

Effect of Molecular Structure on Polyethylene Melt Rheology. III. Effects of Long-Chain Branching and of Temperature on Melt Elasticity in Shear

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Synopsis

The effects of long-chain branching and of temperature on the melt elasticity in shear of polyethylene were investigated using die swell measurements and relating them to recoverable shear strain, normal stress, and shear modulus. Die swell measurements, as a function of shear rate, were obtained for high- and low-density polyethylenes at temperatures ranging from 130° to 225°C. The samples were characterized by GPC and intrinsic viscosity for molecular weight distributions and degrees of long-chain branching. The importance of annealing the extrudates at temperatures above the polymer melting temperature to achieve equilibrium, or strain-free, values of die swell was demonstrated. The effect of long-chain branch was to decrease elastic deformation. At constant shear stress, the melt elasticity of both high- and low-density polyethylene was found to be essentially independent of temperature. Thus, at constant shear rate, elastic deformation decreased with increasing temperature, and it was demonstrated that this decrease could be quantitatively defined in terms of previously determined shear rate-temperature viscosity superposition shift factors.

Introduction

The swelling behavior of molten polymer extruded from an orifice, or die, is of considerable importance both in the fundamental elucidation of polymer flow and in the direct practical control of the processing characteristics of molten plastics. While numerous investigations of "die swell" have been reported,¹ it has not been possible until recently²⁻⁶ to relate the swelling measurement quantitatively to the flow parameters of the system or to the fundamental elastic material properties. Recent confirmation has been obtained for the use of rubber elasticity theory⁶ to relate die swell to recoverable shear strain, shear modulus, and normal stress. In the present paper, die swell measurements on both low- (LDPE) and high-density polyethylene (HDPE) samples over a wide shear rate range and at several temperatures are described and the results are analyzed in terms of recoverable shear strain and shear modulus. The effects of long-chain branching (LCB) and of temperature are discussed.

EXPERIMENTAL

Three commercial LDPE samples polymerized by a high-pressure free-radical process and two commercial HDPE resins polymerized by a low-pressure process were investigated in this study. Of the two HDPE samples, HDPE sample D is an ethylene homopolymer, while HDPE sample E is a copolymer of ethylene with a small amount of 1-butene.

Molecular structure parameters for the five samples were obtained by measuring intrinsic viscosities in *p*-xylene at 105°C and by gel permeation-chromatographic (GPC) analysis using 1,2,4-trichlorobenzene as solvent at 135°C. The method for characterizing both LCB and molecular weight distribution from intrinsic viscosity and GPC analysis has been discussed in detail in two previous papers.⁷ Table I summarizes number- and weight-average molecular weights and LCB indices λ , along with room-temperature densities for the samples. The branching index λ is defined as the number of branches per molecule divided by the molecular weight and is derived directly in the mathematical analysis of the GPC data, as discussed in the above-cited reference. Also given in Table I for comparison with previously published⁸ data are corresponding values of \bar{n}_w , the weight-average number of long-chain branches per molecule.

TABLE I
Molecular Structure Parameters of Polyethylene Samples

Sample	Density	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\lambda \times 10^4$	\bar{n}_w^a
HDPE sample D	0.963	14.0	289	0.25	0.35
HDPE sample E	0.951	15.4	196	~0	~0
LDPE sample 1	0.923	15.8	138	2.3	3.6
LDPE sample 2	0.918	15.8	231	2.8	4.4
LDPE sample 3	0.920	18.7	606	5.7	10.7

^a Calculated from $\bar{n}_w = \lambda \cdot \bar{M}_n$.

Shear stress and die swell measurements were made as a function of shear rate at various temperatures ranging from 130°C to 225°C using an Instron capillary rheometer with a single large *L/D* capillary having the nominal dimensions 0.05 in. in diam., 2.0 in. in length, and 90° entry angle. Not all samples were studied over the entire temperature range noted, since (a) the lowest extrusion temperature for the HDPE samples was 150°C, (b) the lower-viscosity materials were too fluid at 225°C to allow unelongated extrudates to be collected for die swell measurement, and (c) the higher-viscosity materials tended to undergo melt fracture at the lower temperatures, precluding die swell measurement. Actual temperatures investigated for each sample may be seen in the figures. Wall shear stresses τ_w and shear rates $\dot{\gamma}_{tw}$ corrected for non-Newtonian velocity profiles were calculated in the usual manner for capillary viscometry.

