Entry Pressure and Elastic Behavior of a Branched Polyethylene

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SYNOPSIS

Die entry pressures and elastic parameters derived from these have been determined for one low-density polyethylene (LDPE) at four temperatures using three dies having different entry angles. The elongational viscosity shows a somewhat different behavior with respect to temperature than the shear viscosity. Mostly the elastic parameters show a temperature-independent relation to the shear stress but only if the data at the lowest temperature used (130°C) are ignored. The latter data show that the material is much more elastic at this temperature than at higher ones; this is so even when the temperature is increased by only 20°C, after which any further increase gives negligible difference in elasticity. This behavior is probably due to a structural difference which may be a result of increased crosslink sites created by flow-induced crystallization.

INTRODUCTION

Temperature dependence of the flow behavior of melts is most important for processing polymers. A number of studies have been carried out to understand this kind of behavior.[1,2] Studies to date do assist the processor in the drive toward finding the optimal processing temperature (with respect to economical operation and/or product properties). However, a more complete understanding of the temperature dependence of the flow behavior of melts should lead to even further gains in their processing.

Rheological behavior of polyolefins has been much studied in the past.[3,4] Even so, it is not with complete confidence one could say that their flow behavior is well understood. An interesting and bewildering aspect of low-density polyethylene (LDPE) is the long-chain branching which has undoubtedly contributed to some of its flow characteristics. Recently, the author has looked at the shear and elongational behavior of some LDPEs.[5] In addition some elastic parameteres for these polymer melts were also looked at. These were related to the entrance pressure drop. The present work looks at the entrance pressure and the elastic behavior for one LDPE at different temperatures.

ENTRY FLOW

Melts undergo significant pressure drops upon entering a capillary or narrow flow channel from a larger flow section. A common configuration for this kind of study is the capillary rheometer with which we are concerned here. This entrance pressure drop has been ascribed to both shear and elongational flow by Cogswell,[6] who presents a simple method of determining the elongational viscosity from this. Briefly, Cogswell assumes that a material adopts a coni-cylindrical flow pattern when flowing through a converging section into a capillary and that the velocity of the outer boundary of this flow pattern is zero. It is also assumed that the total entrance pressure drop in the converging section is the sum of that due to shear flow, and that due to the extensional flow such that the flow pattern achieved is the one corresponding to the minimum pressure drop.

Several measures based on the entrance pressure drop have been found to be useful in the past.[5,7]

(a) The recoverable shear (refered to as RS below):

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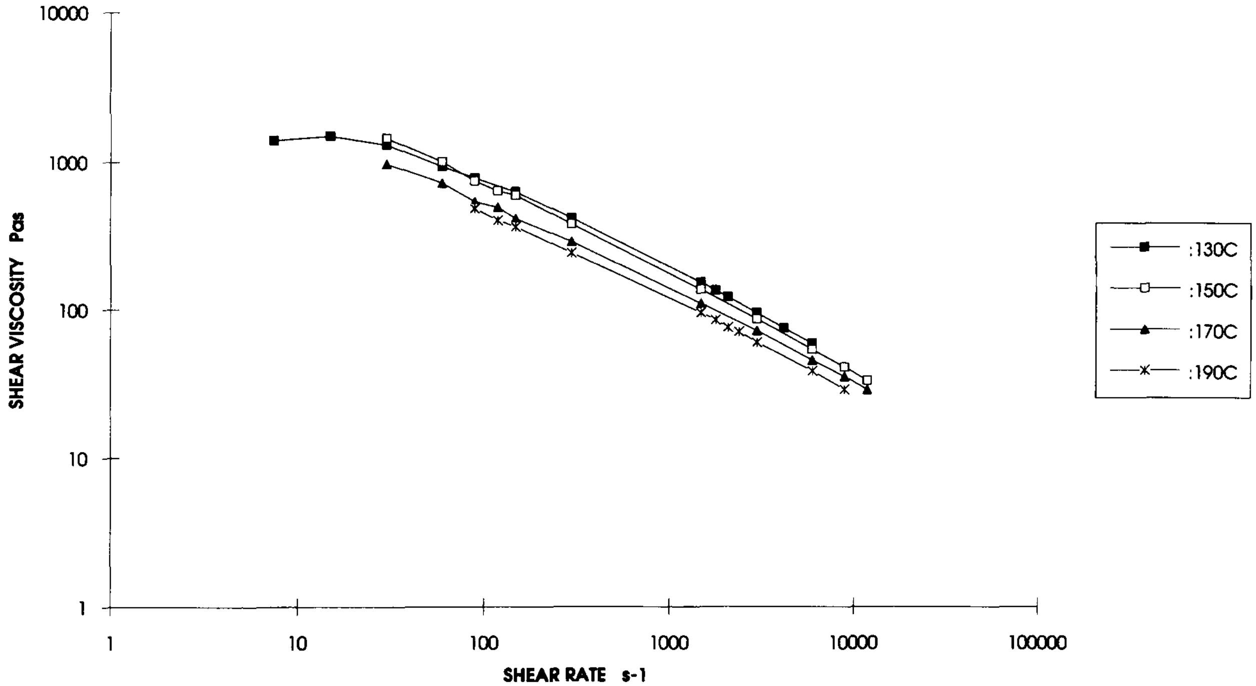

Figure 1 Shear viscosities at different temperatures.

$$\gamma_r = \frac{N_1}{2\sigma_{12}} \tag{1}$$

(b) The compliance:

$$J_s^0 = \frac{N_1}{2\sigma_{12}^2} \tag{2}$$

where N_1 is the first normal stress difference and σ_{12} is the shear stress at the capillary wall.

White and Kondo[8] have found experimentally that the first normal stress difference is half the value of the entrance pressure drop. Therefore the above elastic parameters transform to

$$\gamma_r = \frac{P_0}{4\sigma_{12}} \tag{3}$$

$$J_s^0 = \frac{P_0}{4\sigma_{12}^2} \tag{4}$$

where P_0 is the entrance pressure drop.

