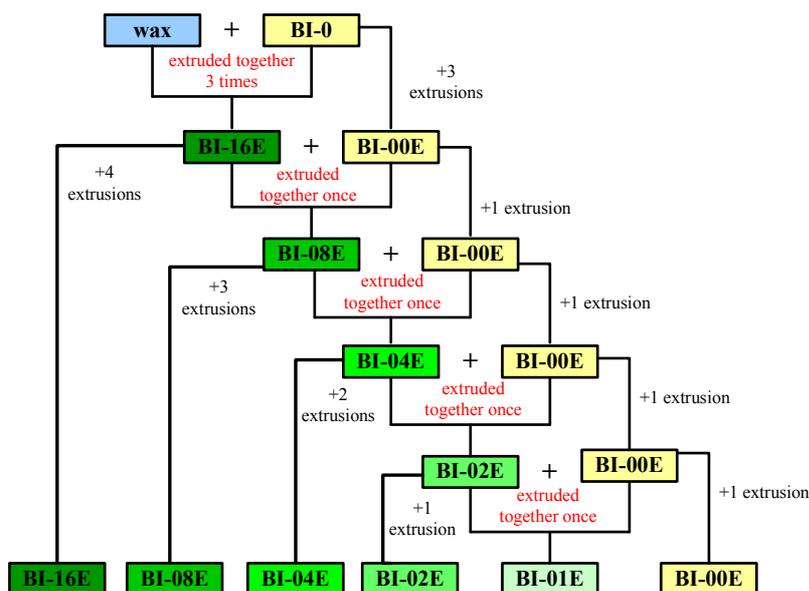


Fig. 4. Flow chart for the blending of bimodal POM with wax at different concentrations.

The list of multimodal materials (bimodal + wax), their notation and thermal properties are shown in Table 2. As with the unmodified monomodal and bimodal POM, the

thermal properties of the POM-wax blends did not differ significantly among each other.

Table 2. Notation and thermal properties of extruded bimodal POM and its wax blends⁽¹⁸⁾.

Notation	Wax Content (wt.%)	Molecular Mass Distribution	Melting Temperature (°C)	Crystallization Temperature (°C)
BI-00E	0	Bimodal	164.6 ± 2.4	135.5 ± 1.2
BI-01E	1	Multimodal	166.6 ± 3.2	135.4 ± 0.5
BI-02E	2	Multimodal	166.9 ± 1.4	136.1 ± 0.7
BI-04E	4	Multimodal	164.3 ± 1.3	135.7 ± 1.0
BI-08E	8	Multimodal	165.3 ± 1.9	135.6 ± 0.9
BI-16E	16	Multimodal	163.6 ± 0.9	135.6 ± 1.2

2.2 Viscosity measurements

Viscosity measurements of all materials in the molten state were performed by means of small amplitude oscillatory shear tests according to ASTM D-4440⁽¹⁹⁾ using a Haake MARS II rotational rheometer (Thermo Scientific, Karlsruhe, Germany). Measurements were performed at 190 °C, which is a commonly used temperature for injection molding of POM. The geometry used was cone-plate with a 20 mm in diameter. Two frequencies sweep were performed in each measurement, the first one increasing from 0.1 s⁻¹ (0.628 rad/s) to 100 s⁻¹ (628.32 rad/s) and the second one decreasing from 100 s⁻¹ to 0.1 s⁻¹, in order to monitor any possible flow instability. The applied stress was set at 200 Pa; such value was previously determined to be within the linear viscoelastic region of the materials at the specified temperature. The reported results are the average of six repetitions for each of the materials studied.

2.3 Creep compliance measurements

Creep measurements in the solid state were performed following the methodology developed at the Center for Experimental Mechanics at the University of Ljubljana⁽²⁰⁾. Cylindrical specimens with diameter $D = 5.80 \pm 0.05$ mm and length $l = 40.0 \pm 1.0$ mm were prepared by gravimetric casting from all of the materials listed in Table 1 and 2. The casting procedure starts by filling up a glass tube with polymer pellets. The material is melted by a movable heater positioned around the glass tube and a pressure of about 1 MPa is applied to the molten polymer using a piston. The temperature of the heater was set at 220

°C. The heater was moved at a relatively slow rate of 2 mm/min. After melting and pressing on the glass cylinder, the polymeric materials were left to naturally cool down to room temperature. Schematics of the procedure are provided elsewhere^{(16) (17) (18) (21)}.