Die swell measurements were made by collecting unelongated extrudates at each shear rate and measuring the diameter of the extrudate approxi-

mately $1/8$ in. from the leading end of the strand. Approximately $1/2$ -in. to $3/4$ -in. sections of the leading end were then cut from the extrudate sample and were annealed in a silicone oil (chosen to match the density of the molten polymer) for 15 min at 150°C for the HDPE samples and at 125°C for the LDPE samples. This procedure was followed in order to achieve equilibrium, or strain-free, values of the swelling ratio B , where B was calculated from the diameter of the annealed extrudate (corrected for density to the temperature of extrusion) divided by the capillary diameter:

$$B = (D_{\text{ext}}/D_c) (\rho v_t)^{1/2} \quad (1)$$

In eq. (1), D_{ext} is the diameter of the annealed extrudate measured at room temperature, D_c is the capillary diameter, ρ is the room-temperature polymer density, and v_t is the specific volume of the molten polymer at the temperature of extrusion. Values of v_t were calculated from the expression

$$v_t = 1.1405 + 9.4 \times 10^{-4} t \quad (t \text{ in } ^\circ\text{C}) \quad (2)$$

obtained by a least-squares fit of the data of Hunter and Oakes.⁹ It had previously¹⁰ been demonstrated that these annealing procedures did, indeed, allow equilibrium values to be obtained in a time period too short for distortion from surface tension to occur. Moreover, neither swelling nor dissolution of the polymer in the silicone oil took place.

RESULTS AND DISCUSSION

Typical of all die swell data obtained, the swelling ratio curves as a function of corrected shear rate are shown for the 170°C data of HDPE sample D and LDPE sample 2 in Figures 1 and 2, respectively. In each of these figures, three curves are shown: the unannealed swelling ratio and the annealed swelling ratio, both uncorrected for density, and the annealed swelling ratio corrected to the density of the extrusion temperature. Of particular note is the very much larger change on annealing in the case of the HDPE sample, denoting the greater frozen-in unrelaxed strain in the unannealed extrudate of this sample. It is clear in both cases, however, that annealing to the strain-free condition is necessary to obtain meaningful measurements of the elastic behavior of the molten polymer.¹¹

Recent theoretical treatment of extrudate swelling as unretarded recovery of elastic strain imparted during the extrusion process⁶ utilizing rubber elasticity theory resulted in the following expressions relating recoverable shear strain S_R and average first normal stress difference $\langle P_{11} - P_{22} \rangle$ to the swelling ratio and the wall shear stress at each shear rate:

$$S_R = (B^4 + 2/B^2 - 3)^{1/2} \quad (3)$$

and

$$\langle P_{11} - P_{22} \rangle = 2/3 \tau_w (B^4 + 2/B^2 - 3)^{1/2} \quad (4)$$