These are utilized below. It is not known what exactly is implied by the recoverable shear and the compliance as calculated using these equations. However, it is clear that both are related quite closely to the elastic behavior of the material concerned.

MATERIALS AND METHODS

An off-line twin-bore capillary rheometer (Rosand Precision Ltd. RH7) was used. The bore–die contraction ratio was 15 : 1. One die was 1 mm diameter and 16 mm long; the other had the same diameter but had an effectively zero length (i.e., an orifice die) giving an entrance pressure drop by extrapolation. Various angled dies were available and have been used though most of the results pertain to flat entry dies (i.e., half entry angle of 90°). Two other dies were also used with half entrance angles of 20° and 60°. Four operating temperatures were chosen: 130, 150, 170, and 190°C.

An LDPE of melt flow index 4 was used. No other data were available for this material. The material has been described by the supplier as suitable for the foam production and that it allows good control of temperature during processing.

RESULTS

Figure 1 shows the shear viscosities for the material at the different temperatures. The viscosities at 130 and 150°C are quite similar. Generally increasing temperature gives lower viscosities as expected.

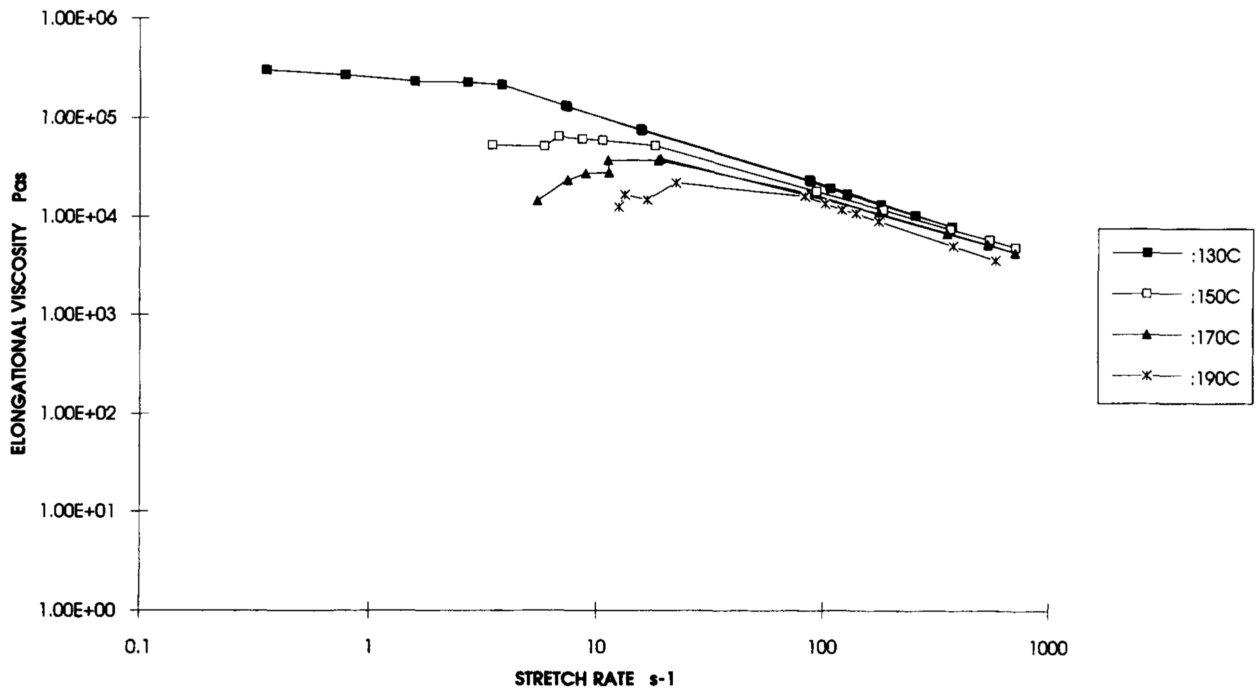

Figure 2 Elongational viscosities at different temperatures.

Figure 2 shows the Cogswell elongational viscosities. As can be seen, there are significant differences at lower stretch rates. The lower temperatures give a somewhat constant viscosity at very low stretch rates while the higher temperatures appear to exhibit some stretch thickening. At higher stretch rates the elongational viscosities have much less variation with respect to temperature. Unlike the shear viscosity data, the elongational viscosities at 130 and 150°C are significantly different at low stretch rates.