After each specimen was prepared, they were annealed at a temperature of 120 °C to erase their thermo-mechanical history. After annealing, torsional creep measurements were performed at the temperature of 110 °C in the time scale of 3 h, under a constant shearing torque (M). The rotational angle caused by this torque was recorded as a function of time ($\varphi(t)$) and then the creep compliance ($J(t)$) of each specimen was calculated using the following equation:

$$J(t) = \frac{\varphi(t)I_p}{lM} \quad (1)$$

where I_p is the polar momentum for the circular cross-section geometry of the cylindrical specimen and l is the length of the specimen. The applied torque was selected to be within the linear viscoelastic region for all POM materials at the specified temperature. Finally, the reported results are the average over two repetitions carried for each of the materials studied.

3. Results and Discussion

3.1 Viscosity

The viscosity of all materials was investigated in frequency domain. Based on these measurements, it is clear that all the materials show a nearly constant magnitude of the complex viscosity at low frequencies,

followed by a drop at higher frequencies, which is commonly referred as a shear-thinning behavior. Figure 5 shows the shear thinning behavior for monomodal and bimodal POM.

The viscosity results can be summarized using two parameters: $|\eta^*|_{\omega \rightarrow \min}$ and $|\eta^*|_{\omega \rightarrow \max}$. The first parameter

represents the magnitude of the complex viscosity at the lowest angular frequency at which experiments were performed (0.628 rad/s), while the second parameter is the magnitude of the complex viscosity at the highest frequency reachable by the experimental set up (628.3 rad/s). The viscosity results are shown in Fig. 6.

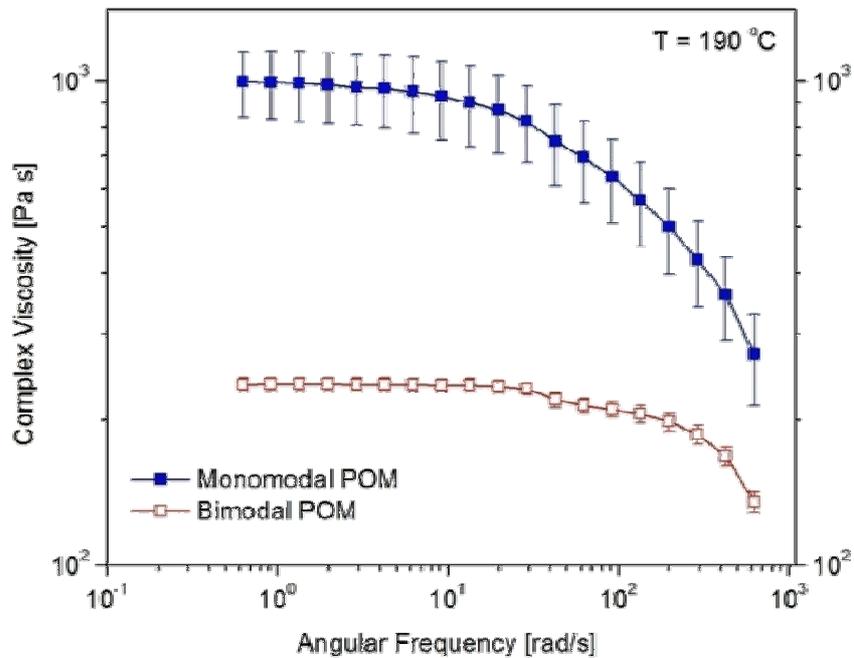


Fig. 5. Shear thinning behavior of monomodal and bimodal POM at 190 °C.

