

PRESSURE EFFECT COMPREHENSION INTO THE FLOW PREDICTIONS OF POWDER INJECTION MOULDING COMPOUNDS

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ABSTRACT

The flow properties of the highly filled polymer compounds intended for production of hard-metal parts by powder injection moulding (PIM) technology were studied. The pure binder, consisted of polyethylene, ethylene-based copolymer and paraffin, and its compounds with hard-metal carbide powder were prepared by melt mixing. The flow properties were investigated in the respect to temperature and pressure using modified capillary rheometer operating flow at constant piston speed. The measures of temperature and pressure sensitivity of PIM compounds, temperature and pressure sensitivity coefficients, were quantified through fitting of the rheological data with Carreau-Yasuda model.

Keywords: PIM technology, rheology, pressure effect

1. INTRODUCTION

Compounds based on hard-metal carbide powder and polymeric binder find application in production of sintered parts by Powder Injection Moulding (PIM) technology. There are many problems that may arise at each stage (mixing, moulding, debinding or sintering) of the PIM technology. It was found (using mainly X-ray analysis) [1] that most of the defects as shape distortions, crack bubbles or density heterogeneities of final parts were initiated during the moulding stage. Therefore, the understanding of the flow properties of such materials is the key to successful processing.

Basic rheological equations qualify the deformation of materials - an elastic solid and a viscous fluid - as a result of an applied stress. These are two limiting cases of material response, which have no examples in the real. Highly filled melts (PIM compounds) belong to the group, where rather complicated flow behaviour is expected.

First, in the region of high shear rates the flow is restricted by instabilities. Second, one cannot ignore the fact that the distribution of filler in the capillary is not homogenous. Kubat and Szalanczi [2] showed that so called Serge-Silberberg effect, i.e. movement of particles from the capillary wall to the centre during flow, achieves a great magnitude, and thus leads to an axial solids concentration gradient. Third, multiphase materials often show apparent slip at the wall, and finally, the matrix can be filtrated out of the compound, which causes the blockage of capillary by the filler.

Recently we have shown [3] that a priori application of the fundamental theories on suspensions in predicting the flow properties of such complicated filled systems should be taken with an extreme caution, because it brings a number of obstacles and limitations.

Flow properties of PIM compounds are strongly affected by processing conditions. Whereas temperature affected viscosity has been commonly taken into account in the flow simulation programs, the effect of pressure on the flow properties has been rather omitted even for unfilled polymer melts. This should not be tolerated for injection moulding, where the theoretical and experimental results will differ significantly.

Pressure affected viscosity can be determined from correlations between pVT and rheological measurements using semi-empirical relations as most recently shown by Sedlacek et al. [4]. If conventional rheometers, as an alternative, are employed, pressure coefficient can be calculated either

from non-linearities occurring in the Bagley plot or from the pressure profile generated during flow in a slit geometry.

2. EXPERIMENTAL

The polymeric binder consisting of three components was used. The particular ones were: Paraffin wax, density 0.900 g.cm^{-3} , Ethylene based block copolymer (Borealis), density 0.927 g.cm^{-3} , Low-density polyethylene (LDPE), Lacqtene 1200 MN 8 (Atochem), density 0.918 g.cm^{-3} .

The composition of the binder was as follows:

21 wt. % of paraffin wax,

26 wt. % of copolymer,

53 wt. % of polyethylene.

The powders used in the experiments described below were composites of tungsten carbide and cobalt. The three employed grades differ in their characteristics as shown in Table 1.

Table 1. Particle size distributions and densities of the powders used.

MATERIAL	BC10U	BC37S	BC55S
Diameter at 10% [μm]	0.45	0.95	1.57
Diameter at 50% [μm]	1.11	3.72	5.28
Diameter at 90% [μm]	3.75	8.18	8.29
Mean diameter [μm]	1.59	4.18	5.14
Tap density [g.cm^{-3}]	4.85	5.99	7.30
Density [g.cm^{-3}]	14.90	14.94	14.94

The rheological behaviour was studied in a capillary rheometer (Göttfert 2001) with a plane capillary entrance. The rheometer was modified by an additional device (Figure 1) generating backpressure, which causes increase of pressure actuating on the tested materials. The detailed description of the equipment and the method can be found in [4]. Pressure dependent viscosity was measured at different values of backpressure in the shear rate range from 35 to 2500 s^{-1} .