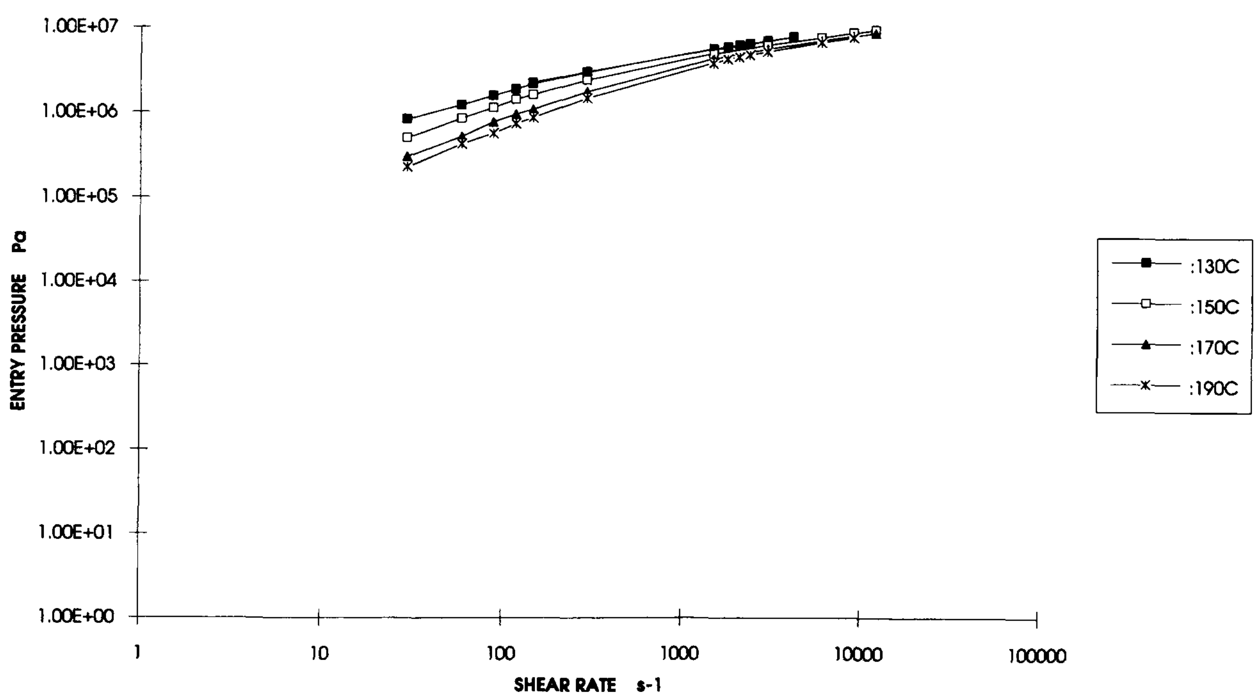

Figure 3 Entry pressure variation with shear rate for 20° die.

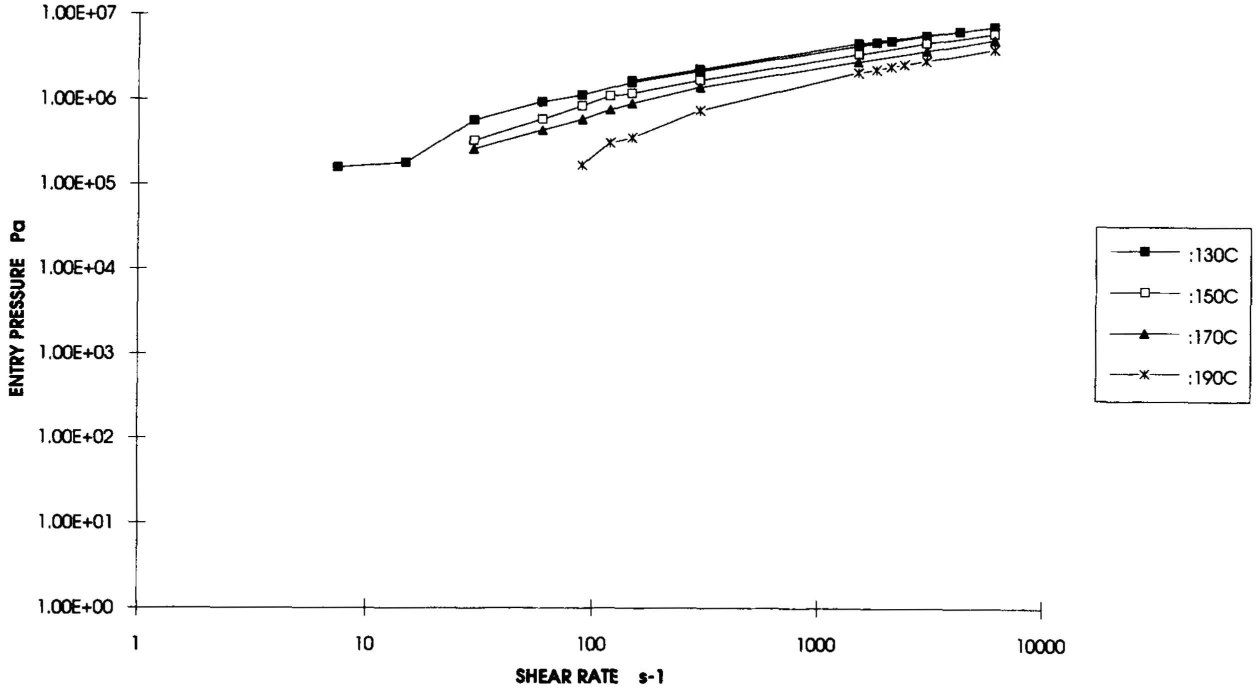

Figure 4 Entry pressure variation with shear rate for 60° die.

Figures 3, 4, and 5 show the data for the entry pressures against shear rates for the four temperatures. For the 20° die, the entry pressures converge, with the lower temperatures giving higher entry pressures as expected. The 60° die showed a lesser degree of convergence with shear rate. The 90° (i.e., the flat entry) die showed a similar behavior to the 20° die.

Figures 6, 7, and 8 show the entry pressures against shear stresses. Previous workers such as