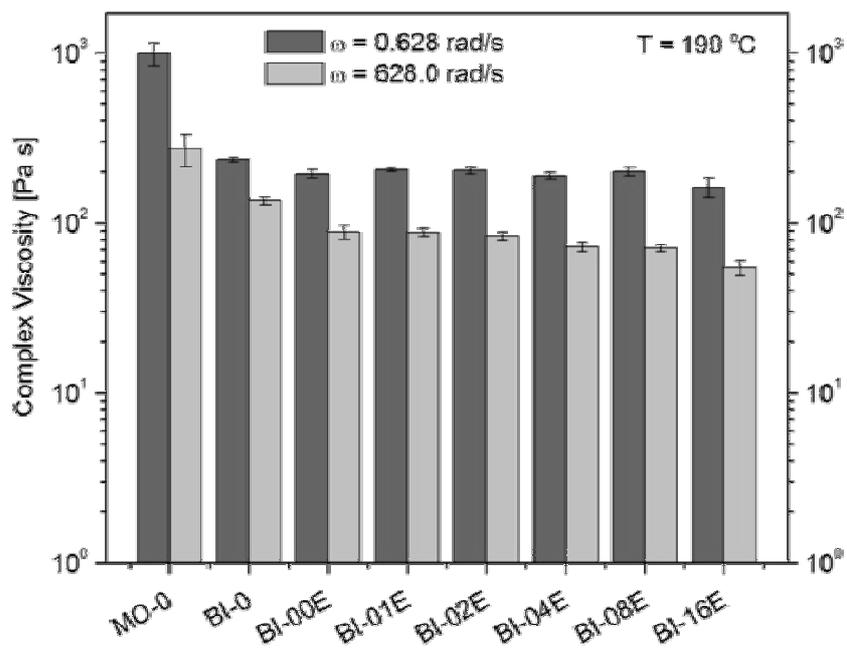


Fig. 6. Complex viscosity at the minimum and maximum frequency studied for all materials investigated at 190 °C.

It is clear that the addition of short polymeric chains resulted in materials with better flowability. The commercial bimodal POM (BI-0), which has a higher content of short polymeric chains, shows a significant decrease in viscosity in both low and high frequencies in comparison to monomodal POM (MO-0). At the lowest frequency bimodal POM has 4 times lower viscosity and at the highest frequency the viscosity is twice smaller. The reduction of viscosity is a consequence of the introduced short polymeric chains, which can act as internal lubricants reducing the friction between the long chains and thus, increasing the flowability of the molten polymer, particularly when subjected to high shear rates. The extrusion protocol used to prepare POM/wax blends led also to a reduction on viscosity; it was observed that BI-00E had about 17% lower viscosity than BI-0 due to the breaking of longer chains during extrusion cycles. Regarding the new formulations proposed in this work, it is possible to notice that the flowability of POM is clearly improved by increasing the concentration of wax added. For instance, by adding 16 wt.% of wax (BI-16E), $|\eta^*|_{\omega \rightarrow \max}$ is reduced by 34% when compared to BI-00E and by 59% when compared to BI-0. As already discussed in this work, improving flow properties is of extreme

importance to mold filling of complex geometries as those usually found in PIM.

3.2 Creep compliance

In Fig. 7 the creep compliance determined at 110° C after 10000 s (~3h) for each of the POM-based materials investigated is shown. Creep compliance values at selected time and temperature enable a direct correlation to process conditions, since both parameters are very similar to those commonly applied during the catalytic debinding process of POM. Therefore, a low value of creep compliance under these conditions is important to ensure minimal deformation of the molded part resulting in a better quality of the sintered product. Bimodal (BI-0) and monomodal POM (MO-0) showed no significant difference in their creep compliance at the measuring conditions. This indicates that the addition of short molecules does not significantly affect the solid mechanical properties of POM. It can be said that the extrusion protocol also showed no significant change in the creep performance of POM, since BI-00E shows only slightly lower creep compliance than neat bimodal POM in the conditions here defined.

