

Extensional Deformation of Polymer Melts**INTRODUCTION**

In recent years, a number of studies of the extensional flow of molten polymers have been reported in the literature.¹⁻¹⁸ The various experimental techniques used in these studies may be broadly classified according to the degree of control of the extensional deformation. The early experiments of Ballman,¹ the more recent work of Vinogradov²⁻⁴ and Meissner,⁵ subsequent experiments involving apparatus similar to that of Meissner,^{6,7} and the studies of Stevenson⁸ may be classified as controlled flow experiments since the sample is subjected to a constant deformation rate. On the other hand, experiments in which apparent extensional viscosities are inferred from data obtained under the nonuniform deformation occurring in a fiber spinning apparatus⁹⁻¹⁵ or in the entrance region of capillary flow¹⁶⁻¹⁸ may be classified as uncontrolled.

The results obtained under controlled flow conditions¹⁻⁸ have generally been presented as plots of apparent extensional viscosity versus time of deformation for a series of constant extension rates. Using this representation, the data have indicated that for low extension rates, the extensional viscosity increases with time until an equilibrium value is attained equal to three times the shear viscosity at zero shear rate. With increasing extension rate, however, a rapid stress growth is generally observed rather than attainment of steady state. Furthermore, the onset of the rapid stress growth has been found^{6,7} to occur at a critical value of the total strain which is approximately independent of the deformation rate. These results are in qualitative agreement with many constitutive theories^{13,19} which predict a solid-like response (i.e., a rapid stress growth) above a critical extension rate.

For the uncontrolled flow experiments,⁹⁻¹⁸ measurements of apparent extensional viscosity have been obtained over very broad ranges of extension rate. In these studies, the results have generally been plotted as apparent extensional viscosity versus extension rate and have indicated a wide variety of material response. Extreme variations in both the magnitude and the extension rate dependence of the extensional viscosity have been observed for various polymers and for the same polymer in different laboratory spinning operations.^{9,14}

In the present note, the wide variety of material response observed in the extensional flow experiments referred to above is shown to be consistent with a single unifying theory. The key point considered is the solid-like nature of the response of viscoelastic materials to rapid deformation and consequently the importance of considering the material strain in interpreting the results. Using a simple, convected Maxwell model, it is shown that for a single material, one may observe extreme variations in both the magnitude and extension rate dependence of the extensional viscosity depending on the level of material strain in the experiment.

THEORETICAL CONSIDERATIONS

In a recent communication,¹⁹ Denn and Marrucci utilized the convected Maxwell model to examine the concept of a limiting extension rate in viscoelastic liquids. Using this model, they obtained the following expression for the extensional viscosity $\bar{\eta}$ at the onset of a constant extension rate in an initially unstressed fluid:

$$\bar{\eta} = \frac{3\mu}{(1 - 2\lambda\Gamma)(1 + \lambda\Gamma)} - \frac{2\mu \exp[-(1 - 2\lambda\Gamma)t/\lambda]}{1 - 2\lambda\Gamma} - \mu \frac{\exp[-(1 + \lambda\Gamma)t/\lambda]}{1 + \lambda\Gamma} \quad (1)$$

Here μ is the zero shear viscosity, λ is the relaxation time, t is the time elapsed since the onset of flow, and Γ is the constant extension rate. These authors then showed that this model predicted a critical extension rate,

$$\Gamma_c = \frac{1}{2\lambda} \quad (2)$$

such that for $\Gamma < \Gamma_c$, the attainment of a steady-state extensional viscosity is predicted, whereas for $\Gamma > \Gamma_c$, a solid-like response is predicted, with the extensional viscosity (stress) increasing rapidly with time (strain).