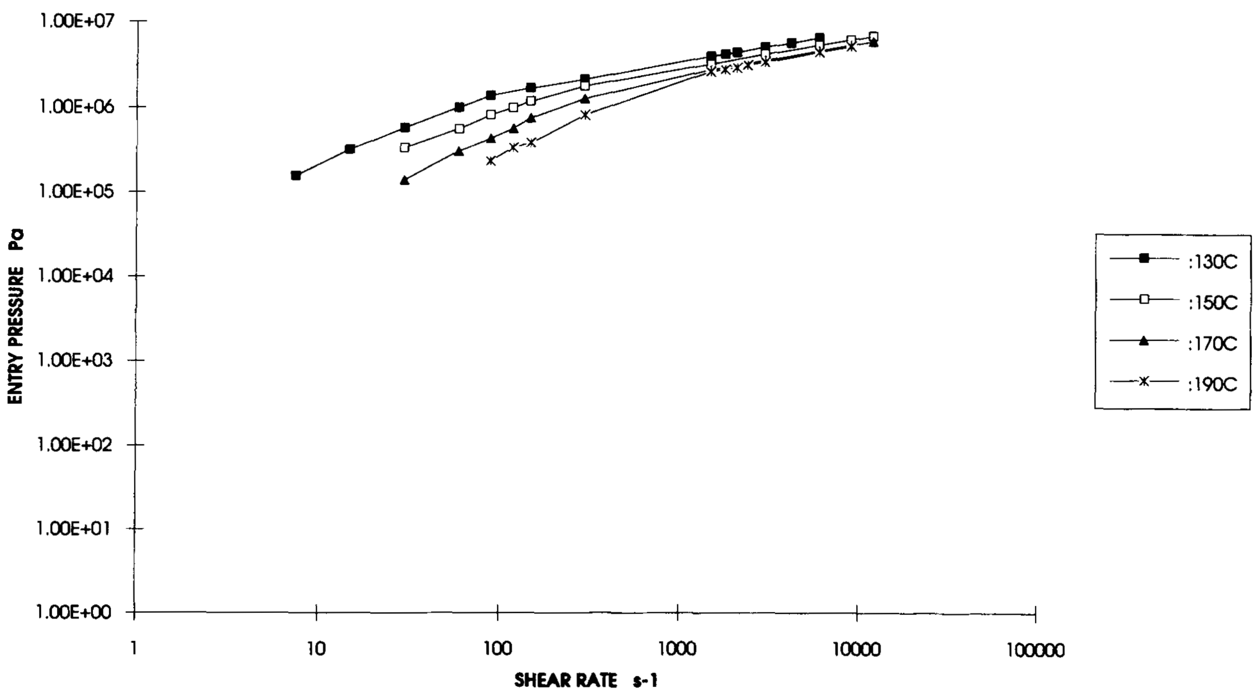

Figure 5 Entry pressure variation with shear rate for 90° die.

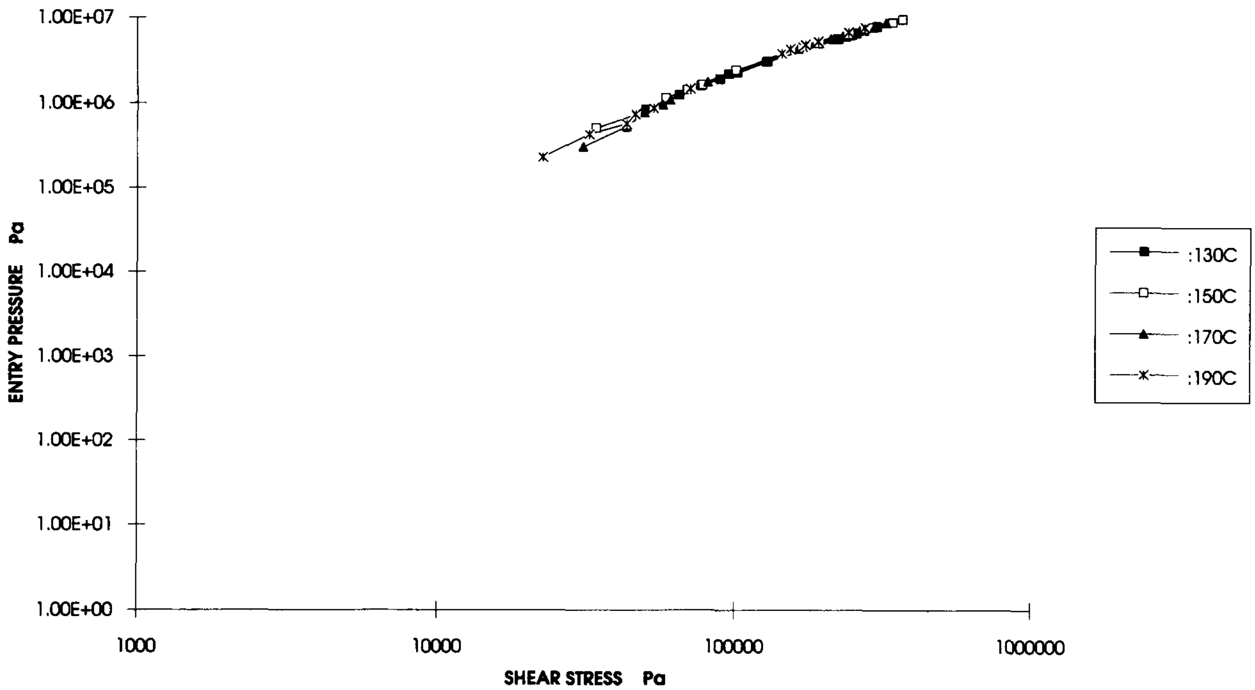

Figure 6 Entry pressure as a function of shear stress for 20° die.

Han[2] have suggested that elastic parameters should show a temperature-independent relation to shear stress for a given material. Indeed Han presents some data showing this for entry and exit pressures for a polyethylene and a polypropylene.

The 20° die (Fig. 6) gave a single curve; the 60° die mostly gave a single curve. The flat entry die (Fig. 8) showed some interesting features. The three higher temperature data (150, 170, and 190°C) fell on a single curve, but the lowest tem-

