

APPARENT WALL SLIP OF TUNGSTEN CARBIDE BASED FEEDSTOCK FOR POWDER INJECTION MOULDING

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ABSTRACT

Highly filled polymeric suspensions, such as those involved in Powder Injection Moulding (PIM), exhibit complex rheological behaviour. A detailed understanding of the rheology of these suspensions is prerequisite for their optimum and safe processing. In present paper, rheological behaviour of highly filled WC-Co compounds during capillary flow was studied with emphasis on apparent slip. Contribution of apparent slip to total volumetric flow decreased with increasing shear stress and increasing capillary diameter.

Keywords: apparent wall slip, capillary flow, powder injection moulding

1. INTRODUCTION

The rheological characterization of concentrated suspensions is complicated by their viscoplasticity [1,2], various types of migration [3,4], structure development effects [5,6] and their ubiquitous apparent slip at the walls of rheometers.

According to Barnes [7], apparent slip occurs in the flow of two-phase (or multi-phase) liquids in viscometers because of displacement of the disperse phase(s) away from solid boundaries, leaving a lower-viscosity, depleted layer of liquid. This is due to physical depletion, because suspended particles cannot penetrate the solid walls. This phenomenon is present even without flow, being called static geometric depletion effect. When flow takes place in the bulk fluid, the resulting hydrodynamic and entropic forces can move particles away from walls. A number of forces are present to oppose this movement of particles away from the wall into the bulk, the most important being osmotic pressure arising from the concentration gradient created. This is so called dynamic depletion. All above mentioned facts lead to the abnormally low apparent viscosities which are exhibited by a fluid mixture in inhomogeneous stress fields or due to direct fluid-wall interactions, when compared with the viscosities measured in uniform stress fields in the absence of direct wall effect. In other words the fluid appears to flow faster than predicted at a given pressure drop or stress level [8].

Any rheometer geometry can show apparent slip effects under appropriate circumstances, but those with smooth walls and high shear gradients are most vulnerable. Liquids giving large slip effects are concentrated solutions of high molecular weight polymers, suspensions of large or flocculated particles and emulsions of large droplet size.

For assessment of the magnitude of any violations of the „no slip“ conditions, fundamental Mooney [9] analysis is seminal. Although variations on the Mooney analysis have been proposed by various investigators [10-15] none offered an improved understanding of the origin of apparent slip flow. Hence the Mooney analysis remains as the most popular method for quantifying apparent slip.

The apparent slip velocity at the walls was also determined directly in rectangular slit flow of concentrated suspensions by using an imaging windows connected to a microscope and high speed camera [16]. Generally, direct measurement techniques, which can be applied to characterize apparent wall slip, including Magnetic Resonance Imaging [17,18] and Laser Doppler Anemometry [19], suffer from spatial resolution problems. More recently, ATR-IR method enabling measurement of particle concentration at very short distances from the wall (0.2-1 μm) was developed [20].

In this preliminary study, we report on effect of solid volume loading on wall slip behaviour of highly concentrated ceramic compounds.

2. EXPERIMENTAL

Materials. The rheological characterization was carried out on hard-metal powder (WC-Co) with 30 and 40 vol. % solids volume loading. Binder consisted of 53 wt. % low-density polyethylene, 26 wt. % polyethylene acrylic acid block copolymer and 21 wt. % paraffin wax. Laboratory kneader Brabender Plasticorder with W50E type of mixing chamber was employed for compounding.

Rheometry. Rheological measurement was performed on the capillary rheometer Göttfert 2001. Data was recorded at the temperature of 160°C. Capillaries with length 20 and diameters of 0.5; 1; and 2 mm, were used for experiments.

Apparent shear rate $\dot{\gamma}$ in a capillary flow can be calculated as: $\dot{\gamma} = \frac{32Q}{\pi D^3}$ (1)

where Q is a volumetric flow and D is a capillary diameter.

