Pressure-dependent viscosity of PIM compounds

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ABSTRACT

A modified single piston capillary rheometer was employed for evaluation of rheological properties of a complex system compounded of three polymeric components (polyethylene, ethylene based copolymer, paraffin wax) and carbide powder. The modified Carreau-Yasuda model was employed to fit the experimental viscosity data and determine temperature and pressure coefficients for ethylene based binder and its compounds with carbide powder.

INTRODUCTION

Injection moulding of the powder-binder compounds demands observance of specific flow features. As it was shown the interpretation of the rheological behaviour of highly filled (typically above 50 vol. %) systems is a difficult task and an application of the fundamental theories to predict the flow properties of such complex systems brings a number of obstacles and limitations and should be taken with an extreme caution[1].

For example, it was demonstrated[2,3] that temperature is the key factor limiting the unstable flow of highly concentrated PIM compounds. It was shown that temperature increase shifts onset of unstable flow of the compounds to lower levels of shear stress, which is in the opposite manner to behaviour of pure polymer melts (e.g. HDPE, LLDPE); moreover it was described that in high temperature region this unstable flow appears almost independently of the filler concentration. This behaviour is caused by the formation and reformation of particles' mat at the capillary entrance. The behaviour, incurred by very low viscosity of binder at high temperature, is known as the mechanism of "filtration effect", and as a possible explanation for flow instabilities of highly filled compounds during capillary flow, was introduced firstly by Yilmazer et al[4].

Another factor complicating flow behaviour of polymeric materials is pressure. Generally, viscosity of a polymer melt increases with pressure arise. In our recent work[5] it was found that increase of the powder loading in the compound diminishes the pressure sensitivity of their flow properties. However, the measurements were carried out only at one temperature and the other limiting factor was filler concentration. The maximum achieved measurable loading was 30 vol. %, because the measurements with higher concentrations than this was complicated by the slip at the wall, resulting in a drag flow.

An intention of this paper is to carry out measurements of pressure-temperature (*P-T*) affected rheological properties with the compounded material of 50 vol.% concentration, thus the material approaching the filling level used for commercial purposes.

EXPERIMENTAL

Materials

In the presented experimental work the only tested powder concentration was 50 vol.%. The employed powder was a composite of cobalt and tungsten carbide (cemented carbide) with average density of

14.38 g.cm^{-3}. The shape of the particles was irregular, having bimodal particle size distribution. The metallic component (cobalt), which only constitutes a minor proportion of the carbide mixture, serves as the matrix for the final sintered part.

The polymer components served as binder were:

- low density polyethylene (LDPE), Lacqtene 1200 MN 8 (Atochem), density 0.918 g.cm^{-3} (53 w%)
- ethylene-acrylic acid block copolymer (EAA), Ex 225 (Exxon), containing 5% of acrylic acid, density 0.929 g.cm^{-3} (26 w%)
- paraffin wax, density 0.9 g.cm^{-3} (21 w%).

Sufficient adhesion between powder and binder was achieved by a copolymer component; paraffin and polyethylene were used 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 minutes indicating that the dispersion process had been completed. This mixing procedure is in accordance with method used for cemented carbides[6].

Rheological measurements

The flow behaviour of the compound was studied using a capillary rheometer (Göttfert 2001) with a plane (180°) capillary entrance. The rheometer was modified by an additional backpressure device increasing pressure in the tested materials. Maximum levels of backpressure generated during experiments reached up to 50 MPa for the pure binder and 70 MPa for the tested composite, thus covering the pressure range used in PIM technology. The detailed description of the equipment and the experimental procedure can be found in[7].

Finally, the Carreau-Yasuda model[8] was employed for fitting of the measured temperature and pressure dependent shear viscosity using commercially available Compuplast software Flow 2000. The constitutive equation of the Carreau-Yasuda model is:

$$\eta(\dot{\gamma}) = \frac{\eta_0 f}{\left[1+\left(K_1 f \sqrt{2\dot{\gamma}}\right)^a\right]^{\frac{1-n}{a}}}$$

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 relation:

$$f = e^{-\alpha(T-T_r)} \text{ or } f = e^{(\beta P)}$$

where α means the temperature coefficient of viscosity, T and T_r are the testing and the reference temperatures, respectively, β is the pressure coefficient of viscosity, and P stands for the gauge pressure.

RESULTS AND DISCUSSION

Shear flow properties of both the pure binder and its compound with 50 vol.%. of powder were examined as functions of temperature and pressure. Experimental data of the flow curves together with the Carreau-Yasuda model fits can be compared in Figs. 1 - 4. The rheological behaviour of binder is shown in Figs. 1 and 2, while the flow curves of filled material are depicted in Figs. 3 and 4.

As can be seen in the Fig. 1, the temperature sensitivity of the used three-component binder is increasing function of pressure. This seems to be very important finding, since in PIM applications it is highly desirable to use low thermal sensitivity binder systems.