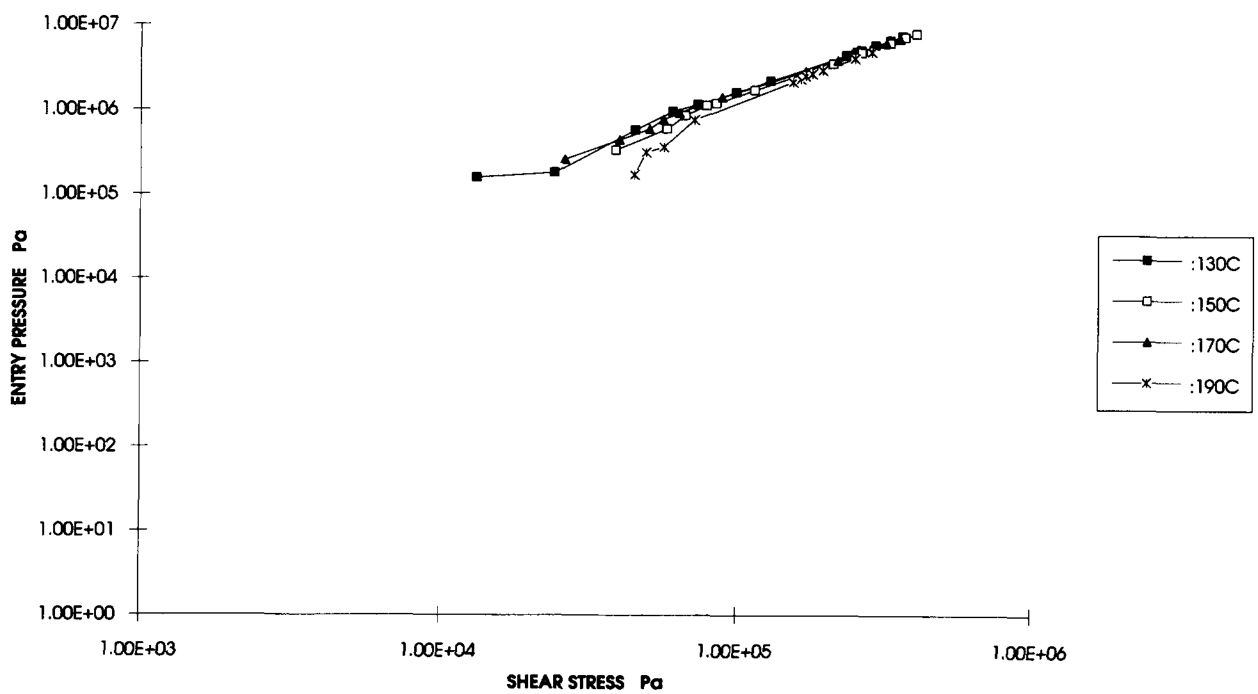

Figure 7 Entry pressure as a function of shear stress for 60° die.

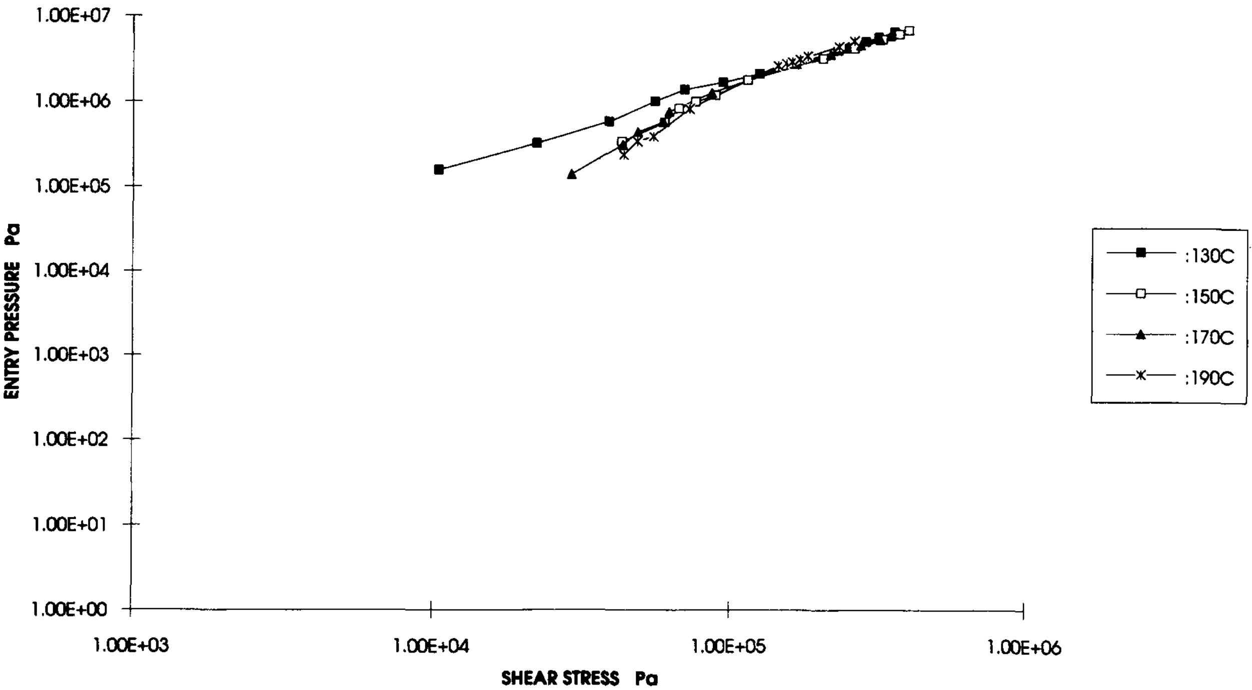

Figure 8 Entry pressure as a function of shear stress for 90° die.

perature entry pressures deviated away from the rest of the data at lower shear stresses. It has been stated by some authors that the elongational contribution to the entrance pressure is greater for larger entry angles;[9] the present author has made numerous calculations using simple models such as that of Cogswell and that of Gibson[9] and has found that the elongational contribution to the entry pressures dominates for most flow rates and is greater for larger entry angles. In view of this, it is expected that the shear contribution to the entry pressure should be highest for the 20° die

