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Pressure-dependent viscosity of powder injection moulding compounds

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Abstract

A single piston capillary rheometer was modified by the addition of a second chamber with a restricting valve (developed at the Polymer Centre, Zlin, Czech Republic), which provides backpressure and increasing the pressure in the melted material during the flow through the die. The Carreau-Yasuda model was employed to fit the measured viscosity data and determine the temperature and pressure coefficients for polyolefin based binder and its compounds with carbide powder. Both temperature and pressure sensitivity coefficients are largely dependent on the structure of a polymer, which should be taken into account for binder- formation's development. Increasing the loading level of the powder in the compound diminishes the pressure sensitivity of their flow properties.

Keywords

Pressure-dependent viscosity • Temperature and pressure coefficients • Modified capillary rheometer • PIM technology

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Introduction

Injection moulding of the powder-binder compounds requires specific flow characteristics to be met. The interpretation of the rheological behaviour of highly filled (typically above 50 vol%) systems is necessarily a difficult task. Recently Honek et al. (2005) have shown that a priori application of the fundamental theories on the 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 rising from both multicomponent character of binder and complex powder characteristics, mainly irregular shape and broad particle size distribution.

Flow properties of PIM compounds are strongly affected by temperature. Hausnerova et al. (1999) and Honek et al. (2002) have demonstrated that temperature is the key factor limiting the unstable flow of highly concentrated PIM compounds manifested as a radical change on their flow curves, accompanied by the distortions of the extruding surface. The temperature affects the onset of unstable flow of the compounds in the opposite manner to polymer melts (e.g. HDPE, LLDPE), almost independently of the filler concentration. At higher temperatures, the formation and reformation of particle's mat at the capillary entrance is enhanced by lower binder viscosity, which supports the mechanism of "filtration effect", as a possible explanation for unstable flow occurring at capillary flow of highly filled compounds, introduced firstly by Yilmazer et al. (1989), and then studied by Yaras et al. (1994) and Suwardie et al. (1998).

Temperature dependence of viscosity has been commonly taken into account in the flow simulation programs, whereas the effect of pressure on the flow properties has been rather omitted even for unfilled polymer melts. This can be tolerated for extrusion, blow moulding, or casting, but not 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 Utracki (1983, 1985) or Sedlacek et al. (2005) semi-empirical relations. If conventional rheometers, as an alternative, are employed, pressure coefficient, β, can be calculated either from nonlinearities occurring in the Bagley plot or from the pressure profile generated during flow in a slit geometry (Duvdevani and Klein 1967; Penwell and Porter 1969, 1971; Penwell et al. 1971; Casale et al. 1971; Kamal and Nyun 1973, 1980; Denn 1981; Laun 1983; Izu et al. 1993; Hatzikiriakos and Dealy 1994; Moldenaers et al. 1996; Hay et al. 1999; Liang 2001).

Another method represents modified rheometers, which are able to cover many flow situations occurring in injection moulding processes. In case of single piston equipments, used by (Choi 1968; Driscoll and Bogue 1990; Baker and Thomas 1993; Thomas 1997; Binding et al. 1998, 1999; Couch and Binding 2000; Carter 2000; Goubert et al. 2001), secondary chamber with a restricting needle is added, while double piston rheometers generate the pressure in the system closed between the two pistons (Maxwell and Jung 1957; Westover 1961, 1966, 1991, 1992; Carley 1961; Ito et al. 1972; Lord 1979; Kadijk and van den Brule 1994; Mackley and Spitteler 1996; Ranganathan et al. 1999). Equipments based on a drag flow as Couette viscometers or sliding plate rheometers were adopted into pressurized versions by Semjonow (1962, 1965, 1967), Cogswell and McGowan (1972), Cogswell (1973), Koran and Dealy (1999).

In the previous paper by Sedlacek et al. (2004), the effect of pressure and temperature on shear and exten- sional viscosities was quantified for various injection moulding grades of polymers. The same modified single piston rheometer is used in this paper, where we report the study of the temperature-pressure-dependent rheological properties of a complex filled system consisting of three polymeric components (polyethylene, polyethylene based copolymer, paraffin wax) serving as binder, and carbide powder used in PIM technology.

Experimental

Materials

The powder used in the experiments described below was a composite of tungsten carbide and cobalt (cemented carbide). The metallic component (cobalt), which constitutes only a minor proportion of the carbide mixture, serves as the matrix for the final sintered part. The average density amounts to 13.2 g cm^{-3}. The powder was supplied by Sandvik Coromant AB, Sweden. The shape of the particles was irregular, with relatively broad particle size distribution.

