

Measurement Note

Measuring the extensional flow behaviour of polyethylenes for plastics processing

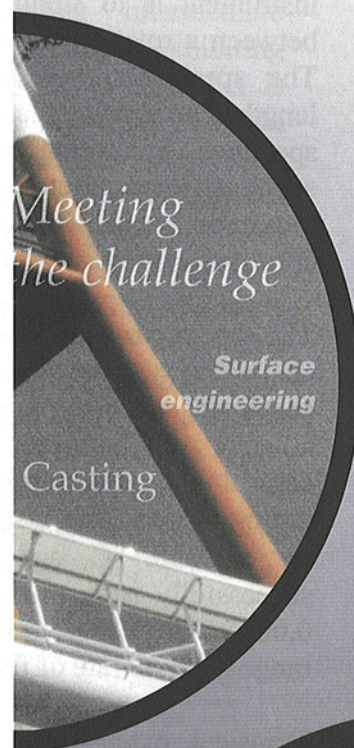
Summary

In many plastics-forming processes the polymer melt undergoes significant extensional flow, for example in extrusion, blow moulding and wire coating. The extensional flow behaviour of materials will therefore have a significant effect on their processability and also on the properties of the product, for example due to stresses generated by the extensional deformation that are subsequently frozen in. However, established rheological techniques predominantly characterize polymer melts in shear and it can prove difficult to relate that behaviour with its behaviour observed in processing where the deformation may be predominantly extensional. An ability to characterize the flow behaviour more appropriately will thus have benefits in materials development and in process and product design.

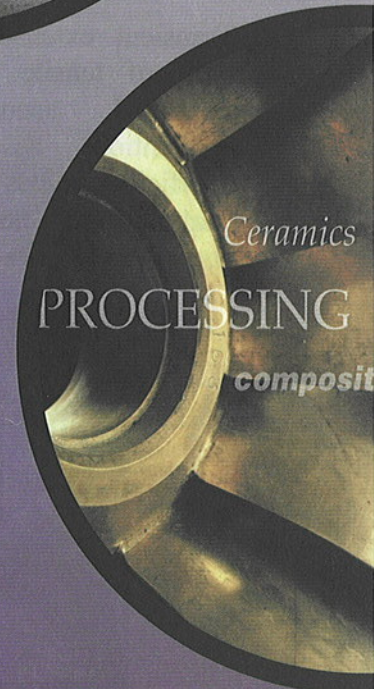
The techniques most suited for characterizing the extensional flow behaviour of polymers are converging and stretching flow methods [1-5]. The converging flow approach can be used to obtain qualitative data but for quantitative data stretching methods must be used. However, suitable stretching techniques are very limited in number.

Low strain rates are important for characterising the flow behaviour of materials. For example, in extrusion, particularly of thick walled products, low rate deformations can occur which result in slump of the product causing an unacceptable variation in wall thickness. A knowledge of the appropriate rheological behaviour can therefore be used to design out this problem. However, testing at low strain rates presents further experimental difficulties due to the very low forces and long test durations involved. Results of an industrial case study carried out with GPS Ltd on four HDPEs used for thick-walled pipe extrusion are presented. The objective was to identify differences in their low rate extensional flow behaviour that may be correlated with their processability.

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Casting



NPL 
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Low rate extensional rheometer

An instrument for measuring the extensional viscoelasticity of polymer melts was developed to operate at low strain rates, Figure 1. The operating principle of the instrument is to stretch a molten specimen between a rotating clamp and a fixed clamp. The specimens were typically 80 mm in length. The rotating clamp, by winding up the specimen, controlled the rate at which the specimen was stretched. The fixed clamp measured the tensile force developed in the specimen during stretching.

The specimens were fixed to the clamps using an epoxy adhesive. After loading, the specimen and clamps were immersed into a silicone oil bath to provide temperature control and also support for the specimen during testing. The instrument has been used up to 230 °C and measurements have successfully been made at strain rates from 0.001 s^{-1} to 100 s^{-1} , giving the instrument a range in strain rate of five decades.

Transient extensional viscosity values (the ratio of tensile stress to strain rate) are presented, according to nomenclature convention, as tensile stress growth coefficient values [6]. Details of the method, analysis and nomenclature are presented elsewhere [4].

