On the Rheological Interpretation of Die Swell in Molten Polymers

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Synopsis

The reasons are given for the failure of the momentum method due to Metzner et al. to predict correct orders of magnitude in normal stress difference of polymer melts in simple shearing flow, and an expression is given for calculating the normal stress difference of polymer melts in steady fully-developed flow from "exit pressure" measurements.

INTRODUCTION

Extrudate swelling has been known for many years to be typical of viscoelastic fluids. In the past, some studies[1,2] were made to correlate die swell ratio with the normal stress difference of the material under investigation. On the other hand, some studies[3-5] report that the same method does not predict correct orders of magnitude in normal stress difference, in particular when the method is applied to die swell data of molten polymers.

The purpose of this paper is to point out the reasons why the momentum method of Metzner et al.[1] fails to predict correct orders of magnitude in normal stress difference of polymer melts. The author then suggests the use of a general expression which is obtained by removing some of the assumptions made in the derivation by Metzner et al.[1] The newly suggested expression is tested with experimental data, yielding correct orders of magnitude in normal stress difference of molten polymers.

THEORY

Take a force balance between the exit of the tube and a position downstream in the extrudate, at which the elastic stress has been relaxed and the velocity has also become uniform (neglecting gravitational and surface forces). This gives

$$(P_{11} - P_{22})_{R,L} = - (\tau_{22})_{R,L} + \frac{\rho D^2 \dot{\gamma}_R^2}{64n}$$
$$\times \left[\frac{(3n + 1)(n + 1)}{(2n + 1)} - \frac{1}{\chi^2} \left(1 + n + \frac{dln\chi}{dln\dot{\gamma}_R} \right) \right]. \quad (1)$$

Here, $-(\tau_{22})_{R,L}$ is the total normal stress in the radial direction at the tube wall at the exit of a tube, which is called the "exit pressure," P_{11} and P_{22} are deviatoric components of normal stresses in the axial and radial direction, respectively; χ is the die swell ratio d_j/D with d_j being the extrudate diameter; D is the tube diameter; n is the flow index in the power law flow model; ρ is the fluid density; and $\dot\gamma_R$ is the wall shear rate.

When the first term, $-(\tau_{22})_{R,L}$ on the right hand side is assumed to be zero, eq. (1) reduces to

$$(P_{11} - P_{22})_{R,L} = \frac{\rho D^2 \dot\gamma_R^2}{64n} \left[\frac{(3n + 1)(n + 1)}{(2n + 1)} - \frac{1}{\chi^2}\left(1 + n + \frac{d\ln\chi}{d\ln\dot\gamma_R}\right)\right], \quad (2)$$

which is the expression used by Metzner et al.[1,2] in calculating the values of $(P_{11} - P_{22})$ from the die swell data of dilute polymeric solutions. The same expression has recently been used by La Nieve and Bogue[4] for die swell data of polyethylene and by Graessley et al.[5] for die swell data of polystyrene melt, resulting in exceedingly small values of $(P_{11} - P_{22})$, several orders of magnitude smaller than what would be expected. Vinogradov and Prozorovskaya[6] also calculated $(P_{11} - P_{22})$ from die swell data of polypropylene melt by the use of eq. (2), reported reasonable orders of magnitude in $(P_{11} - P_{22})$. However, these authors[6] appear to have made errors in their calculation.

It should be noted in eq. (2) that the following assumptions are made: (1) the Weissenberg assumption is valid; (2) the isotropic pressure at the center of the exit plane of the capillary, $p(O,L)$, is zero; (3) the flow is fully developed at the exit plane of the capillary. The first two assumptions eliminated the radial normal stress term, $-(\tau_{22})_{R,L}$, from eq. (1). Although the third assumption is subject to question as well, this assumption does not enter into the final expression.

RESULTS AND DISCUSSION

Recently, Han et al.[7] measured both the "exit pressure," $-(\tau_{22})_{R,L}$, and die swell ratio for high density polyethylene and polypropylene melts. Figure 1 shows the plot of die swell ratio versus shear rate for high density polyethylene (Union Carbide DMDJ 4309) at 180°C in flow through a circular tube of L/D equal to 20 ($D = 0.125$ in.). Figure 2 shows the plot of the "exit pressure" versus shear rate for the same material. It can be easily shown from these experimental data that the die swell term, the second term on the right hand side of eq. (1), is several orders of magnitude smaller than the "exit pressure" term, and that eq. (1) is reduced to

$$(P_{11} - P_{22})_{R,L} \cong -(\tau_{22})_{R,L}, \quad (3)$$

at least for all polymer melts met in practice. Table I gives some numerical values of $(P_{11} - P_{22})$ calculated from eq. (1), that is, essentially from eq.