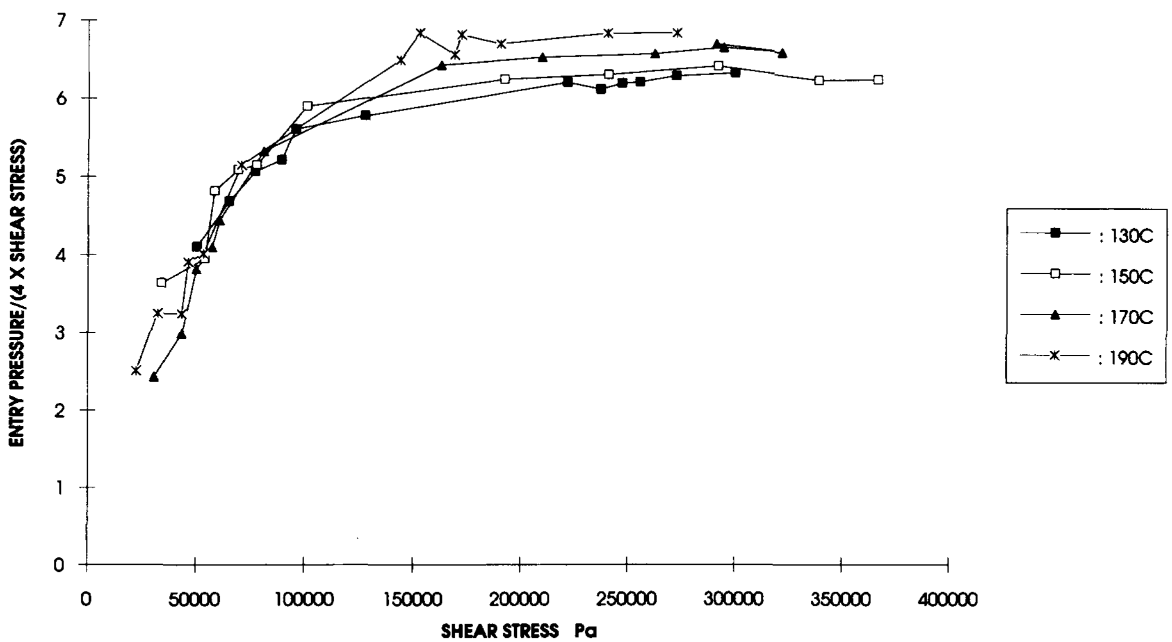

Figure 9 Recoverable shear for 20° die.

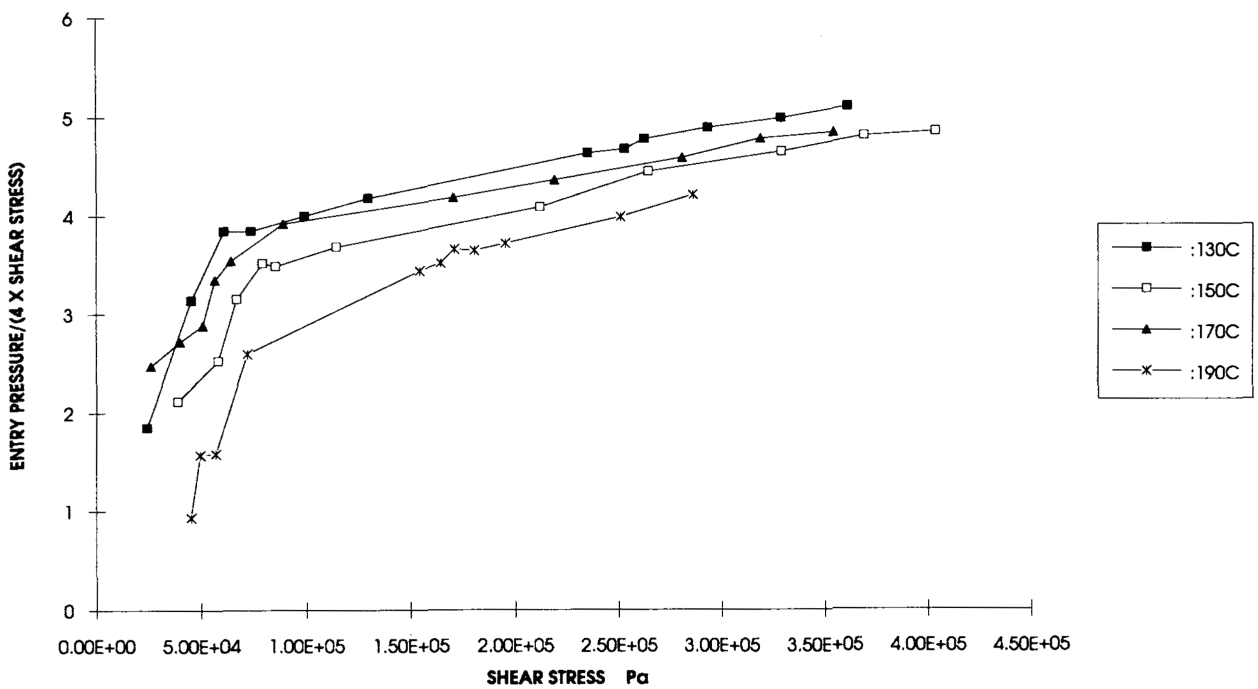

Figure 10 Recoverable shear for 60° die.

and least for the flat entry die for a given flow rate. It is suspected that the material exhibits some structural differences at the lowest temperature used here (130°C). The lower entry angled dies gave a largely temperature-independent relationship. There is still an incomplete understanding of the vortex behavior for different angled dies at present and these results also suggest that without a further proper such understanding one has to speculate to a certain extent.