The apparent shear stress τ_a for a capillary of given D and L is a function of the pressure drop Δp :

$$\tau_a = \frac{\Delta p D}{4L} \quad (2)$$

In order to correct the data for a pressure drop at the entrance to the capillary, Bagley procedure is employed. The true shear stress is then expressed: $\tau_w = \frac{\Delta p_c D}{4L}$ (3)

where Δp_c is corrected pressure drop.

The Mooney analysis for determination of slip velocity is based on plotting apparent shear rate $\dot{\gamma}$ versus $1/D$ at constant shear stress at the wall, which requires measurements with capillaries of different diameters. The Mooney analysis should produce straight lines, whose slopes are proportional to the slip velocity V_s :

$$\left[\frac{\partial \left(\frac{32Q}{\pi D^3} \right)}{\partial \left(\frac{1}{D} \right)} \right]_{\tau_w} = 8V_s \quad (4)$$

Slip velocity V_s is a function of the wall shear stress. Linear as well as power law dependencies have been published [21,22]:

$$V_s = \alpha \tau_w \quad (5)$$

$$V_s = \alpha \tau_w^m \quad (6)$$

where α is a slip coefficient.

The contribution of slip Q_s to the total volumetric flow Q is often quantified through Q_s / Q ratio,

where: $Q_s = \frac{\pi D^2 V_s}{4}$ (7)

$$Q = \frac{\pi D^2 V}{4} \quad (8)$$

It is obvious, that Q_s / Q ratio is equal to zero for materials flowing without slip and, on the other hand, it equals one if the flow is due to slip only.

3. RESULTS AND DISCUSSION

Figure 1 shows flow curves of compounds containing 30 and 40 vol. % of the powder. Pseudoplastic behaviour was observed for both systems. For the mixture filled with 40 vol. % of the WC-Co

powder, stresses level off at approximately 130 kPa at 1000 s^{-1} , whereas lower stresses (70 kPa maximum) were observed at 30 vol. % of the filler. It should be noted, that the rheological measurement was restricted to the shear rate range of $35\text{-}1000 \text{ s}^{-1}$, since the compound exhibited large pressure oscillations beyond this region.

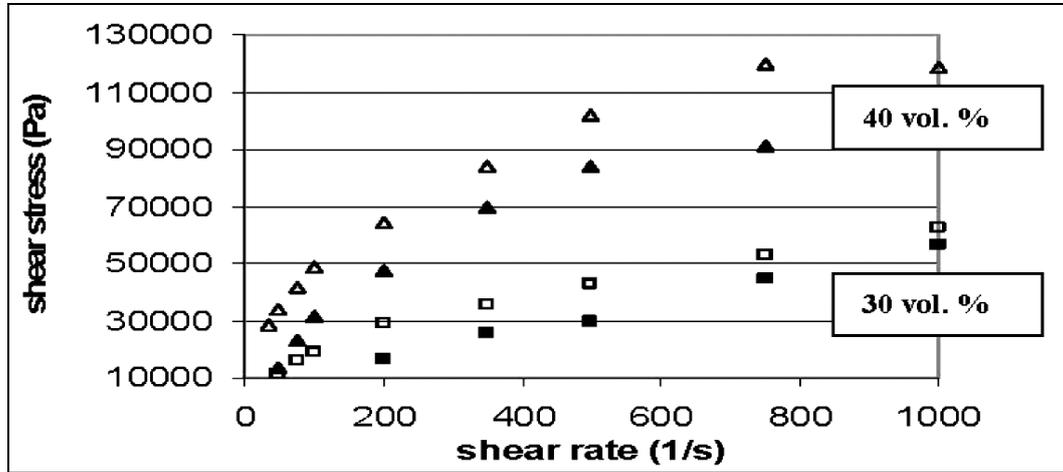


Figure 1. Bagley corrected flow curves for 30 and 40 vol. % WC-Co suspensions, capillary diameter $D = 0.5 \text{ mm}$ (■, ▲), $D = 1 \text{ mm}$ (□) and $D = 2 \text{ mm}$ (Δ); $L/D = 20$.