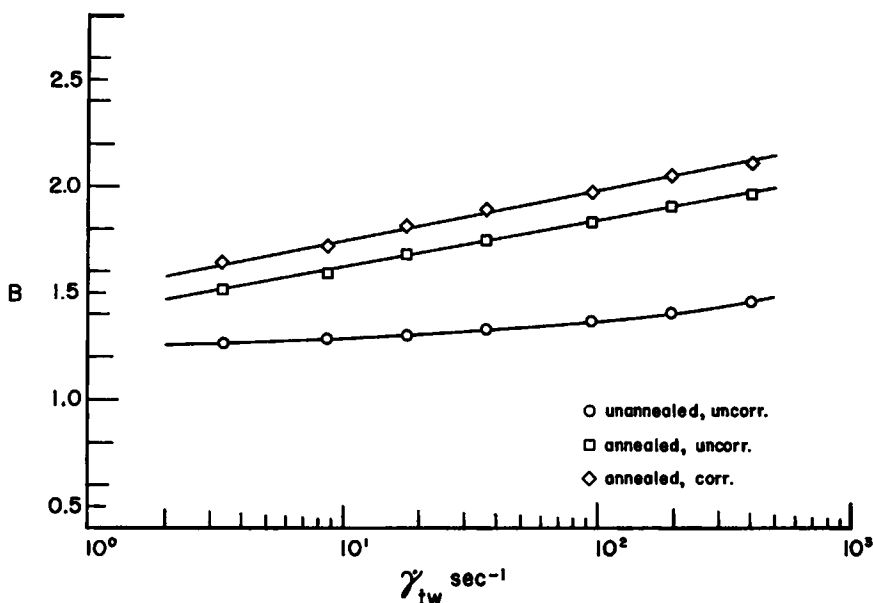


Fig. 1. Comparison of swelling ratio data for HDPE sample D at 170°C, with and without extrudate annealing (with and without density correction).

where the factor $2/3$ arises from consideration of the average shear stress (taken for a Newtonian velocity profile across the capillary cross section) as being the appropriate value to relate to the average normal stress difference. Moreover, the shear modulus is given by

$$G = 2/3 \tau_w / S_R. \quad (5)$$

A more detailed discussion of this treatment, along with the results of two other mechanistic models, with experimental confirmation, is given in reference 6.

A direct evaluation of the effect of LCB in the absence of other significant variations in molecular structure may be made by comparing HDPE sample E and LDPE sample 2. The GPC molecular weight distribution curves of the two resins are seen in Figure 3 to be almost identical. This relatively good agreement of distribution over all molecular species is probably more significant than comparison of averages only, as in Table I. The elastic behavior in shear of the two resins is shown in Figure 4 where S_R is plotted against τ_w at all extrusion temperatures. The sample containing LCB is clearly seen to have undergone less elastic deformation at a given shear stress. A further assessment of the effect of LCB is to be found comparing LDPE samples 1 and 3 to HDPE sample D (itself containing a very low, but apparently real, amount of LCB). Figure 5 shows comparative GPC plots for these samples indicating the differences in molecular weight distribution. Figure 6 compares the S_R -versus- τ_w curves at all temperatures for the three samples, demonstrating that the high

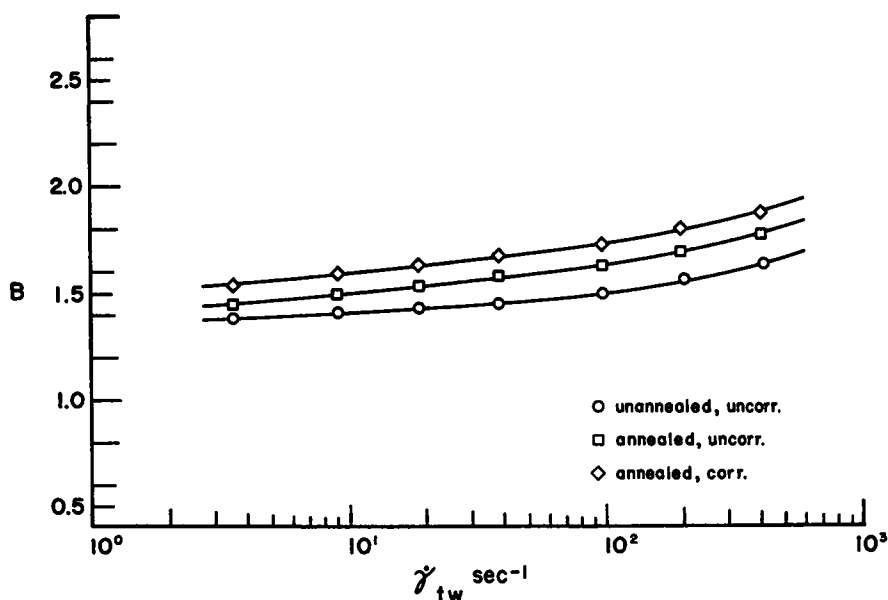


Fig. 2. Comparison of swelling ratio data for LDPE sample 2 at 170°C, with and without extrudate annealing (with and without density correction).

