Flow Properties of Polymeric Systems. XX. Shear Rate–Temperature Superposition for Low Molecular Weight Polyethylenes

Mendelson has reported a method of superpositioning viscosity shear rate data of polyethylene melts as a function of temperature.[1] Later, he demonstrated that the method is applicable to polypropylene melts.[2] The superposition method requires, for each polymer, a series of shear stress–shear rate flow curves at several temperatures. One temperature is arbitrarily picked as the reference. The shift factors A_T are obtained by choosing a shear rate on the reference flow curve and shifting the corresponding constant shear stress of the other flow curves to coincide with the shear rate, $\dot{\gamma}$. The values of A_T can then be calculated from

$$A_T = \frac{\dot{\gamma}(\text{Ref})}{\dot{\gamma}(\text{T})}$$

For polyethylenes, Mendelson found that different shift factors were required for high-density and low-density polyethylenes. The low-density polyethylenes reported by Mendelson[1] had $\bar{M}_n$ values of 27.3×10^3–37.8×10^3 with $\bar{M}_w$ ranging from 55.6×10^3 to 1580×10^3. This work tests the applicability of the superposition principle to much lower molecular weight polyethylenes.

The physical properties of the two low-density polyethylenes are given in Table I.

TABLE I
Properties of Polyethylenes

$\bar{M}_v$	$[\eta]$ (in Decalin, 70°C), dl/g	Approx. melting temp, °C	Density, g/ml	
			110°C	135°C
3300	0.154	104	0.802	0.787
8300	0.301	104	0.802	0.788

Viscosity measurements were made with an Instron capillary rheometer; the capillary employed had a length of 4.008 in. and a diameter of 0.03093 in. Flow studies were made at 110°C and 125°C on the sample with a molecular weight of 3300; measurements were made at 110°C and 150°C on the polyethylene of 8300 molecular weight.

The shift factors used were taken from a least-square fit of data in Table IV of reference 1 expressed as

$$\log A_T = \frac{2.313 \times 10^3}{T(°\text{K})} - 5.465$$

Results are shown in Figure 1. The agreement for the two polymers is good, approximately the same scatter as that observed by Mendelson. It is not possible to compute shift factors from these measurements as they did not extend to sufficiently low shear rates. From the limited results, the method appears to be applicable to very low molecular weight, low-density polyethylenes. This significantly extends the useful range of the method.
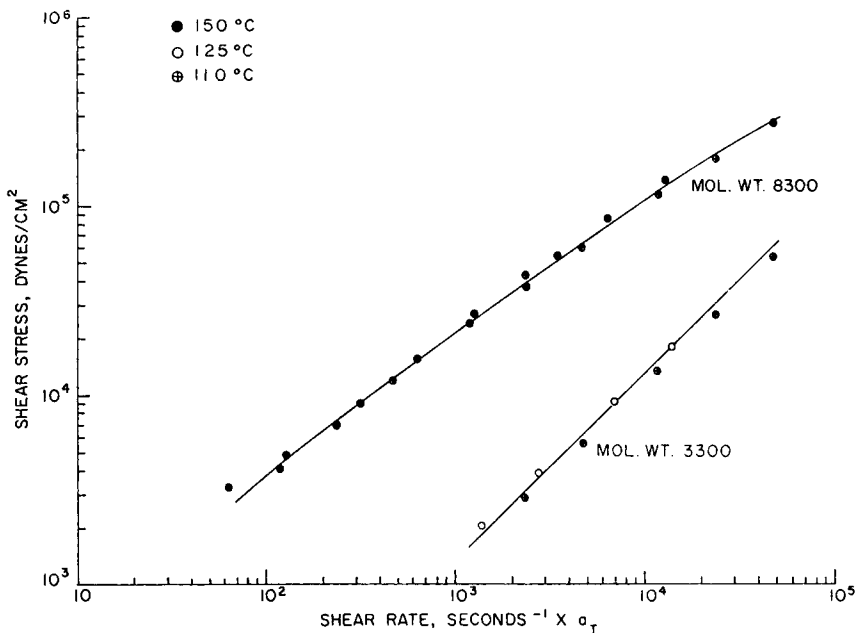
Fig. 1. Shear rate–temperature superposition of low-density polyethylenes.

References

1. R. A. Mendelson, *Trans. Soc. Rheol.*, **9:1,** 53 (1965).
2. R. A. Mendelson, *J. Polym. Sci. B*, **5,** 295 (1967).

JULIAN F. JOHNSON*

Chevron Research Company
Richmond, California 94802

* Present address: University of Connecticut, Storrs, Conn. 06280