Figure 2. describes the dependence of slip velocity on wall shear stress. As can be seen, slip velocity increases with increasing shear stress. In addition, slip velocity is considerably lower for compound with higher solid volume loading. These observed dependencies could be fitted by power-law relationship with parameters $\alpha = 7.692 \times 10^{-8}$, $m = 2.121$ (30 vol. %) and $\alpha = 3.246 \times 10^{-8}$, $m = 1.791$ (40 vol. %).

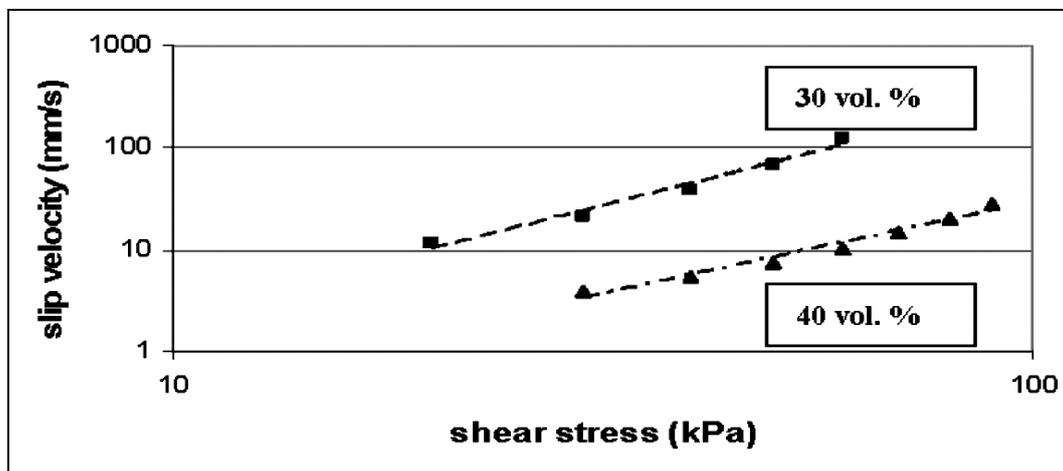


Figure 2. Dependence of slip velocity on wall shear stress; data fitted through Eq. 6.

It is obvious (Figure 3) that slip is more significant for smaller capillary diameter and Q_s/Q ratio decreases over whole range of shear stresses. Dubus and Burlet [21] observed more significant decrease of Q_s/Q ratio for alumina suspension. They reported plug flow at very low shear stresses and shear flow at high stresses at the wall. On the other hand, opposite trend was described in work of Yilmazer and Kalyon [22]. In their paper, plug flow occurred above critical shear stress and it was relatively independent on capillary diameter. Cohen and Metzner [8] and Barnes [7] proposed equations describing dependence of Q_s/Q on shear stress. In general, contribution of slip to total volumetric flow increases with increasing shear stress for shear thickening fluids and decreases for shear thinning fluids

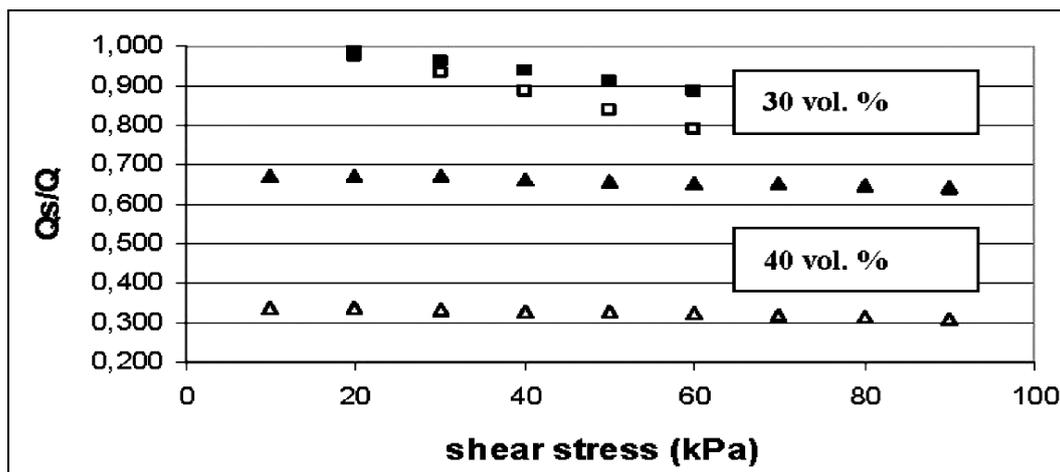


Figure 3. Contribution of wall slip to total volumetric flow; capillary diameter $D = 0.5$ mm (■, ▲), $D = 1$ mm (□) and $D = 2$ mm (△); $L/D = 20$.