molecular weight branched sample undergoes less elastic deformation than the more linear (HDPE) lower molecular weight sample, but more elastic deformation than the lower molecular weight branched sample. Considerable difficulty was encountered in obtaining adequate reproducibility of GPC data for HDPE sample D, and it is possible, particularly in view of the LCB calculated to be present, that the \bar{M}_w (and breadth of distribu-

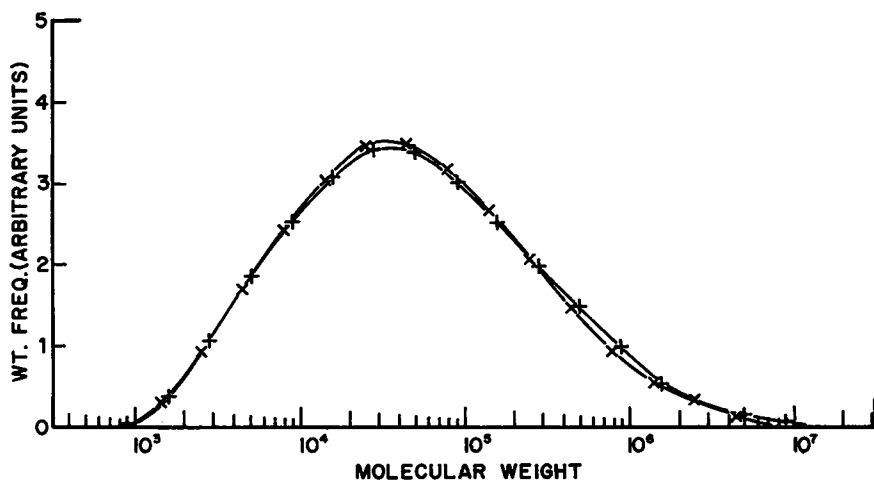


Fig. 3. Comparative GPC molecular weight distribution curves for HDPE sample E (X) and LDPE sample 2 (+).

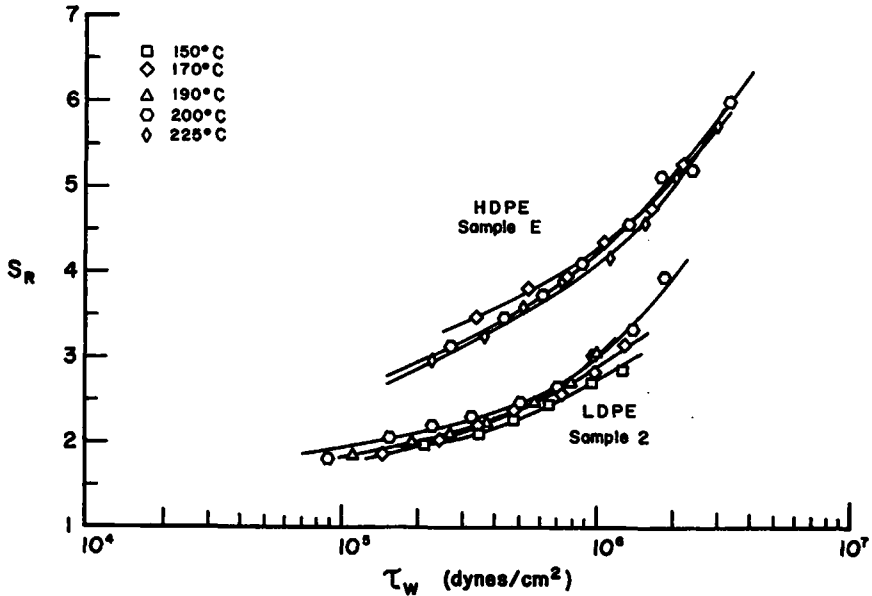


Fig. 4. Comparison of S_R vs. $\log \tau_w$ at various temperatures for HDPE sample E and LDPE sample 2.

tion) may be somewhat high. However, rather than mitigating against the conclusion concerning the effect of LCB on melt elasticity, the possibility that the assigned molecular weight of HDPE sample D may be too high only dramatizes the effect of LCB in decreasing the melt elasticity of the LDPE samples.