(3).   One can see that the magnitude of $(P_{11} - P_{22})$ is reasonable from the physical point of view.   It may be worth making a few remarks about the implications of eq. (3).   First, the momentum method does not give a meaningful expression which can be used for correlating die swell ratio with normal stress difference for polymer melts.   Secondly, the two assumptions made in the derivation of eq. (2) are not valid, at least for polymer melts.
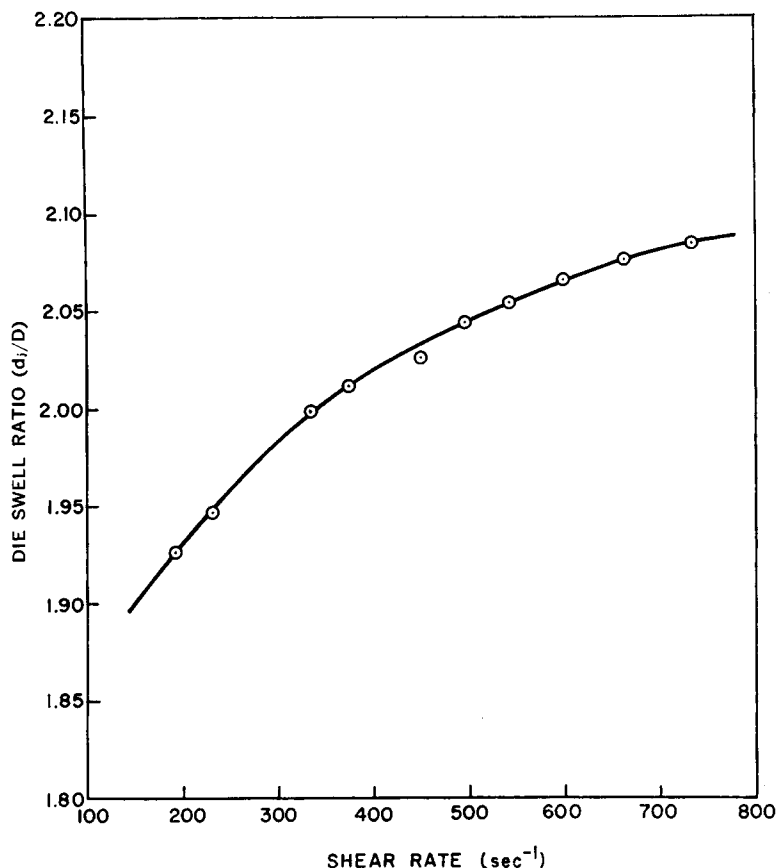

Fig. 1. Plot of die swell ratio versus shear rate for high density polyethylene at 180°C ($L/D = 20$; $D = 0.125$ in.).

Lastly, instead of die swell measurement, the "exit pressure" measurement should be made in order to use the momentum method for calculating the normal stress difference for polymer melts.

In order to demonstrate that the magnitudes of the normal stress difference calculated from the "exit pressure" measurements are of the correct orders, we shall consider below: (1) the evaluation of material constants in a 3-constant Oldroyd model, and (2) the calculation of normal stress difference from die swell data, by use of rubber elasticity theory.[8]   For simple

TABLE I
Comparison of the Calculated Values of the Normal Stress
Difference from Eqs. (3) and (5)[a]

True wall shear rate, $\sec^{-1}$	True wall shear stress, psi	Exit pressure $-(\tau_{22})_{R,L}$ psi	Measured die swell ratio	Calculated $(P_{11} - P_{22})$ from eq. (5), psi	Calculated $(P_{11} - P_{22})$ from eq. (3), psi
200	15.1	19.0	1.929	55.64	19.0
250	16.1	21.0	1.957	61.11	21.0
300	17.1	23.0	1.982	66.62	23.0
350	18.0	24.8	2.002	71.58	24.8
400	18.8	26.5	2.018	75.79	26.5
450	19.5	28.0	2.032	79.74	28.0
500	20.1	29.5	2.045	83.48	29.5
550	20.7	30.9	2.056	87.13	30.9
600	21.3	32.1	2.065	90.03	32.1
650	21.9	33.3	2.074	93.39	33.3
700	22.4	34.5	2.081	96.41	34.5

[a] The material used is high density polyethylene, and the data are obtained with a capillary length-to-diameter ratio (L/D) of 20 at 180°C ($D = 0.125$ in.).

shearing flow, the 3-constant Oldroyd model gives the following expression[9]:

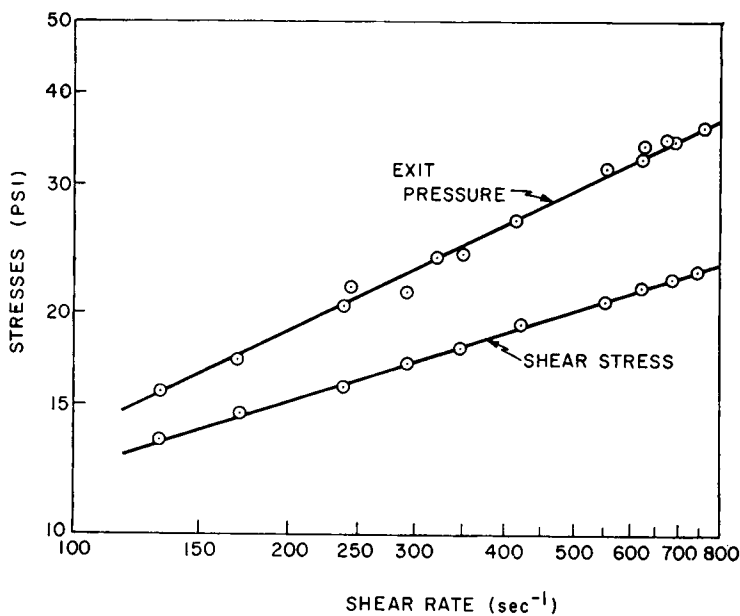$$(P_{11} - P_{22}) = \frac{2\eta_0(\lambda_1 - \lambda_2)\dot{\gamma}_R{}^2}{1 + \frac{2}{3}\lambda_1{}^2\dot{\gamma}_R{}^2} \qquad (4)$$