The polymer components served as binder were:

- LDPE, Lacqtene 1,200 MN 8 (Atochem), peak melting temperature 107 °C, density 0.918 g cm^{-3}
- ethylene-acrylic acid block copolymer (EAA), Ex 225 (Exxon), containing 5% of acrylic acid, peak melting temperature 100 °C, density 0.929 g cm^{-3}
- paraffin wax, peak melting temperature 56 °C, density 0.900 g cm^{-3}.

The binder composition contained:

- 53 w% low-density polyethylene
- 21 w% paraffin wax
- 26 w% EAA.

Sufficient adhesion between powder and binder is achieved by a copolymer component; paraffin and polyethylene are likely to decrease compound's viscosity due to their low molecular weight.

Blending procedure

The compounds were prepared in a laboratory kneader (Brabender Plasticorder PL-2000-6, mixer type W 50E) at 150°C and 80 rpm. The mixing chamber was filled by 70-80% of its volume. Firstly, a small portion (1/5) of the polymer binder was preheated in the mixer. Then the powder and remaining binder were added by turns during the first minute and the suspension was mixed for about 5 more minutes. The kneader torque was always constant over the last 2-3 min indicating that the dispersion process had been completed. This mixing procedure is in accordance with Youseffi and Menzies (1997), where it has been used for cemented carbides.

Methods

The rheological behaviour of the compounds was studied in a capillary rheometer (Gottfert 2001) with a plane (180 °) capillary entrance. As introduced by Sedlacek et al. (2004), the rheometer was modified by an additional device (Fig. 1) generating backpressure, which causes an increase of pressure actuating on the tested materials. It consists of a chamber with restricting needle valve moving horizontally by means of screw thread in order to set the level of pressurization applied on the material during its flow through the die.

The pressure values were taken at two points: in the reservoir closely upstream from the entrance to the capillary

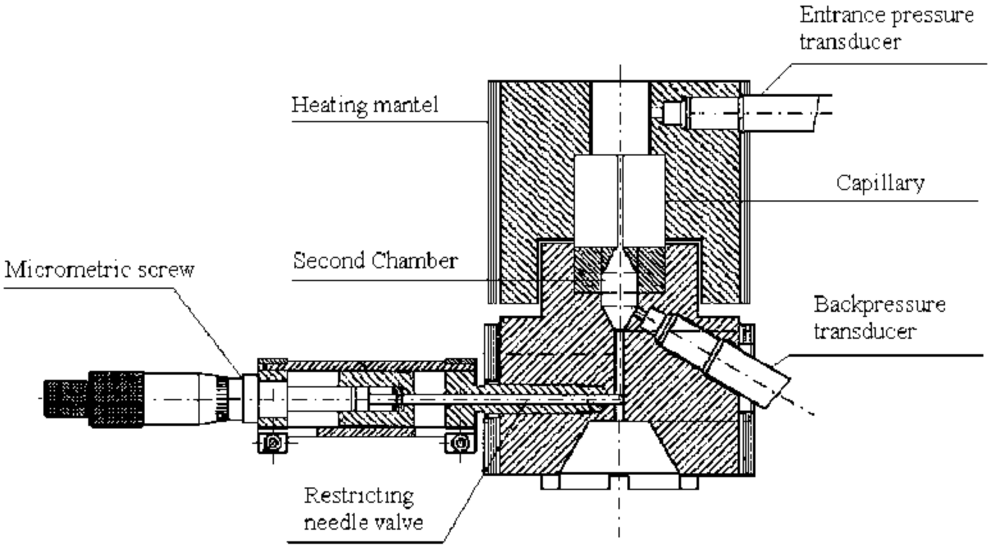

Fig. 1 Schematic diagram of backpressure device

(entrance pressure), and in the second chamber (backpressure). Maximum levels of backpressure generated during experiments reached up to 50 MPa, thus covering the pressure range used in PIM technology.

Experiments were done with two capillaries: long (L/ D = 20/1) and orifice (L/D = 0.12/1). Pressure transducer Dynisco MDA 462-1/2 with nominal range 70 MPa was used for the measuring of backpressures, the entrance pressures were recorded by transducer Gottfert GFT 048B with nominal range 100 MPa. Pressure-dependent viscosity was measured at different values of backpressure in the shear rate range from 35 to 2,500 s^{-1}. The tests were carried out at 140, 150 and 160 °C. Temperature during experiments was controlled by separate sources of heating of the rheometer as well as of the additional chamber.