These results, i.e., reduction of melt elastic deformability with increasing LCB, are in agreement with earlier results⁸ obtained by the direct measure-

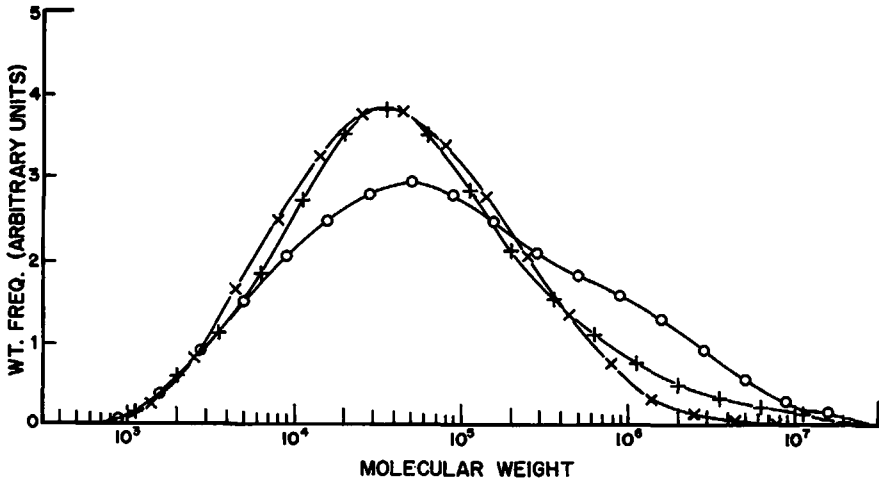


Fig. 5. Comparative GPC molecular weight distribution curves for HDPE sample D (+), LDPE sample 1 (x), and LDPE sample 3 (o).

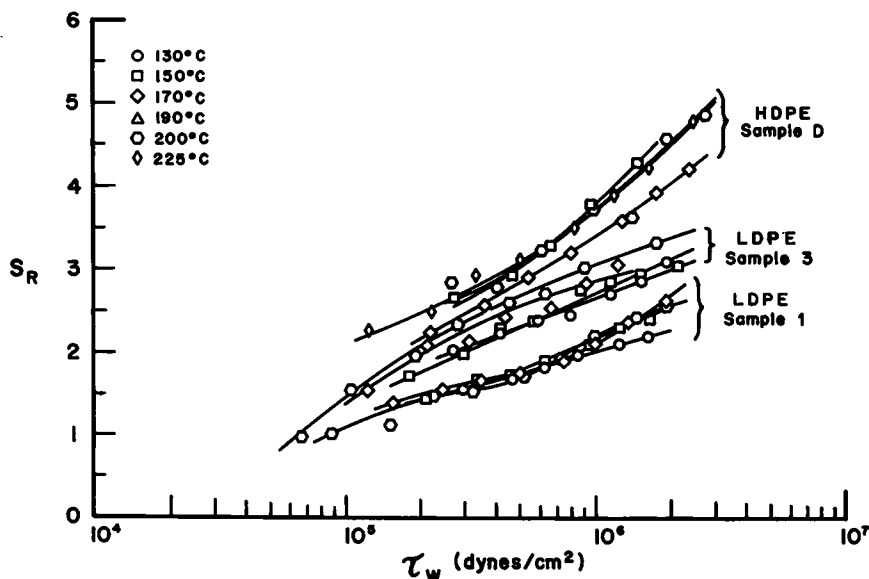


Fig. 6. Comparison of S_R vs. $\log \tau_w$ -data at various temperatures for HDPE sample D, LDPE sample 1, and LDPE sample 3.