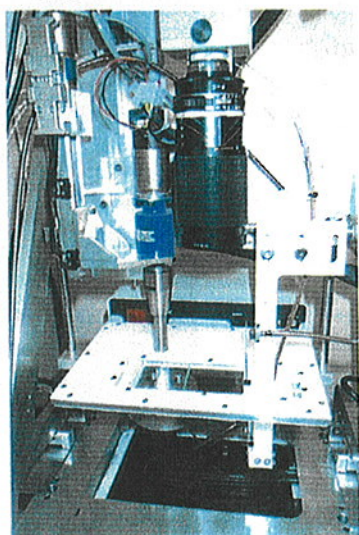


Figure 1: NPL extensional rheometer for testing molten polymers at low rates.

Extensional viscosity results for four similar polyethylenes

Four samples of HDPE having similar properties were tested for an industrial case study. The NPL references for these materials were: HGZ000, HHA000, HHB000 and HHR000. An example of the low strain rate transient stress growth coefficient results is presented, Figure 2. Greatest strain hardening was observed for HHA000, followed by HGZ000, HHR000 and then HHB000 (strain hardening was most significant at the lowest strain rate). Comparing the results for the four grades at a strain rate of 0.01 s^{-1} , Figure 3, indicated that the material HHA000 had lower transient extensional stress growth values at strains up to approximately 0.4 (time $\approx 40 \text{ s}$). However, at higher strains the transient extensional stress growth values were similar for all materials, this being due to the greater additional strain hardening of HHA000.

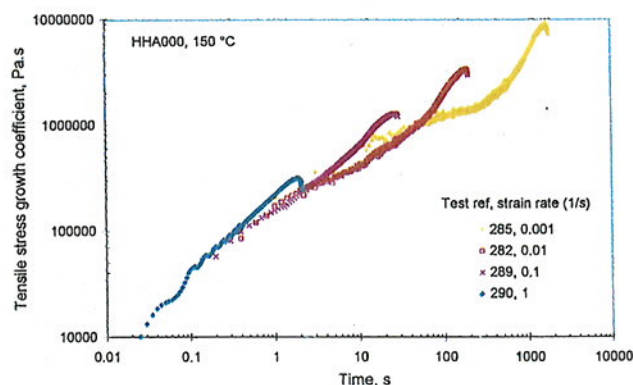


Figure 2: Extensional viscosity data for a HDPE (HHA000).

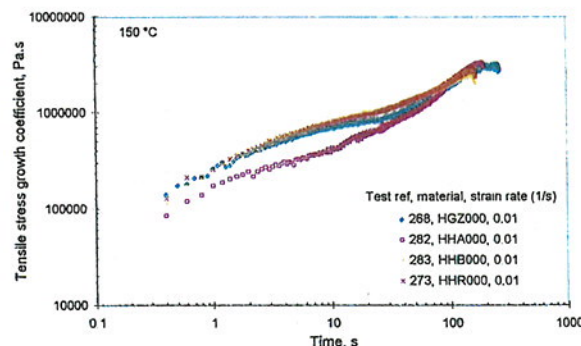


Figure 3: Comparison of the extensional viscosities of four similar HDPEs.

The differences between the three materials HGZ000, HHB000 and HHR000 were relatively small although the values for HGZ000 were slightly lower. Further detailed analysis of this and additional strain rate data used to compile master curves [8] suggested that the data at 0.01 s^{-1} were reasonable for HHB000 and HHR000, but possibly a little high (by $\approx 10\%$ to 20%) at low times ($< 10 \text{ s}$) for HGZ000, and possibly a little low for HHA000 (by $\approx 10\%$). Taking these factors into considerations would give HGZ000 intermediate transient extensional stress growth values. However the differences in values between HHR000, HHB000 and HGZ000 were still small.

Measurement of the draw-down of extrudate using a melt flow rate instrument to determine approximate extensional viscosity values was also carried out. The measurements were made using a standard Ray-Ran Test Equipment Limited's 5MPCA Advanced Melt Flow System instrument. Automated, non-contact extrudate swell measurements were made using a Mitutoyo Laser Scanning Micrometer (LSM-3000) mounted on the melt flow rate instrument and also on the cooled extrudate using a hand-held digital micrometer after completion of the test.