The sketch of both used capillaries for the backpressure device is depicted in Fig. 2. Entrance pressure drop (orifice die), ΔP_O, pressure drop through the long capillary, ΔP_L, and mean pressure of the long capillary, P_M, are calculated from:

$$\Delta P_O = P_{1O} - P_{2O}, \tag{1}$$

$$\Delta P_L = P_{1L} - P_{2L}, \tag{2}$$

$$P_M = \frac{P_{1L} + P_{2L}}{2}, \tag{3}$$

where subscripts 1 and 2 correspond to measured pressures at the capillary entrance and exit, respectively, O and L represent orifice and long capillaries, respectively.

Both ΔP_O and ΔP_L are the functions of temperature, volume flow rate and mean pressure. The following equations to get the true values of shear stress, σ_C, shear rate $\dot{\gamma}_C$, and shear viscosity, η_C, were used:

$$\sigma_C = \frac{(\Delta P_L - \Delta P_O)R}{2L}, \tag{4}$$

$$\dot{\gamma}_C = \frac{4Q}{\pi R^3}\left(\frac{3n+1}{4n}\right), \tag{5}$$

$$\eta_C = \frac{\sigma_C}{\dot{\gamma}_C} \tag{6}$$

where *R* and *L* are the capillary radius and the length, respectively. The slope of log-log plot of true shear stress versus apparent shear rate, *n,* is evaluated properly through second order polynomial function fit within measured shear rate and mean pressure ranges.

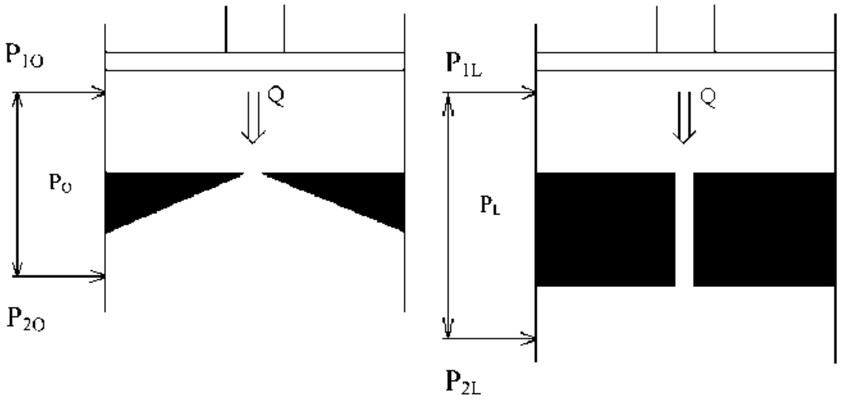

Fig. 2 Sketch of the orifice (L/ D = 0.12) and long (L/D = 20) capillaries

Finally, the Carreau-Yasuda model (Yasuda et al. (1981) was employed for fitting the measured temperature and pressure-dependent shear viscosity. The Carreau-Yasuda model is a few-parametric model (see Table 1), reliably representing experimental data of steady shear viscosity in a wide range of shear rates with even a single relaxation mode. Its constitutive equation was expressed analytically by Barnes and Roberts (1992). It gives the excellent description of the transition region. For the fitting procedure commercially available software (Flow 2000, Compuplast Int., Czech Republic) was employed. The method used was based on minimizing the summation of the squares of the residuals. This was accomplished through nonlinear regression employing the Marquardt-Levenberg algorithm.

The constitutive equation of the Carreau-Yasuda model is:

$$\eta(\dot{\gamma}) = \frac{\eta_0 f}{[1+(K_1 f\dot{\gamma})^{a}]^{1-n/a}}, \tag{7}$$

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 temperature and pressure sensitivity.

We have chosen the simplest exponential expression widely used in polymer engineering calculations and modeling of nonisothermal injection molding flows for the determination of α coefficient:

$$f = e^{-\alpha(\mathrm{T}-T_r)}, \tag{8}$$

where α means temperature coefficient of viscosity, and T and T_r are testing and reference temperatures, respectively.

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

$$f = e^{(\beta P)}, \quad (8)$$

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

Results and discussion

Shear flow properties of the pure binder were examined as the functions of both temperature and pressure, and the obtained results fitted through Carreau-Yasuda model are depicted in Figs. 3 and 4.