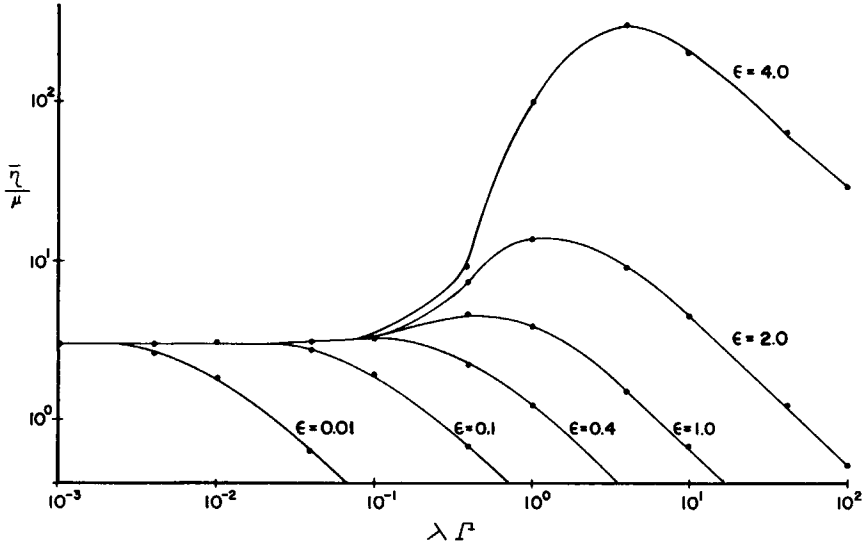


Fig. 1. Theoretical predictions of extensional viscosity vs. extension rate for indicated constant strain levels.

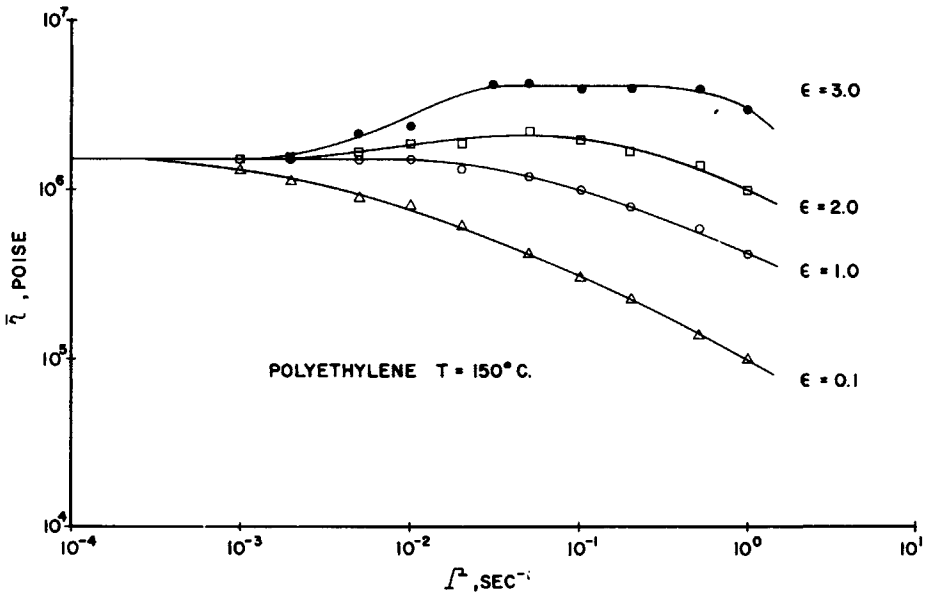


Fig. 2. Extensional viscosity vs. extension rate for indicated constant strain levels (data of Meissner⁵).

For the kinematics considered in the Denn and Marrucci communication, the total Hencky strain, ϵ , is given by

$$\epsilon = \Gamma t \tag{3}$$

Thus, from eq. (1), we may obtain an expression for $\bar{\eta}$ as a function of the total strain ϵ and the product $\lambda\Gamma$ (which may be identified with the recoverable extensional strain²⁰):

$$\bar{\eta} = \frac{3\mu}{(1 - 2\lambda\Gamma)(1 + \lambda\Gamma)} \dots \frac{2\mu \exp[-(1 - 2\lambda\Gamma)\epsilon/\lambda\Gamma]}{1 - 2\lambda\Gamma} - \frac{\mu \exp[-(1 + \lambda\Gamma)\epsilon/\lambda\Gamma]}{1 + \lambda\Gamma} \tag{4}$$