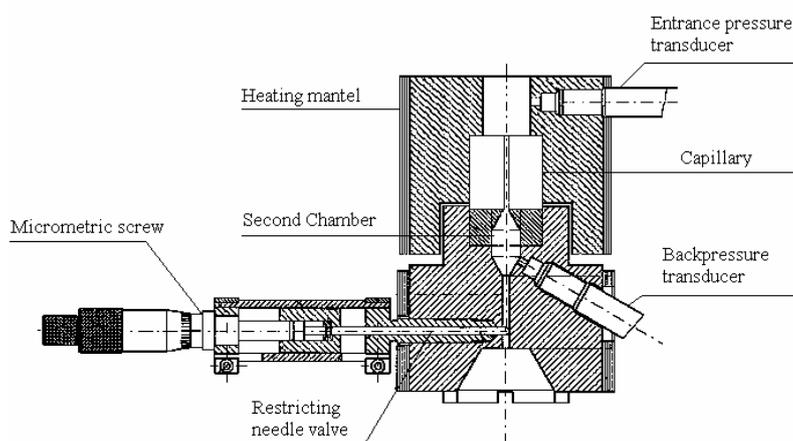


Figure 1. Schematic diagram of backpressure device [4].

3. RESULTS AND DISCUSSION

Highly filled polymers generally show high sensitivity to variations in shear rate, even if the polymer matrix behaves in a Newtonian fashion. This trend is more pronounced as the concentration of the filler increases [5,6], see schematically in Figure 2. Depending on the type of the dispersed particles, especially on their particle size, a yield point may appear at low shear rate. The presence of yield stresses is indicative of a particle network structure within the melt, which is relatively stable at the lower shear rates. At higher shear rates, however, this structure is broken and the viscosity is dominated by hydrodynamic interactions [7]. At stresses above the yield point, there is an initial

decrease in viscosity as the shear rate increases (shear thinning behaviour), indicating particle and polymer orientation and ordering with flow.

Many highly filled suspensions, especially those containing irregularly shaped particles, show dilatant flow, as we have shown in [5]. There is still considerable uncertainty about the source of such behaviour. Jansma and Qutubuddin [8], who studied this phenomenon using different viscometers, showed that it could not be an experimental artefact due to the slip effect. The shear dilation appears to depend on the matrix wetting characteristics and solids loading.

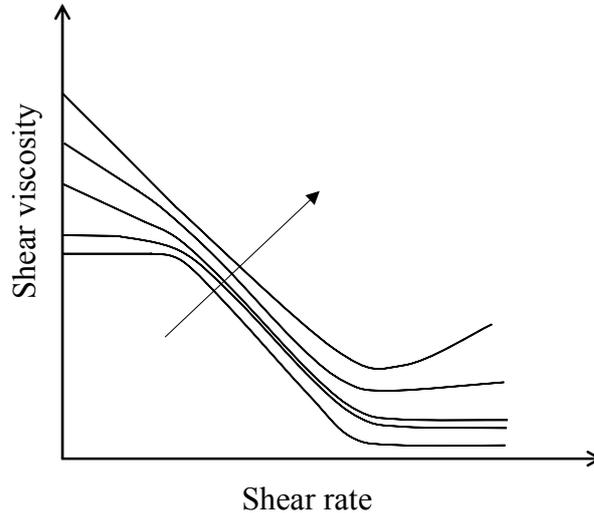


Figure 2. Scheme of the flow behaviour of filled systems. The arrow shows direction of concentration rise.

Temperature is clearly the key factor to influence the course of the flow behaviour. The activation energy is not constant for filled systems, but it varies with volume fraction of solids. High activation energy values indicate high sensitivity of system to temperature change. Two different explanations of dependence of activation energy on filler content can be found in the literature. German [9] suggests that activation energy increases with increasing filler content. His idea is based on the explanation that the relative rate of viscosity decrease is typically faster in the loaded system, because of the superimposed change in volume fraction of solids associated with difference in thermal expansion coefficients. On the other hand, data from our investigations [10], confirmed by Shenoy [11], suggest opposite dependence of the activation energy on the filler content. According to his work viscosity of filled system is less temperature sensitive than that of pure polymeric binder, because the fillers provide very little free volume change with temperature in relation to the binder. In order to strengthen our findings, T-p flow behaviour has been investigated.

Pressure effect on viscosity was evaluated using the Carreau-Yasuda model [12]:

$$\eta(\dot{\gamma}) = \frac{\eta_0 f}{\left[1 + (K_1 f \dot{\gamma})^a\right]^{\frac{1-n}{a}}} \quad (1)$$

where η_0 means zero-shear viscosity, $\dot{\gamma}$ is shear rate, $\eta(\dot{\gamma})$ represents the shear rate-dependent viscosity, K_1 , n , and a are empirical constants, and f stands for the exponential relations embracing the pressure sensitivity.