4. CONCLUSION

Capillary flow measurement of the highly filled WC-Co compounds was performed. This revealed that wall slip appears during flow of both 30 and 40 vol. % materials. Slip velocity increased with increasing wall shear stress and the dependence was described by power-law relationship. Slip velocities were significantly higher at lower solid volume loading. In addition, the significance of slip slightly decreased with increasing wall shear stress, which was quantified through Q_s/Q ratio. Whereas the contribution of slip to total volumetric flow of 40 vol. % suspension was about 60%, plug flow of suspension containing 30 vol. % of powder was observed at low shear stresses.

5. ACKNOWLEDGEMENT

This work has been financially supported by the Ministry of Education, Youth and Sports of the Czech Republic MSM 7088352101. B.H. is a laureate of L'Oréal "For Women in Science" 2006.

6. REFERENCES

- [1] E.C. Bingham: Fluidity and plasticity (McGraw Hill, London), p. 231, 1922.
- [2] R. B. Bird, G. C. Dai, and B. J. Yarusso: Rev. Chem. Eng. 1, p.1, 1983.
- [3] F. Gadala-Maria, A. Acrivos: J. Rheol. 24, p. 799, 1980.
- [4] D. Leighton, A. Acrivos: J. Fluid Mech. 275, p. 155, 1987.
- [5] A. B. Metzner: J. Rheol. 29, p.739, 1985.
- [6] D. M. Kalyon, H. Gevgilili, R. Yazici, P. Yaras, S. Railkar: Rheol. Acta. 43, p. 396, 2004
- [7] H.A. Barnes: J. Non-Newtonian Fluid Mech. 56, p. 221, 1995.
- [8] Y. Cohen, A.B. Metzner: J. Rheol. 29(1), p. 67, 1985.
- [9] M. Mooney: J. Rheol. 30, p. 210, 1931.
- [10] Z. B. Jastrzebski: Ind. Eng. Chem. Fundam. 6, p.445, 1967.
- [11] G. Astarita, G. Marrucci, and G. Palumbo: Ind. Eng. Chem. Fundam. 3, p.333, 1964.
- [12] W. C. Kozicki, S. M. Pasari, A. R. K. Rao, and C. Tiau: Chem. Eng. Sci. 25, p.41, 1970.
- [13] J. G. Oldroyd: J. Colloid Sci. 4, p. 333, 1949.
- [14] D. C. H. Cheng: Ind. Eng. Chem. Fundam. 13, p. 394, 1974.
- [15] P. J. Carreau, Q. H. Bui, and P. Leroux: Rheol. Acta. 18, p. 606, 1979.
- [16] D. M. Kalyon, H. Gokturk, P. Yaras, B. Aral: Annu. Tech. Conf.-Soc. Plast. Eng. 41, p.1130, 1995.
- [17] A.E. Kaiser et al.: Proceedings of XIIIth International Congress on Rheology, Cambridge, UK, p. 227, 2000.
- [18] M. Han, C. Kim, M. Kim, S. Lee: J. Rheol. 43(5), p. 1157, 1999.
- [19] S. Jana., B. Kapoor, A. Acrivos: J. Rheol. 39, p. 1123, 1995.
- [20] P.J.A. Hartman Kok et al.: J. Colloid and Interface Sci. 280, p. 511, 2004.
- [21] M. Dubus, H. Burlet: J. Eur. Cer. Soc. 17, p. 191, 1997.
- [22] U. Yilmazer, D.M. Kalyon: J. Rheol. 33(8), p.1197, 1989.