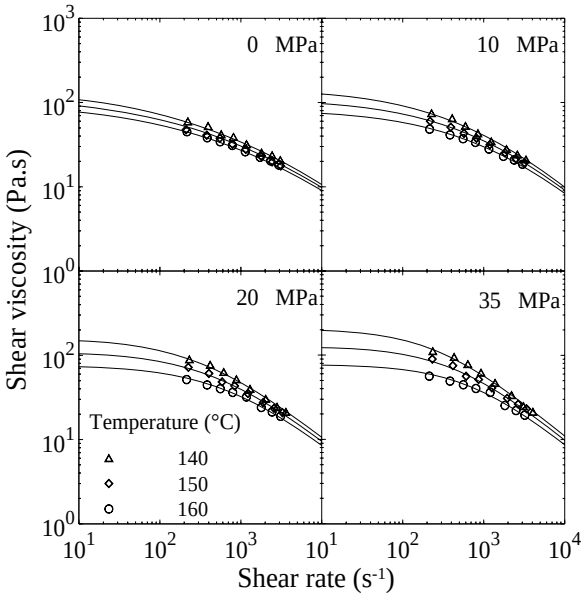

Figure 1. Temperature-dependent viscosity vs. shear rate curves of pure binder at various pressures together with the Carreau-Yasuda model fit.

In addition, it is obvious from Fig. 2 that the pressure dependencies of the binder are highly sensitive to the temperature. In other words it means that at higher temperatures the flow properties of binder are less affected by pressure, which is favourable for the PIM processing. Nevertheless, it should be considered that at elevated temperatures the flow will be most probably complicated by instabilities as described in[3].

Table 1. Temperature sensitivity coefficients at various pressure conditions.

Pressure, P (MPa)	Filler content (vol.%)	
	0	50
	Temperature coefficient, α (10^{-3} °C^{-1})	
0	18.8	17.4
10	28.4	17.8
20	37.2	18.3
35	48.8	18.9
50	59.4	19.2
70	-	20.9

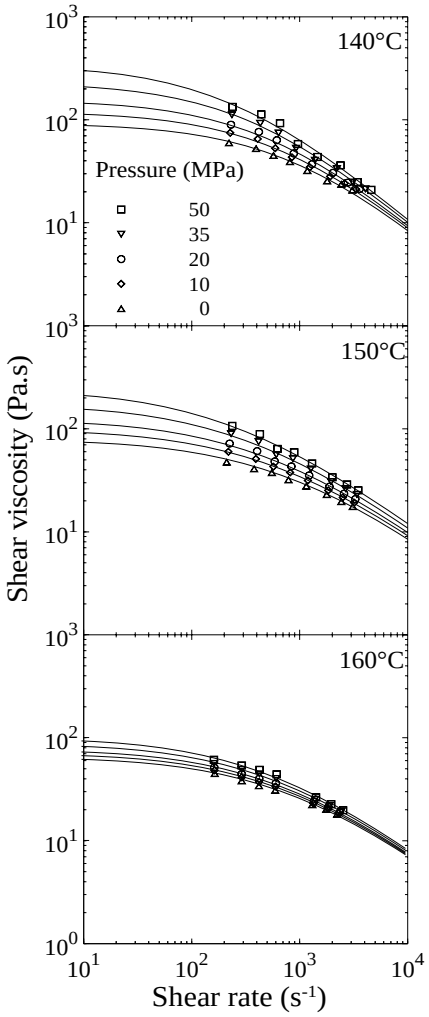

Figure 2. Pressure-dependent viscosity vs. shear rate curves of pure binder at different temperatures together with the Carreau-Yasuda model fit.

The temperature-dependent viscosity data for carbide powder compounds of 50 vol.% of carbide powder at selected constant pressures fitted by the Carreau-Yasuda model are depicted in Figure 3. It is obvious that the sensitivity of the temperature coefficient, α, to pressure is diminished comparing to sensitivity of pure binder. The reason of this is probably caused by the fact that flow behaviour at so high filler concentration is given and controlled by the filler presence more than binder itself.

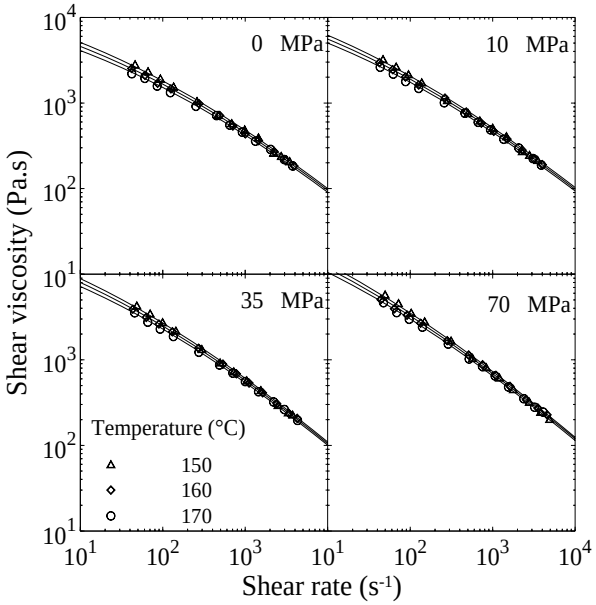

Figure 3. Temperature-dependent viscosity vs. shear rate curves of powder compound (50 vol.%) at various pressures together with the Carreau-Yasuda model fit.