ment with a Weissenberg rheogoniometer of $(P_{11} - P_{22})$ and shear stress for a series of narrow molecular weight distribution samples of LDPE having varying amounts of LCB at constant molecular weight and constant molecular weight distribution. These earlier results were shown in Figure 10 of reference 8 as S_R versus shear rate. More recently, Han et al.¹² compared "exit pressure" measurements for a LDPE sample against those for several HDPE samples of lower molecular weight and concluded that, at constant shear stress, the long-chain branched sample had higher melt elasticity. The S_R data for the samples containing systematically varied amounts of LCB from reference 8 have been replotted here in Figure 7 to show that, at constant shear stress as well as at constant shear rate, melt elasticity decreases with increasing LCB.

Figures 4 and 6 also demonstrate the effect of temperature on melt elasticity. It is apparent from these figures that, at constant shear stress, the temperature dependence is not large and may be negligibly small. Moreover, whatever temperature dependence may be present does not vary significantly between HDPE and LDPE. This is in direct contrast to the temperature dependence of the viscosity which, as is well known, decreases exponentially with increasing absolute temperature and which shows approximately twice the "activation energy" for LDPE as for HDPE. Moreover, since little or no change in melt elasticity occurs with temperature at constant shear stress, it must decrease with increasing temperature at constant shear rate. This will be considered quantitatively later in the paper. The observation of essentially temperature-independent melt

elasticity at constant shear stress for polyethylene is consistent with results of Meissner¹³ and of Han¹⁴

There appears to be a barely perceptible trend in the data shown in Figures 4 and 6 toward an increase in S_R with increasing temperature. This would imply a slight decrease in modulus at constant shear stress with increasing temperature, see eq. (5). Calculated shear moduli at four temperatures from 130° to 200°C are plotted as a function of shear stress for LDPE sample 1 in Figure 8 and, if any variation of G with temperature exists, it is too small to be observed. However, it is clear from Figure 8 that G is not constant with changing shear stress (or shear rate), i.e., that "Hooke's law in shear" is not obeyed. The conformational statistical

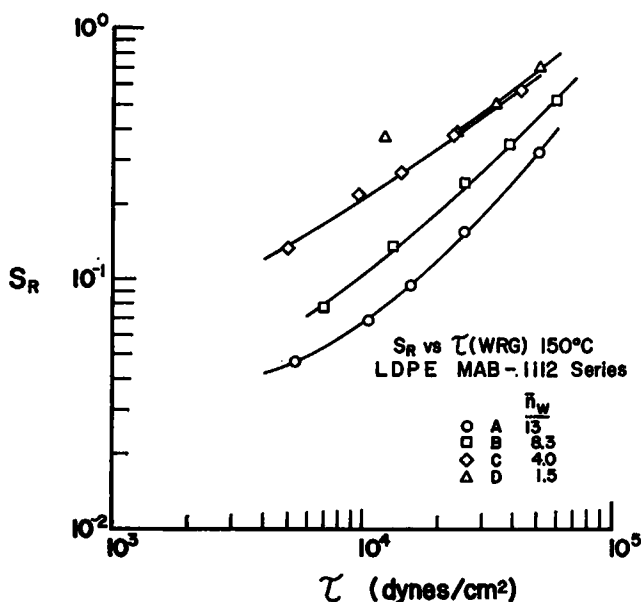


Fig. 7. S_R vs. $\log \tau$ curves at 150°C for four LDPE samples (MAB-1112A, B, C, and D) having equal \bar{M}_n and \bar{M}_w values and varying weight-average number of LCB (\bar{n}_w) as indicated (data from ref. 8).

theory of the rubber elasticity of permanently crosslinked chains predicts that G should be proportional to the product of density and absolute temperature and inversely proportional to the molecular weight between crosslinks. For the 70° spread in temperature from 130°C to 200°C, this would predict an 11% increase in G (M_c constant and using eq. (2) to obtain densities). This is essentially within the experimental error of the measurements. Thus, the experimental results appear to be relatively consistent with the prediction of temperature dependence from rubber elasticity theory. Indeed, since these polymers are entangled, rather than permanently crosslinked, if the experimental results do show a slight decrease in modulus with increasing temperature, this might be explained as owing