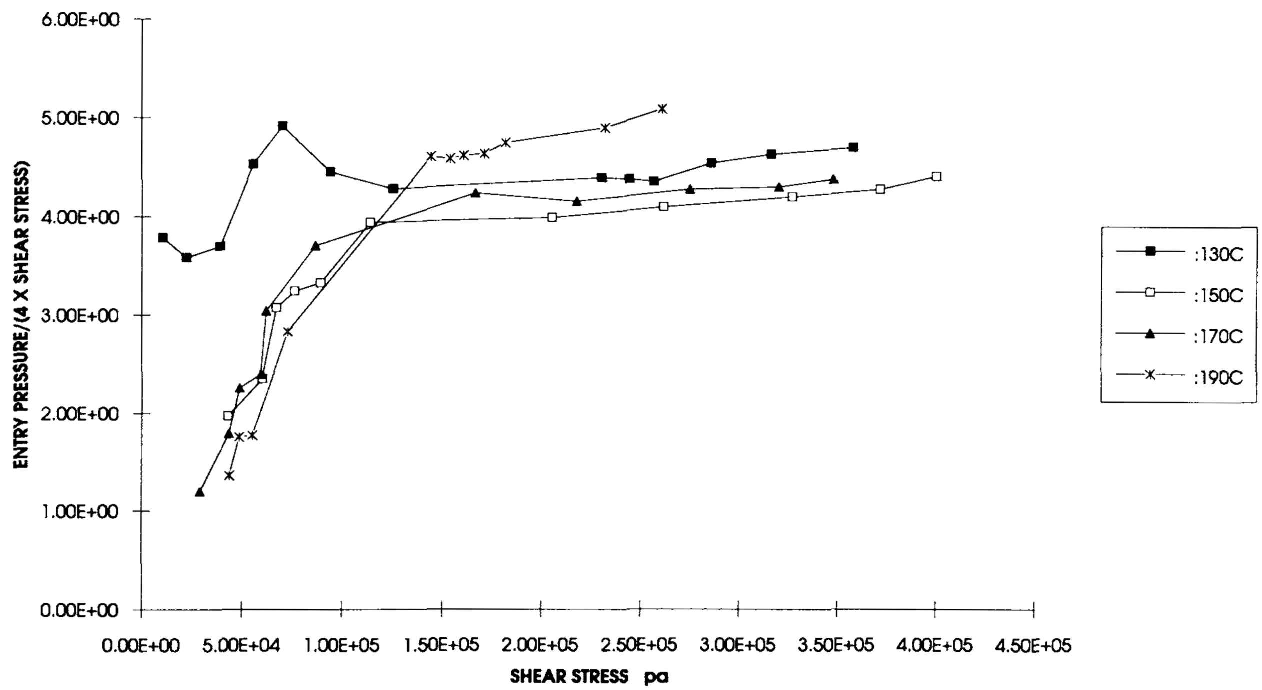

Figure 11 Recoverable shear for 90° die.

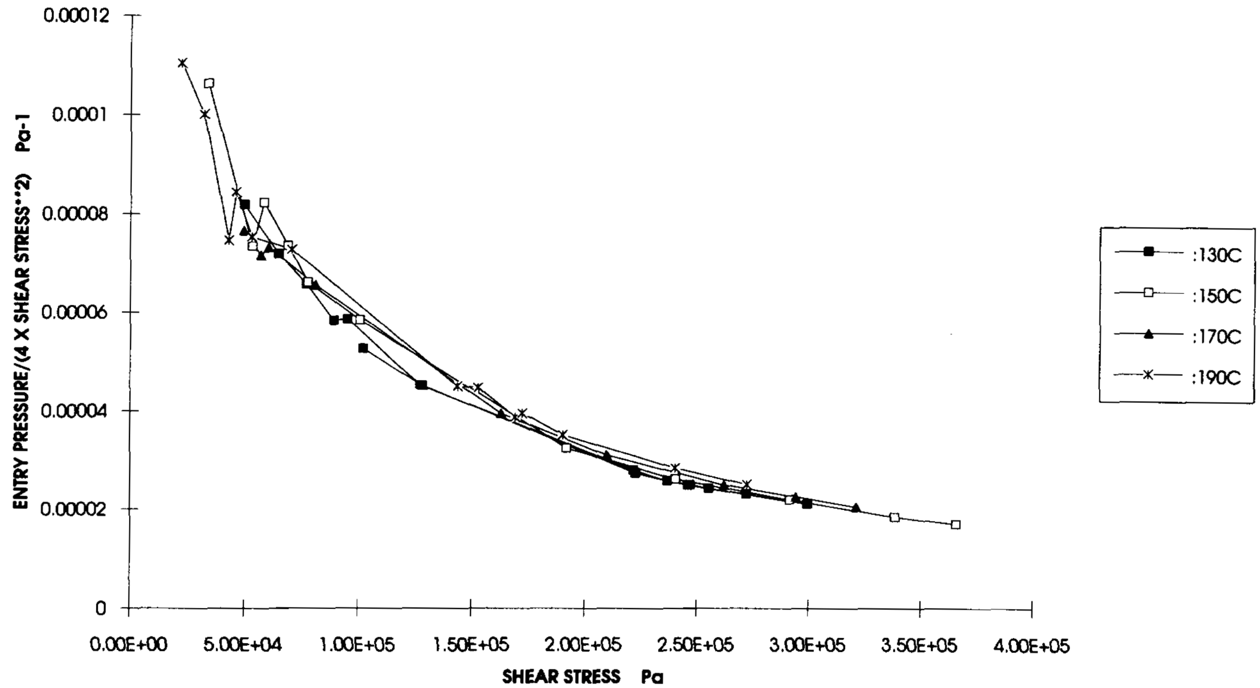

Figure 12 Compliance for 20° die.

Figures 9, 10, and 11 show the results for the recoverable shear for the three dies. The 20° die (Fig. 9) gave largely similar RS values for the four temperatures. This was not the case for the 60° die (Fig. 10) for which at lower shear stresses there was significant variation for the different temperatures. Figure 11 for the flat die shows similar RS values for the three higher temperatures especially at lower shear stresses; the lowest temperature (130°C) gave a distinctly different behavior at lower stresses. The flat entry data suggest