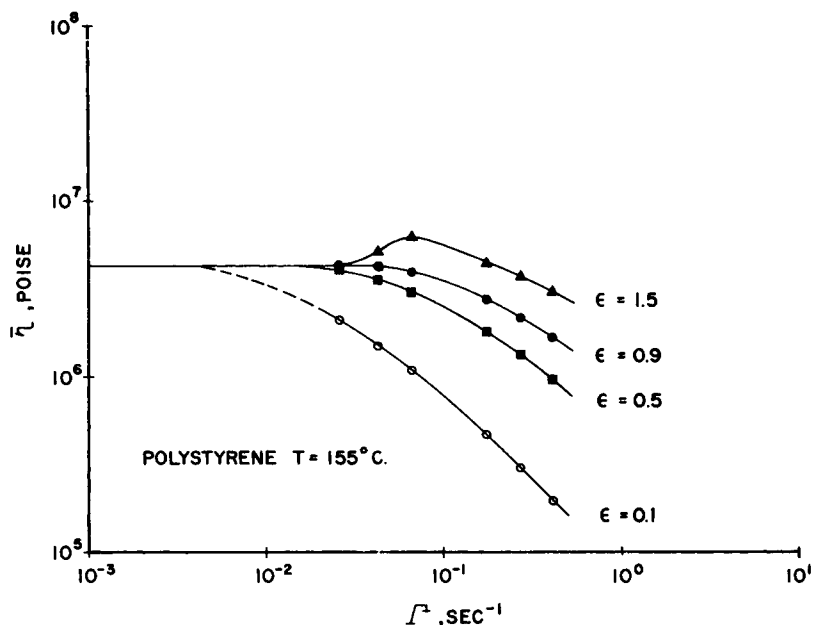


Fig. 3. Extension viscosity vs. extension rate for indicated constant strain levels (data of Everage and Ballman⁷).

Consider now a series of experiments in which a constant extension rate is imposed on an initially unstressed fluid of constant shear viscosity μ and single relaxation time λ . For a given extension rate, we may compute from eq. (4) the apparent extensional viscosity of the Maxwell fluid for any given constant total strain. Furthermore, for a series of experiments covering a range of constant extension rates, we may compute the apparent extensional viscosity at the instant of time in each experiment at which the specified value of the total strain is achieved. Thus, we may construct a series of dimensionless plots of $\bar{\eta}/\mu$ versus $\lambda\dot{\Gamma}$ using constant values of the total strain as a parameter. A plot of this type is presented in Figure 1, and the results clearly illustrate the variety of material response one may observe under conditions of constant total strain with varying strain rate.

The results in Figure 1 are easily interpreted in terms of the simple spring-dashpot model. For very high extension rates, the apparent viscosity decreases with extension rate for all strain levels. In this case, the total deformation occurs over a short time and involves primarily a stretching of the spring with little movement of the dashpot. As long as the extension rate is high enough that one has only the stretching of the spring, the spring stress is constant and independent of the rate at which the strain is achieved. Consequently, a constant stress divided by an increasing strain rate leads to a decrease in apparent viscosity (i.e., in this case the "viscosity" of the spring) with strain rate.

For the other extreme of small extension rates, the total deformation occurs over a long time and involves primarily dashpot motion. As a consequence, the apparent viscosity is that for a Newtonian fluid (i.e., $\bar{\eta}/\mu = 3.0$).

The nature of the transition from the constant extensional viscosity at low extension rates, which is dominated by dashpot motion, to the decreasing extensional viscosity at high extension rates, which is dominated by the spring stress, is strongly dependent on the level of total strain in the experiment. For total strains less than approximately 1.0, the model predictions indicate an abrupt transition from the constant viscosity at low extension rates to the decreasing viscosity at high extension rates. For total strains greater than approximately 1.0, however, the stress in the spring may (depending on the extension rate) become greater than $3\mu\dot{\Gamma}$ and thus result in an increase in apparent extensional viscosity with extension rate over a range of intermediate extension rate levels. In this case, with further increases in extension rate, a maximum occurs in the apparent viscosity-versus-extension rate curve as the region of high extension rates is encountered and, as discussed above, the viscosity ultimately decreases with increasing extension rate.

COMPARISON WITH EXPERIMENT

Previously published extensional viscosity results obtained in controlled flow experiments may be easily replotted in the form of Figure 1. Figures 2 and 3 illustrate in this form the results of Meissner⁵ for low-density polyethylene melt and the data of Everage and Ballman⁷ for polystyrene melt. In both plots, the results are qualitatively quite similar to the predictions of the convected Maxwell model. The major quantitative difference is a distinct flattening of the experimental curves in the area of the maximum for the polyethylene data, in contrast to a relatively sharp peak in the model predictions. This is very probably a consequence of the assumed single relaxation time in the model representation.

