

Rheological Behavior of Linear Polyethylene at Low Shear Rates

Ford et al.¹ have recently reported that several linear polyethylenes undergo crosslinking during low-shear-rate processing, resulting in an increase in melt viscosity. In compression-molding operation (a low-shear-rate process), their polyethylene samples showed a sharp drop in melt index (ASTM D1238-65T). We report here a similar phenomenon observed in a cone-and-plate viscometer for some linear polyethylenes of high melt index. The mechanism for this behavior, we believe, is the same as that stated by Ford et al.

The rotational viscometer used for the low-shear-rate measurements was Farol Research Engineers' Weissenberg rheogoniometer² in which a cone-and-plate configuration was employed. The sample is placed between a lower rotating cone and a stationary upper plate. The platen diameter is 7.5 cm and the cone angle is $1^{\circ}30'$. The torque delivered to the upper plate is sensed by a torsion bar-transducer arrangement, and recorded continuously by a strip chart recorder. In this particular experiment, the samples were evaluated at a low speed (shear rate = 0.0023 sec^{-1}) for more than 140 min at a constant temperature of 220°C .

Figure 1 shows the torque versus time relationships of three different polyethylene samples having similar melt indexes (around 15.0 g/10 min). They show various degrees of "crosslinking" as a function of time indicated by the continuous increase of torque with time. The melt viscosity of sample A increases tenfold after 140 min over the pseudo-steady value at 20–40 min. The torque reached after 140 min by sample A is about three times that observed for sample C at the same shear rate and temperature. An interesting, but apparently not related, phenomenon in connection with this low-shear-rate viscosity behavior of linear polyethylene is that injection-molded articles from sample C exhibit more brittleness than those made from samples A and B.

These data support the hypothesis of Ford et al. that linear polyethylene apparently contains reactive sites which can lead to both chain scission and crosslinking reactions depending on shear rate and temperature. At low shear rates, crosslinking appears to be dominant. It is also apparent that the molecular homogenization theory of Heit-miller et al.³ would not explain the anomalous behavior of linear polyethylenes shown by our data.

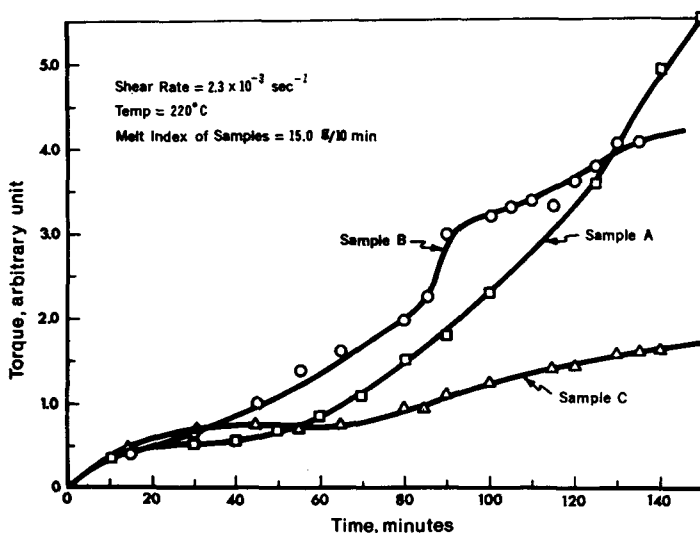


Fig. 1. Torque vs. time relationships for linear polyethylene.

References

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