The pressure-dependent viscosity data of PIM compounds for 50 vol.% of carbide powder at constant temperature fitted by the Carreau-Yasuda model can be seen in Figure 4. Analogous to temperature behaviour of the PIM compounds, also the variation in pressure effects is reduced as the carbide powder was added. As it is obvious from confrontation of Fig. 2 and 4, in contrast to rather high temperature sensitivity of pressure coefficient of the tested three-component binder, the sensitivity of polymeric compound manifests much less declines in β coefficients.

Table 2. Pressure sensitivity coefficients at various temperatures.

Temperature, T (°C)	Filler content (vol.%)	
	0	50
	Pressure coefficient, β (GPa^{-1})	
140	26.1	-
150	16.4	24.1
160	8.7	19.6
170	-	18.3

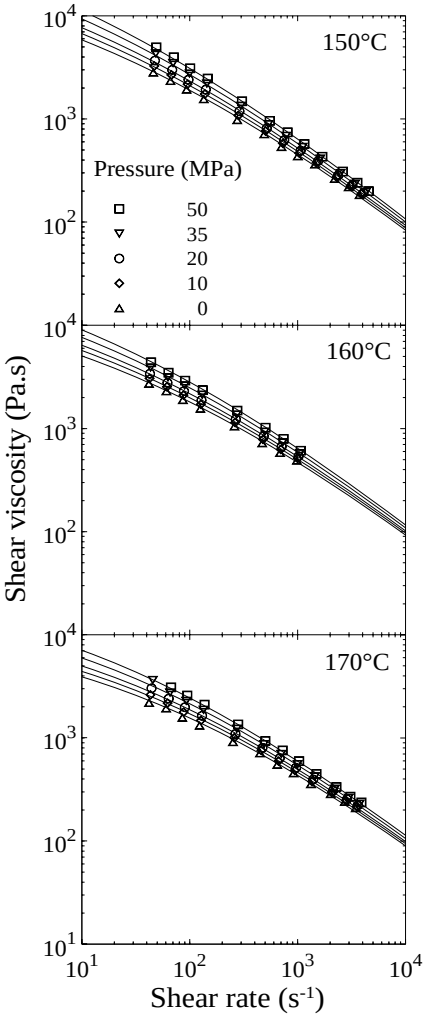

Figure 4. Pressure-dependent viscosity vs. shear rate curves of powder compound (50 vol.%) at different temperatures together with the Carreau-Yasuda model fit.

The exact values of sensitivity coefficients α and β of both tested concentration at specific pressure and temperature conditions are given in Table 1 and 2.

It is noteworthy that values of temperature coefficients, α, of both tested materials are almost indifferent at ambient pressure and diverge significantly only at elevated pressures. This observation together with obtained low pressure sensitivity of α of filled material are positive results adverting to easier prediction of flow behaviour of highly filled materials contrary to viscosity predictions of pure binder.

Another interesting result arises from comparison of levels of pressure coefficients, β. As it shows Table 2 the pressure coefficient of compound at 150°C is higher than β of used binder at the same temperature condition. This finding is out of accord with the results of recent work[5], where it was described, that increase of the powder loading level in the compounds (namely 10 and 30 %) diminishes the pressure sensitivity of their flow properties. The observed increase of pressure coefficient can be due to different particle size distribution, or due to dominant role of 50 vol.% filler concentration on the flow behaviour, where viscosity increase in highly filled materials is further supported by more remarkable suppression of interparticle motion. Furthermore, volume fraction of particles, which is slightly changed due to high pressurization, because of great discrepancy between bulk moduli of the powder and the binder, can play indispensable part in the whole task. Nevertheless, as in the case of temperature sensitivity, it can be stated that the lower variation in β with temperature change is positive aspect for estimation of rheological properties of PIM compounds.

Finally, it should be mentioned that till now the reason of described temperature and pressure dependencies of pressure and temperature effects on flow behaviour, respectively, is unknown. Namely, *P-T* dependent flow behaviour described for presented three-component binder as well as for PP and PS in the work of Sedlacek et al.[7] is in contrast to independent behaviour of LDPE, LLDPE and HDPE in the same study. However, as it was shown the dependency of *P-T* behaviour of highly filled is negligible in comparison to pure material. These results should be kept in the mind in the case of binder-formation's development.

CONCLUSION

The effect of pressure and temperature on the flow properties of the PIM compounds containing 50 vol%. of carbide powder and three-component polyolefin based binder was studied in the presented work using modified capillary rheometer. The influence of pressure and temperature on shear viscosity of the binder system has been quantified through pressure and temperature sensitivity coefficients, which were found to be functions of temperature and pressure, respectively. Concerning the highly filled PIM compounds (50 vol%.), the lower sensitivity of pressure and temperature dependencies of flow behaviour on temperature and pressure, respectively, was described comparing sensitivity of pure binder, which is positive result adverting to easier prediction of flow behaviour of PIM compounds.

ACKNOWLEDGEMENT

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