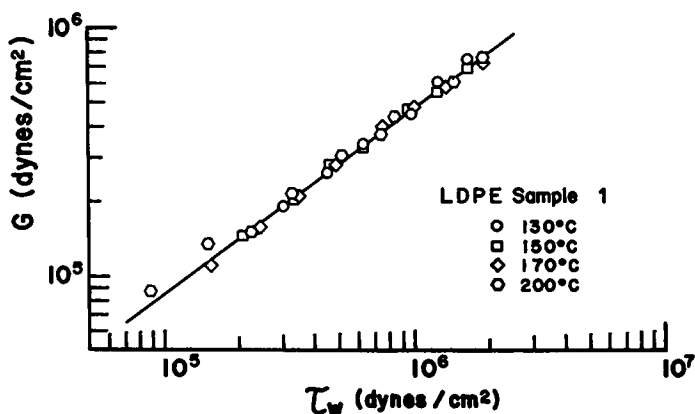


Fig. 8. Die swell-derived $\log G$ vs. $\log \tau_w$ data at various temperatures for LDPE sample 1.

to an increase in the effective molecular weight between entanglements with increasing temperature.

If the approximation may be made that S_R is independent of temperature at constant shear stress, it immediately becomes possible to predict the dependence of S_R or of die swell on temperature as a function of shear rate, a result of considerable practical importance since most polymer processing operations in which postextrusion swelling is important are carried out at explicit rates rather than stresses. This dependence of die swell or recoverable shear strain on temperature as a function of shear rate becomes precisely the dependence of the shear stress on temperature (for the above assumption of S_R independent of temperature at constant shear stress). Thus, the dependence of S_R on temperature at constant shear rate may be quantitatively defined in terms of the same constants which define the temperature dependence of viscosity at constant shear stress.

A particularly useful method for expressing this viscosity dependence in terms of shear rate-temperature superposition has been demonstrated previously.^{15,16} In this method of superposition of shear stress-shear rate curves, the necessary shear rate-temperature shift factors were found to be independent of molecular weight and molecular weight distribution and to be dependent upon type of polymer, i.e., LDPE or HDPE, only. Consequently, one set of constants may be used for all HDPE materials and another set for all LDPE materials. These constants are obtained from the Arrhenius-type equation for the shift factor a_T as a function of absolute temperature T ,

$$a_T = B \exp (E_a/RT) \quad (6)$$

where the shift factor is defined by

$$a_T = \dot{\gamma}(\text{ref})/\dot{\gamma}(T) \quad (\text{at constant } \tau). \quad (7)$$