Fig. 2. Plot of the exit pressure vs. shear rate for high density polyethylene at 180°C ($L/D = 20$; $D = 0.125$ in.).

in which η_0, λ_1, and λ_2 are three material constants. Now one can evaluate the numerical values of these three material constants by curve fitting techniques, from use of eqs. (3) and (4) and Figure 2. The numerical values obtained thereby ($\eta_0 = 0.8 \times 10^5$ poise, $\lambda_1 = 0.0568$ sec, and $\lambda_2 = 0.0029$ sec) are considered to be of reasonable magnitudes, from the physical point of view. One may note at this point that if eq. (2) were used together with Figure 1 to calculate numerical values of material constants, one would obtain exceedingly small values of material constants. Metzner et al.[10] took such an approach to evaluate material constants in an 8-constant Oldroyd model[11] from die swell data of polyethylene and polypropylene melts, and they indeed reported exceedingly small values of material constants, which are physically unacceptable.

Spencer and Dillon[12] introduced the concept of recoverable shear strain for correlating die swell data of polymer melts with recoverable shear. Since then, many researchers have used one form or another of the same concept for analyzing the die swell data of polymer melts. Very recently, Graessley et al.[5] and Bagley et al.[13] have used the concepts of rubber elasticity theory[8] for analyzing their die swell data. According to these authors,[5,13] the die swell ratio is related to the normal stress difference by

$$P_{11} - P_{22} = \tau_{12}\sqrt{\chi^4 - \frac{1}{\chi^2}} \tag{5}$$

where τ_{12} is the shear stress. It should be noted that the derivation of eq. (5) is based on several simplifying assumptions which are subject to question.

The values of the normal stress difference calculated from eq. (5) and Figure 1 are given in Table I, together with those calculated from eq. (3) and Figure 2. It is seen that the two approaches predict the same orders of magnitude in ($P_{11} - P_{22}$), but the prediction based on eq. (5) is almost three times that based on eq. (3).

SUMMARY

In summary, reasons are given for the failure of the momentum method of Metzner et al.[1,2,10] to predict correct orders of magnitude in normal stress difference of polymer melts, and an expression is given for calculating the normal stress difference of polymer melts from the "exit pressure" measurement. The suggested method is demonstrated with experimental data, yielding correct orders of magnitude in normal stress difference. However, more experimental work is needed in this area, in particular with systems of highly concentrated polymeric solutions. A work is in progress by the author on the measurement of the "exit pressure" with concentrated polymeric solutions.

References

1. A. B. Metzner, W. T. Houghton, R. A. Sailor, and J. L. White, *Trans. Soc. Rheology*, **5**, 133 (1961).

2. A. B. Metzner, W. T. Houghton, R. E. Hurd, and C. C. Wolfe, Paper Presented at the International Symposium on Second-Order Effects in Elasticity, Plasticity and Fluid Dynamics, Haifa, Israel, April 21–29, 1962.

3. J. G. Savins, *J. Appl. Polym. Sci.*, **6**, S67 (1962).

4. H. L. La Nieve and D. C. Bogue, *J. Appl. Polym. Sci.*, **12**, 353 (1968).

5. W. W. Graessley, S. D. Glasscock, and R. L. Crawley, Paper Presented at the 1969 Annual Meeting of the Society of Rheology, St. Paul, Minn., Oct. 1969.

6. G. V. Vinogradov and N. V. Prozorovskaya, *Rheologica Acta*, **3**, 156 (1964).

7. C. D. Han, M. Charles, and W. Philippoff, *Trans. Soc. Rheology*, in press.

8. L. R. G. Treloar, *The Physics of Rubber Elasticity*, Oxford University Press, Cambridge, 1958.

9. M. C. Williams and R. B. Bird, *Phys. Fluids*, **5**, 1126 (1962).

10. A. B. Metzner, E. L. Carley, and I. K. Park, *Mod. Plastics*, **37** (11), 133 (1960).

11. J. G. Oldroyd, *Proc. Roy. Soc., Ser. A*, **245**, 278 (1958).

12. R. S. Spencer and R. E. Dillon, *J. Colloid Sci.*, **4**, 241 (1949).

13. E. B. Bagley and H. J. Duffey, Paper Presented at the 1969 Annual Meeting of the Society of Rheology, St. Paul, Minn., Oct. 1969.