The temperature sensitivity of the binder is increasing the function of pressure, which can be seen from the values of temperature coefficient, α, depicted in Table 2. This is very important finding since in PIM applications it is highly desirable to use low thermal sensitivity binder systems.

Accordingly, the pressure coefficients, β, of the tested three-component binder (shown in Table 3) are highly sensitive to the temperature. At higher temperatures the flow properties of binder are less dependent on pressure, which is favourable for the PIM processing. On the other hand, in this temperature region the flow is complicated by instabilities.

Similar trends of T—P-dependent flow behaviour, as found with the tested polyolefin based binder, were observed in the previous work of Sedlacek et al. (2004) for PP and PS, while α and β of LDPE, LLDPE or HDPE were found to be constant. Overall, the knowledge concerning temperature dependencies of pressure coefficients is still not clear; it has been found by Liang (2001) and Christensen and Kjaer (1999) to be decreasing or increasing (Ito et al. 1972) the function of temperature as well as temperature independent as shown by Binding et al. (1998, 1999).

The pressure-dependent viscosity data for carbide powder compounds up to 30 vol% of carbide powder at constant temperature 140 °C was fitted by the Carreau-Yasuda model (Fig. 5). The pressure sensitivity

Table 1 Parameters of Carreau-Yasuda model

Material	Parameter	η_0 [Pa.s]	n	K_1X10^{-3}	a
Binder	Pressure (MPa)				
	50	245.32	0.10	1.88	0.57
	35	175.28	0.10	1.23	0.60
	20	125.24	0.10	1.34	0.61
	10	100.10	0.26	2.00	0.68
	0	80.00	0.39	2.77	0.71
	Temperature (°C)				
	160	65.84	0.21	1.10	0.66
	150	80.00	0.22	1.34	0.64
	140	92.53	0.10	1.14	0.71
Compound	Concentration (vol%)				
	10	211.10	0.10	1.15	0.41
	30	447.37	0.53	26.8	2.69

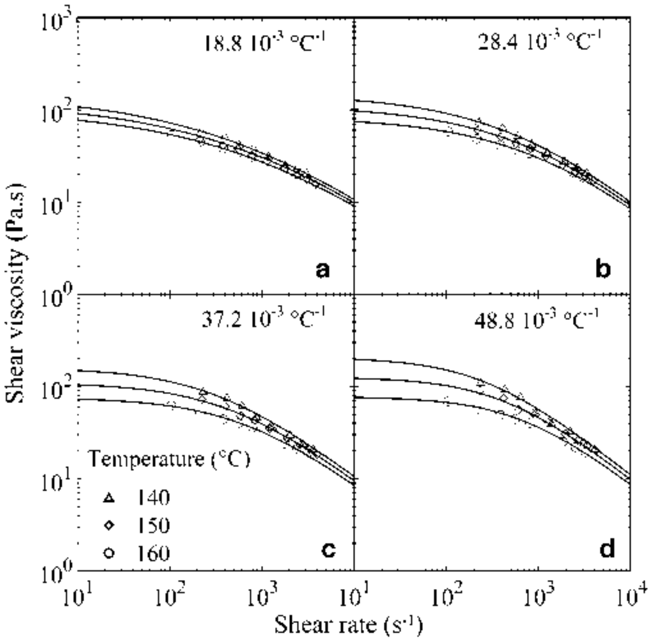

Fig. 3 Temperature-dependent viscosity versus shear rate curves of pure binder as a parameter of pressure **a** 0, **b** 10, **c** 20, **d** 35 MPa. *Solid lines* represent data fitting by the Carreau-Yasuda model

coefficients are demonstrated in the Table 4. Typically, during flow of highly filled materials, after overcoming yield point at the low shear rates, particles start to order themselves in the flow direction to allow interparticle motion resulting in higher maximum packing fraction and lower viscosity. Pressure suppresses this effect resulting in higher viscosity. At high shear stresses (rates), volume increases because particles cannot form layers and slide over each other as proposed by Hoffman (1972). With an increase of particles volume in the suspensions, the rheological dilatancy might be connected as discussed by Yilmazer and Kalyon (1991).

Finally, it should be mentioned that volume fraction of particles is also slightly changed due to pressurization, because of a great discrepancy between bulk moduli of the powder and binder.

Apparently, the pressure sensitivity of the PIM compounds is reduced as the amount of carbide powder in the compound rises. The measurement of the pressure-dependent viscosity at powder concentrations higher than 30 vol. % was complicated by the slip at the wall, resulting in a plug flow.