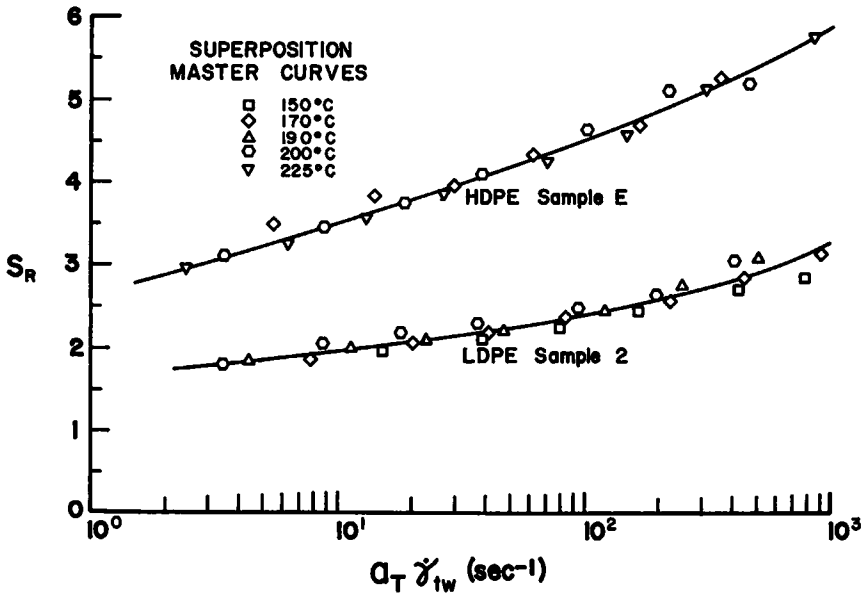


Fig. 9. 200°C Master curves of S_R vs. $\log a_T \dot{\gamma}_{tw}$ for HDPE sample E and LDPE sample 2 obtained by superposition using generalized shear rate-temperature shift factors for HDPE and LDPE, respectively.

In eq. (7), $\dot{\gamma}(\text{ref})$ is the shear rate at the reference temperature at some shear stress τ ; and $\dot{\gamma}(T)$ is the corresponding shear rate at the same shear stress measured at temperature T . The constants in eq. (6), taken from reference 16 for a reference temperature of 200°C (473°K) are $B = 3.88 \times 10^{-6}$ and $E_a = 11.7$ kcal/mole for LDPE, and $B = 1.12 \times 10^{-3}$ and $E_a = 6.3$ kcal/mole for HDPE.

These constants, obtained from earlier viscosity studies, were applied in the present paper to test the shear rate-temperature superposition of recoverable shear strain-shear rate curves. Figure 9 shows two 200°C master curves of S_R versus $\log a_T \dot{\gamma}_{tw}$ obtained by superimposing the HDPE sample E data at three temperatures and the LDPE sample 2 data at four temperatures (where $\dot{\gamma}_{tw}$ is the "true" wall shear rate, i.e., the shear rate corrected for non-Newtonian velocity profile), using a_T values calculated from eq. (6) and the appropriate values of the constants. It may be seen that reasonably good superposition was achieved. However, superposition can only be expected to be as good as the constancy of S_R with temperature at constant shear stress, so that, from Figure 6, it would be expected that poorer superposition of S_R - $\dot{\gamma}_{tw}$ data would be obtained for HDPE sample D and LDPE sample 3. Nonetheless, in general, it appears that, within the limitations of larger experimental error or only approximate validity to the assumption of constant S_R with temperature at constant shear stress, recoverable shear strain-shear rate data at various temperatures may be superimposed to a single

master curve for a given resin using a unique set of shift factors derived directly from viscosity data. This further implies that, given a recoverable shear strain–shear rate curve for a given resin at one temperature, it is possible to construct the corresponding curve at any other temperature in essentially the same way as is discussed for viscosity curves in reference 16. It is important to note that the foregoing discussion, of course, applies equally well to the direct relation between die swell and shear rate as a function of temperature, i.e., master curves of swelling ratio versus reduced shear rate may be constructed and swelling ratio curves at various temperatures may be predicted.

SUMMARY

Comparison of recoverable shear strain data derived from die swell measurements for LDPE and HDPE demonstrated that long-chain branching caused a reduction of melt elasticity in shear for materials having the same molecular weight and molecular weight distribution. This result confirmed earlier direct measurement of recoverable shear strain using cone-and-plate rheometry for a series of LDPE samples also of constant molecular weight and distribution, but having differing amounts of long-chain branching. Moreover, the linear polymer was shown to have higher elastic deformability than branched polymer of considerably higher molecular weight. These results were seen to be valid whether comparison was made at constant shear stress or constant shear rate.

Conclusions concerning the effect of temperature on melt elasticity depend upon specification of constant shear stress or constant shear rate. The results at various temperatures indicated that melt elasticity, expressed as die swell, recoverable shear strain, or modulus, is at least to a first approximation independent of temperature when compared at constant shear stress. It follows necessarily that, at constant shear rate, melt elasticity decreases with increasing temperature, and this decrease may be expressed quantitatively in terms of shear rate–temperature superposition shift factors previously shown to define the viscosity dependence on temperature.

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