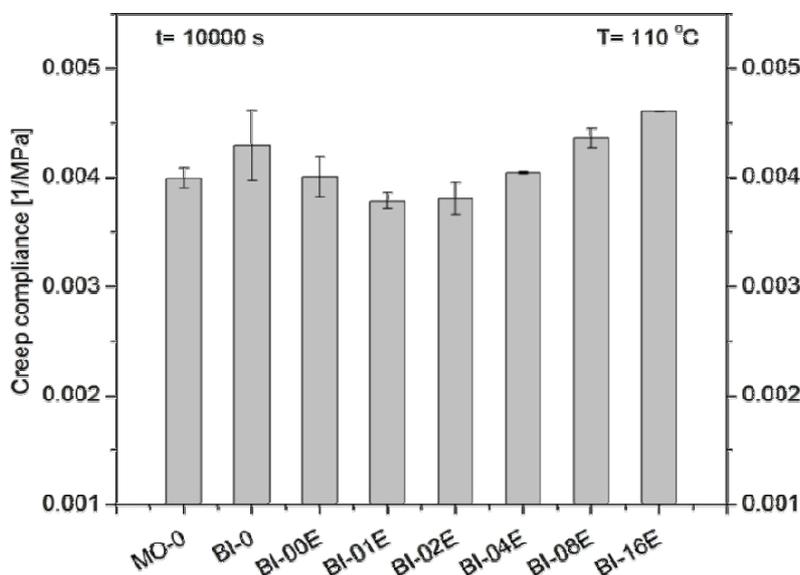


Fig. 7. Creep compliance measured at 110 °C, after 10⁴ seconds, for all materials investigated.

From another standpoint, the addition of up to 2 wt.% of wax yielded no significant change in creep compliance, it appears as if BI-01E and BI-02E have a slight improvement in the resistance to deformation as compared to BI-00E, but the change cannot be considered significant. On the other hand, materials BI-04E and BI-08E have shown creep compliances slightly higher than BI-01E and BI-02E, but at the same level as the extruded bimodal POM.

Finally, the highest creep compliance, and consequently, the lowest resistance to deformation among all materials investigated was observed for BI-16E.

The possible explanation for the observed behavior could be that the smaller molecules arrange themselves in the spaces between the larger ones when in the molten state. As the material solidifies a more closely packed structure is obtained, such tighter structure prevents the material

from creeping. This hypothesis is supported by the polarized micrographs presented by Emri and von Bernstorff⁽¹⁶⁾ and Kubyshkina *et al.*⁽¹⁷⁾ for PA6 and by Stringari *et al.*⁽¹⁸⁾ for POM-wax mixtures, which shows a finer structure for the materials with the higher content of shorter chains. However, when the content of shorter molecules exceeds a certain concentration, they may actually facilitate the movement of larger chains and as a result the materials start to creep more.

4. Conclusions

This work has shown that macroscopic properties of POM are sensitive to the addition of short polymeric chains. For instance, the commercial bimodal POM (BI-0) which has a larger content of short polymeric chains presents time-dependent properties in solid state similar to those shown by standard monomodal POM (MO-0) with larger molecular chains. However, BI-0 exhibits a much better flowability, which is extremely important for filling the cavities of complex geometries as those usually encountered during the powder injection molding process. The extrusion protocol has shown no negative effects in both, binder's flowability and its resistance to deformation. These results suggest that not only the ratio between long and short chains affects the time-dependent properties of POM, but also the distribution and interactions between them.

Also, for the blends of bimodal POM and wax, it was observed that the addition of short polymeric chains to bimodal POM showed a further decrease in molten viscosity. At low wax content (up to 4 wt.%), the solid creep properties of the blends remained almost unchanged. However, the addition of higher concentrations, for instance 16 wt.%, already shows a relatively larger increase in creep compliance. The investigated mixture of bimodal POM and 8 wt.% wax had viscosity values (at 190 °C) up to 19% lower than the commercial bimodal material submitted to the same extrusion protocol. At the same time the creep compliance of the same mixture is only 9% higher at the conditions here studied (at 110 °C, after 10⁴ s), which is still lower than the 14% increase when the content of wax reached 16 wt.%. So it can be said that a compromise was reached at 8 wt% wax content, lower viscosity and not so high increase in creep compliance.

In general, it can be concluded that the addition of short polymeric chains may be an interesting tool for the optimization of binders designed to be used in powder injection molding technology, and that measuring the time-dependent properties of binder in solid and molten state can be an important tool for determination of the optimal formulation of a PIM binder.

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