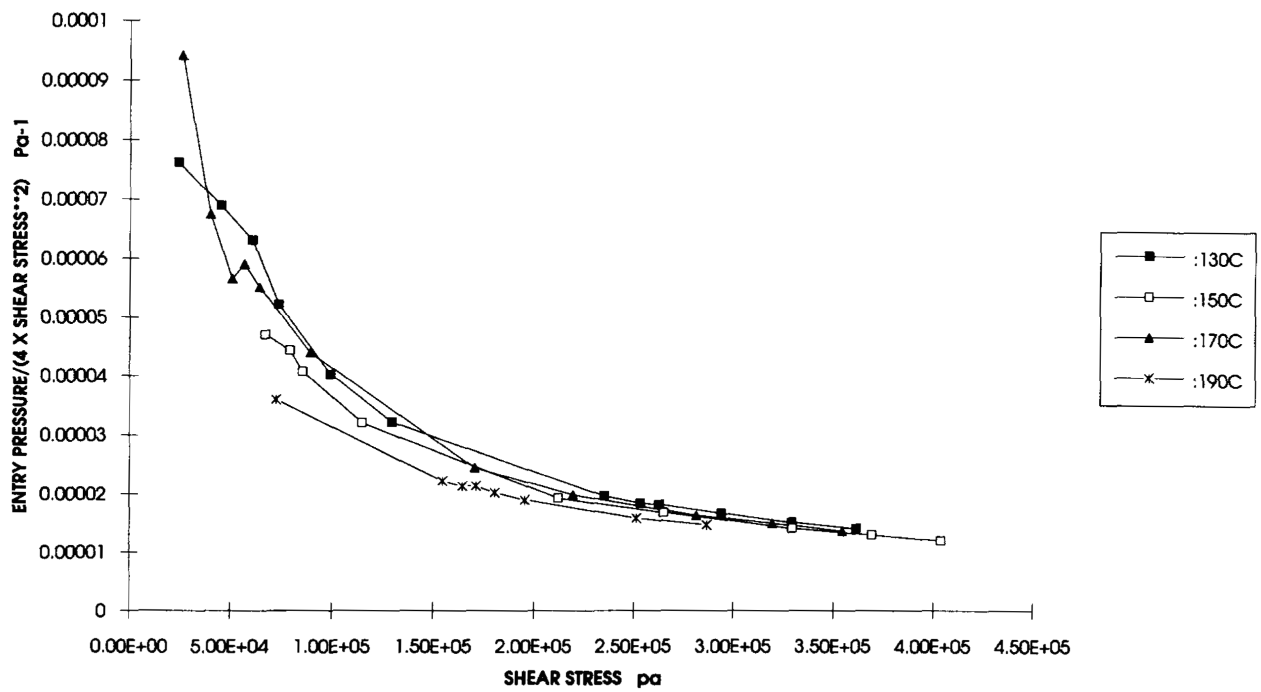

Figure 13 Compliance for 60° die.

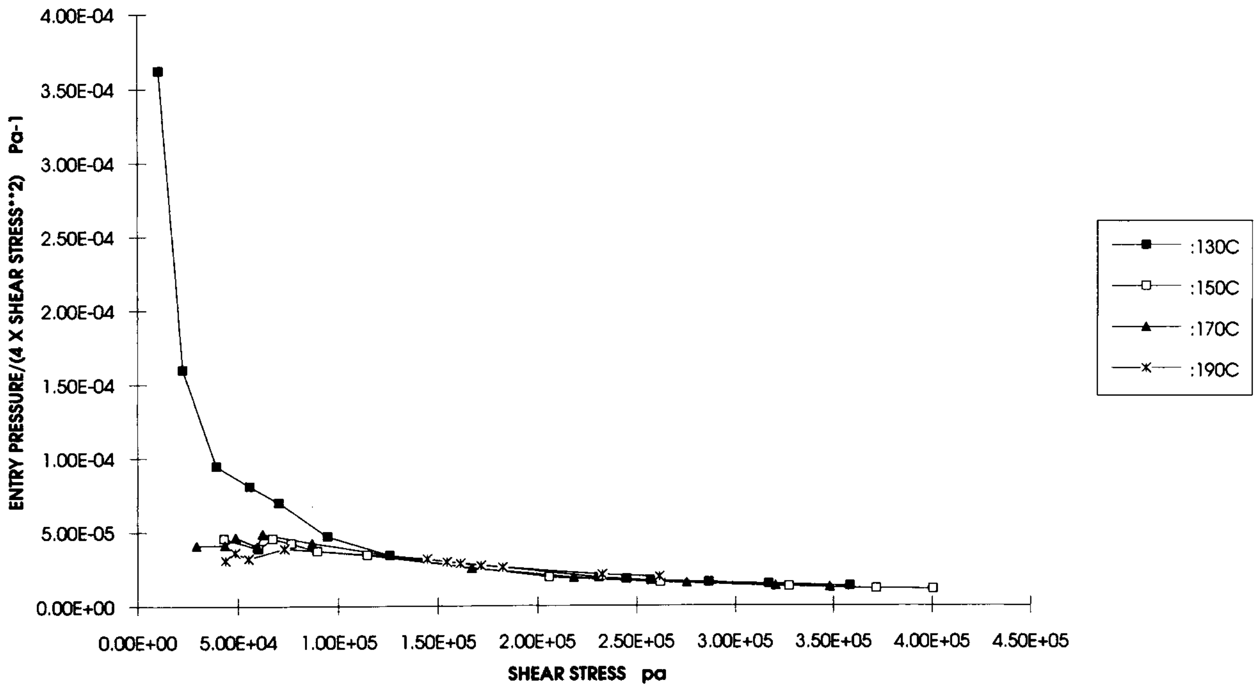

Figure 14 Compliance for 90° die.

that at lower shear stresses the material is more elastic at 130°C and is largely temperature-independent for higher temperatures than 130°C.

Figures 12, 13, and 14 show the results for the compliance for the three dies. The 20° die gave a largely temperature-independent compliance-shear stress relationship. The 60° die (Fig. 13) gave a somewhat similar result though there was a wider scatter of the data. The flat entry data in Figure 14 showed that except for 130°C, the results gave a temperature-independent relationship. This was also found for the recoverable shear above. As for the RS data, the material at 130°C is much more elastic at lower shear stresses. This increased elasticity may be due to flow-induced crystallization resulting in increased crosslink sites.

CONCLUSION

The entry pressure and two elastic parameter data for a branched polyethylene at four temperatures and for three dies have been presented. The entry pressure, in the past, has largely been ascribed to the elasticity of the material. Some previous publications have suggested that any elastic parameters should show temperature-independent relation to shear stress. This has largely been found here except if the data at the lowest temperature used are considered. It is suggested that at this temperature the material has some structural differences with that at higher temperatures. Perhaps this is due to flow-induced crystallization at lower melt temperatures which could lead to increased sites for crosslinks.

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