

NOTES

*The Flow of Partially Crystalline Polyethylene**

Low molecular weight amorphous polymers generally exhibit a constant viscosity up to high stresses and shear rates, $\sim 10^4 \text{ sec.}^{-1}$.¹ Non-Newtonian flow can be observed, however, for low polymers at temperatures below their normal melting points. A temperature range for melting provides an interval for studying the anomalous flow induced by partial crystallinity. A range of softening temperatures is characteristic of many polymers, and low density polyethylenes are known particularly for melting over a broad range. The effect of crystallites on polyethylene rheology is known to be both important and striking.²

Figure 1 shows a plot at several temperatures of viscosity vs. shear rate for a low density polyethylene. This soft-wax polymer, obtained from Allied Chemical Corporation, has a specific gravity of 0.92 and becomes a true liquid only above 103°C., as indicated by a constant coefficient of thermal expansion. This polymer has a viscosity average molecular weight of 2800 as determined by intrinsic viscosity.^{1,3} Figure 1 shows that viscosities measured in the true liquid range for this polyethylene are Newtonian. This conclusion holds generally for polyethylenes with molecular weights below 5000.¹

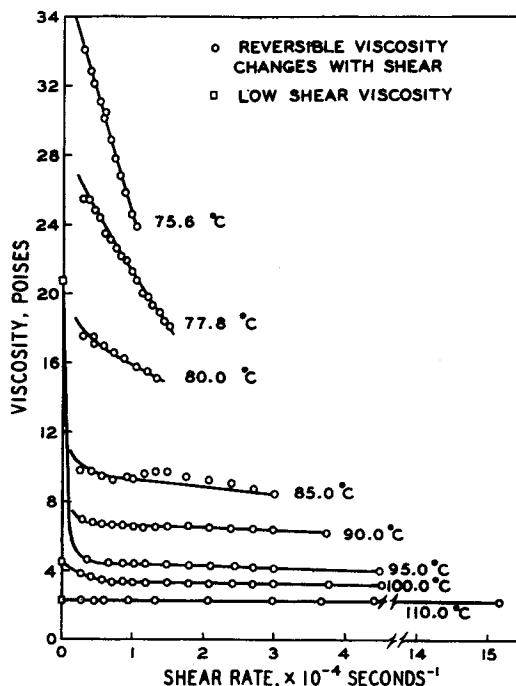


Fig. 1. Viscosity vs. shear for a low density low molecular weight polyethylene.

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In contrast, measurements at lower temperatures in the partially crystalline region are non-Newtonian. The shear curves are entirely reversible and reproducible, indicating that no polymer degradation occurred during tests. Shear heating effects are known to be inconsequential in these tests. Equilibrium was attained at each shear rate in less than one second, with no apparent hysteresis. Low density polyethylenes studied by another method also indicate reversible viscosity changes with shear but with perhaps longer times required for obtaining equilibrium.³

Only about 5% crystallinity is required to produce the prominent shear-dependent viscosities shown in Figure 1.³ Interpretation of the results, however, is difficult because of molecular complexity. Low density polyethylenes exhibit extensive chain branching in addition to a molecular weight distribution. Moreover, the theoretical effect of stress on partially crystalline polymers is also far from understood.² Because of these uncertainties, the limits of viscosity changes with shear exhibited by partially crystalline polyethylene have been evaluated empirically.

Figure 2 shows a reinterpretation of the data in Figure 1 with additional low shear viscosities. High shear data were obtained with a thin-film, double-thermostated, rotational, concentric cylinder viscometer.⁴ The low shear viscosities were obtained with a modified and calibrated Brookfield viscometer. The abrupt change in low shear viscosities and the transition from Newtonian to non-Newtonian flow occur as temperature is decreased below the polymer melting point of 103°C.

The limiting high shear viscosities of partially crystalline polyethylene are found empirically to be approximated by extrapolating the viscosity-temperature scale from the

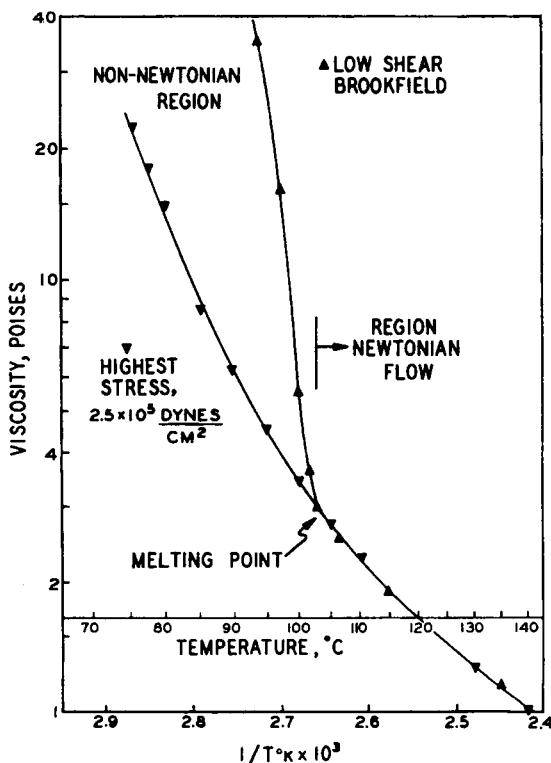


Fig. 2. Viscosity vs. temperature for a low density low molecular weight polyethylene.

true liquid into the partially crystalline range. This behavior is remarkably similar to that recently reported for certain liquid crystals.⁶ One-component cholesteryl ester systems, which form cholesteric and smectic-type mesophases, have limiting high shear mesophase viscosities which can also be predicted from the viscosity-temperature plot for the corresponding true liquid, as in Figure 2. The smectic and cholesteric, layer-type mesophases thus may represent an experimental model for evaluating the general flow of partially crystalline polymer.

Figure 2 indicates that apparent flow activation energies, proportional to the slope, and viscosities increase with decreasing temperature and shear. Below the melting point, limiting low shear viscosities are extremely high, as this soft-wax polyethylene would normally be considered a solid below 103°C. Indeed, Ueberreiter, in studying similar polymers in the same temperature range, found that low shear viscosities extend to as high as 10^{10} poises as measured by a drawn rod technique. Ueberreiter also found that high shear viscosities were low, yielding values in general agreement with the high shear viscosities reported in Figure 2.

The flow of partially crystalline polyethylene is also experimentally (see Fig. 2), if not phenomenologically, similar to the flow of high polymer solutions. At high shear, high molecular weight polymers contribute only minutely to solvent viscosity. Analogously, partially crystalline aggregates behave as polymer of higher molecular weight in an amorphous polymer matrix which may be considered the aggregate solvent. It has been suggested that non-Newtonian flow is the result of shear destruction of crystallites.³ Peck and Kaye describe confirming evidence which indicates that the drawing of crystalline polymer involves at least partial unfolding of the molecules from the crystalline lamellae.⁵ Thus, both reversible shear orientation and destruction of crystallites will contribute to the non-Newtonian effects observed here for partially crystalline polyethylene. The shear effect on crystallites represents for this system the only possible contribution to non-Newtonian flow.¹

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ROGER S. PORTER
JULIAN F. JOHNSON

California Research Corporation
Richmond, California

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