The pressure effect was determined utilizing the exponential relation in a form:

$$f = e^{(\beta P)} \quad (2)$$

where β is the pressure coefficient of viscosity, and P stands for the gauge pressure.

In our recent work [13] pressure and temperature sensitivity coefficients of PIM materials were found to be functions of temperature and pressure, respectively. While pressure sensitivity coefficient was decreasing function of temperature, which is positive for PIM, temperature coefficient was thereby raised by pressure, which is opposite to the PIM demands. Further, both the pressure and the temperature sensitivities of the PIM compounds are reduced as the amount of carbide powder in the

compound rises. Nevertheless, comparing of the results obtained for the compounds differing in powders used showed a strong effect of filler characteristics on p-T dependent flow behaviour, and therefore we take it into consideration here.

The pressure-coefficients of 50 vol.% compounds with carbide powders differing in their particle size distributions are depicted in Table 2.

Table 2. Pressure sensitivity coefficients and parameters of Carreau-Yasuda model.

Material	β [1/GPa]	η_0 [Pa.s]	n	T_r [°C]	$K_1 10^{-3}$ [s]	a
BC10U	32.96	4051.7	0.10	0	8.932	0.289
BC37S	19.25	1373.8	0.10	0	3.226	0.444
BC55S	18.30	787.7	0.10	0	2.548	0.435

Increasing the loading level of the carbide powder seemed to diminish the pressure sensitivity of their flow properties. When an influence of filler size distribution is considered, it is found that the shape of the particle size distribution curve determines basic viscosity behaviour. Zero-shear viscosity is increased for powder (BC10U) containing the highest portion of small particles (around 1 μ m). At the same time such compound shows the most pronounced sensitivity to pressure.

During flow of highly filled materials particles dilate to allow interparticle motion. Pressure suppresses this effect resulting in higher viscosity. It seems that the pressure sensitivity of the PIM compounds might be modified via tailoring of filler characteristics.

4. ACKNOWLEDGEMENT

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5. REFERENCES

- [1] Edirisinghe M.J., Evans J.R.G.: Properties of ceramic injection molding formulations. 1. Melt rheology, J. Mater. Sci. 22, 2267, 1987.,
- [2] Kubát J., Szalanczi A.: Flow instabilities in capillary flow of concentrated suspensions, Polym. Eng. Sci. 14, 873, 1974.,
- [3] Honek T., Hausnerova B., Saha P.: Relative viscosity models and their application to capillary flow data of highly filled hard-metal carbide powder compounds, Polym. Comp. 26, 29, 2005.,
- [4] Sedlacek T., Cermak R., Hausnerova B., Zatloukal M., Boldizar A., Saha P.: On pVT and rheological measurements of polymer melts: Correction of the hole fraction-viscosity relationship, Intern. Polym. Proc. 20, 286, 2005.,
- [5] Hausnerová B., Saha P., Kubát J.: Capillary flow of hard-metal carbide powder compounds, Int. Polym. Proc. 14, 254, 1999.,
- [6] Hausnerová B., Saha P., Kubát J., Kitano T., Becker J.: Rheological behaviour of hard-metal carbide powder suspensions at high shear rates, J. Polym. Eng. 20, 237, 2000.,
- [7] Husband D.M., Aksel N.: The existence of static yield stresses in suspensions containing noncolloidal particles, J. Rheol. 37, 215, 1993.,
- [8] Jansma J.B., Qutubuddin S.: Rheological behaviour of concentrated calcium phalophosphate suspensions, J. Rheol. 39, 161, 1995.,
- [9] German R.M.: Powder Injection Molding, MPIF, Princeton, 1990.,
- [10] Honek T., Hausnerova B., Saha P.: Temperature dependent flow instabilities of highly filled polymer compounds, App. Rheol. 12, 72, 2002.,
- [11] Shenoy, A.V.: Rheology of Filled Polymer Systems, Kluwer Academic Publishers, 1999.,
- [12] Yasuda K., Armstrong R.C., Cohen R.E.: Shear flow properties of concentrated solutions of linear and star branched polystyrenes, Rheol. Acta 20, 163, 1981.,
- [13] Hausnerová B., Sedláček T., Slezák R., Saha P.: Pressure-dependent viscosity of powder injection moulding compounds, Rheol. Acta 45, 290, 2006.