For the case of the uncontrolled flow experiments, it is difficult to compare directly the model predictions with experimental results, since in this case the extensional viscosity data are obtained from measurements along a spinline where the deformation history in the spinneret influences rheological responses and the material strain and strain rate vary over a wide range of values. However, the results in Figures 1-3 strongly suggest that variations in total strain (i.e., draw ratio) may play a major role in the variety of material response which have been observed in spinning experiments.

In a recent publication,²¹ solutions were obtained by Denn and co-workers for the equations which describe steady-state isothermal spinning of a Maxwell fluid. These results indicated that for the industrially important case of an applied take-up stress which is large compared to the modulus of the Maxwell material, a linear velocity profile (i.e., a constant extension rate) is predicted to occur along the spinline. As also noted by Denn and co-workers, nearly linear velocity profiles have been observed experimentally for the case of large imposed stress.^{13,22} Under these conditions of constant extension rate, the results obtained in the present note clearly have direct application to spinning experiments, assuming any effects of upstream deformation history may be neglected. For example, a spinning operation in which the draw ratio is maintained constant (by adjusting the final filament diameter) while the total throughput of material varies is a constant total strain operation with the strain rate changing with polymer throughput. In this case, the present theory indicates that with increasing polymer throughput (i.e., strain rate), changes in take-up tension ranging from effectively zero to an exponential increase may occur depending on the total strain involved.

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References

1. R. L. Ballman, *Rheol. Acta*, **4**, 138 (1965).
2. G. V. Vinogradov, A. I. Leonov, and A. N. Prokunin, *Rheol. Acta*, **8**, 482 (1969).
3. G. V. Vinogradov, B. V. Radushkevich, and V. D. Fikhman, *J. Polym. Sci. A-2*, **8**, 1 (1970).
4. G. V. Vinogradov, V. D. Fikhman, B. V. Radushkevich, and A. Ya. Malkin, *J. Polym. Sci. A-2*, **8**, 657 (1970).
5. J. Meissner, *Trans. Soc. Rheol.*, **16**, 405 (1972).
6. C. W. Macosko and J. M. Lortson, Paper presented at SPE ANTEC, Montreal, P.Q., Canada, May 9, 1973.
7. A. E. Everage, Jr., and R. L. Ballman, *J. Appl. Polym. Sci.*, **20**, 1137 (1976).
8. J. F. Stevenson, *A.I.Ch.E. J.*, **18**, 540 (1972).
9. J. N. Dalton, M.S. thesis, University of Tennessee, Knoxville, 1971.
10. D. Acierno, J. N. Dalton, J. M. Rodriguez, and J. L. White, *J. Appl. Polym. Sci.*, **15**, 2395 (1971).
11. L. E. Abbott, M.S. thesis, University of Tennessee, Knoxville, 1971.
12. I.-J. Chen, G. E. Hagler, L. E. Abbott, D. C. Bogue, and J. L. White, *Trans. Soc. Rheol.*, **16**, 473 (1972).
13. J. A. Spearot and A. B. Metzner, *Trans. Soc. Rheol.*, **16**, 495 (1972).
14. C. D. Han and R. R. Lamonte, *Trans. Soc. Rheol.*, **16**, 447 (1972).
15. R. R. Lamonte and C. D. Han, *J. Appl. Polym. Sci.*, **16**, 3285 (1972).
16. F. N. Cogswell, *Rheol. Acta*, **8**, 187 (1969).
17. F. N. Cogswell, *Trans. Soc. Rheol.*, **16**, 383 (1972).
18. F. N. Cogswell, *Polym. Eng. Sci.*, **12**, 64 (1972).

19. M. M. Denn and G. Marrucci, *A.I.Ch.E. J.*, **17**, 101 (1971).
20. A. E. Everage, Jr., and R. L. Ballman, *J. Appl. Polym. Sci.*, **18**, 933 (1974).
21. M. M. Denn, C. J. S. Petrie, and P. Avenas, *A.I.Ch.E. J.*, **21**, 791 (1975).
22. F. Kanel, Ph.D. dissertation, University of Delaware, Newark, 1972.

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