Conclusion

The effect of pressure and temperature on the flow properties of the materials intended for powder injection moulding (PIM) technology was studied using a singlepiston capillary rheometer modified by additional backpressure chamber. The influence of pressure and temperature on shear viscosity of the three-component polyolefin based binder has been quantified through pressure and temperature sensitivity coefficients, which were found to be the functions of temperature and pressure, respectively. While pressure sensitivity coefficient

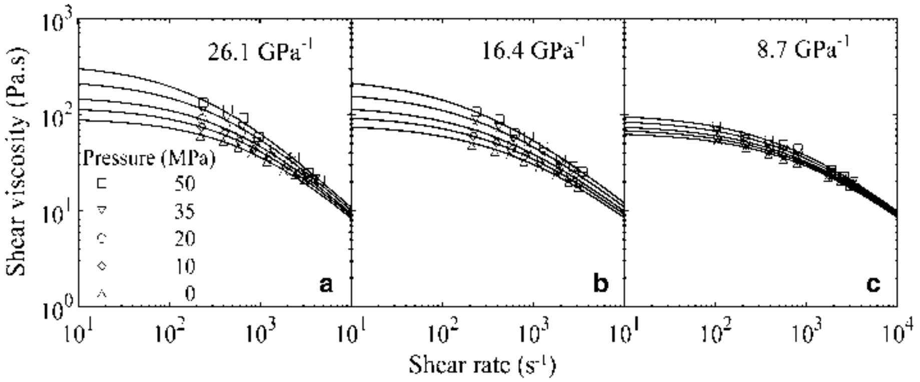

Fig. 4 Pressure-dependent viscosity versus shear rate curves of pure binder as a parameter of temperature **a** 140, **b** 150, **c** 160 °C. *Solid lines* represent data fitting by the Carreau-Yasuda model

Table 2 Temperature sensitivity coefficients of the binder at various pressure conditions

Pure binder

Pressure, *P* (MPa)	0	10	20	35
Temperature coefficient, α (10)$^{-3o}$ C^{-1})	18.8	28.4	37.2	48.8

Table 3 Pressure sensitivity coefficients of the binder at various temperatures

Pure binder

Temperature, *T* (^{o}C)	140	150	160
Pressure coefficient, β (GPa^{-1})	26.1	16.4	8.7

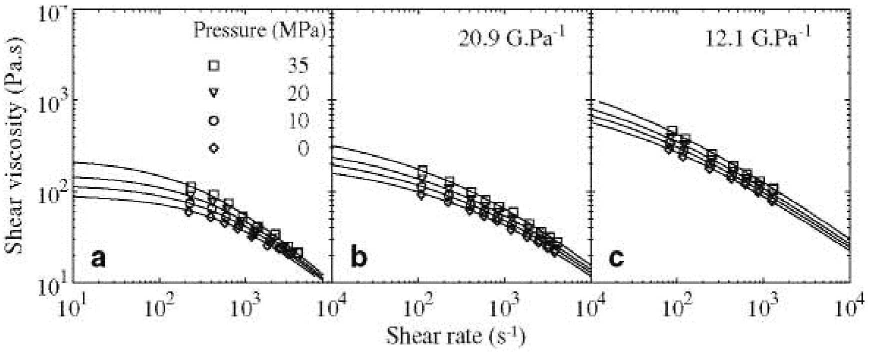

Fig. 5 Pressure-dependent viscosity versus shear rate curves of **a** 0, **b** 10 and **c** 30 vol.% carbide powder compounds at 140 °C. *Solid lines* represent data fitting by the Carreau-Yasuda model

Table 4 Effect of filler content on pressure sensitivity coefficients of the PIM compounds

PIM compound at 140 °C			
Filler content, ϕ (vol%)	0	10	30
Pressure coefficient, β (GPa^{-1})	26.1	20.9	12.1

is decreasing the function of temperature, which is positive for PIM, temperature coefficient is thereby raised by pressure, which is opposite to the PIM demands. Thus, both effects should be taken into account for the development of the binder formulations. Concerning the PIM compounds, increasing the loading level of the carbide powder seems to diminish the pressure sensitivity of their flow properties. However, for this particular carbide powder, the flow at the concentrations higher than 30 vol. % was complicated by wall slip verging into plug flow, and therefore precluding substantial clarification of the pressure effect.

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