The results obtained using the hand-held micrometer clearly showed, the decrease in extrudate diameter as the test progressed, due to the effect of the mass of extrudate already formed drawing down the molten extrudate, Figure 4. The gradient of the line of extrudate diameter versus position can be related to the extensional viscosity of the material. A greater (negative) gradient implies the more easily it draws down, the lower its resistance to extensional deformation and thus the lower its extensional viscosity. The greatest negative gradient was exhibited by HHA000, followed by HGZ000 and then HHB000 and HHR000, the latter two having very similar gradients. An analysis was developed to interpret the drawing down of the extrudate in terms of an approximate extensional viscosity [7]. The extensional viscosities, determined

from the hand-held micrometer measurements of extrudate swell, are presented in Figure 5. This shows that there is a difference of approximately $\times 3$ in the approximate extensional viscosity values of the four materials with HHA000 exhibiting the lowest values, HGZ000 exhibiting intermediate values and HHB000 and HHR000 exhibiting the highest values. It is noted that this is consistent with the trend in values obtained using the NPL extensional rheometer. Furthermore the magnitude of the extensional viscosity values obtained using the melt flow rate method (in the range 10^5 Pa.s to 10^6 Pa.s) were similar to that obtained using the more elaborate NPL extensional rheometer, although precise comparison is made difficult due to the non-isothermal and non constant strain rate nature of the melt flow rate draw-down method. For full presentation and discussion of the results, including that of an uncertainty analysis see reference [8].

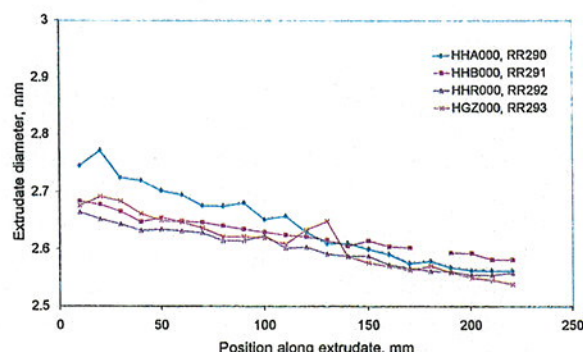


Figure 4: Extrudate swell behaviour of four similar HDPEs using a hand-held micrometer.

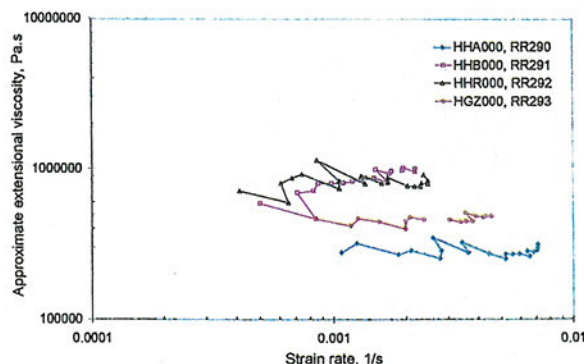


Figure 5: Interpretation of extrudate swell measurements as approximate extensional viscosities for four similar HDPEs.

Conclusions

The four HDPEs exhibited differences in extensional flow behaviour, with one grade being clearly lower in extensional viscosity at low strain values than the others. Analysis of these four grades using the extrudate draw down method revealed similar trends in behaviour as had been identified using the NPL extensional rheometer. Furthermore, the approximate extensional viscosity values thus determined were similar to those obtained using the more elaborate extensional rheometer.

Acknowledgements

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References

1. Rides, M., Allen, C.R.G., and Chakravorty, S., Review of extensional viscoelasticity measurement techniques for polymer melts, NPL Report CMMT(A)44, October 1996.
2. Rides, M. and Chakravorty, S., Review of converging flow methods for determining the extensional flow behaviour of polymer melts, NPL Report CMMT(A)80, August 1997.
3. Rides, M. and Allen, C.R.G., Measurement of the extensional flow properties of polymer melts using converging flow methods, NPL Measurement Good Practice Guide No.16, January 1999.
4. Rides, M. and Allen, C.R.G., Measurement of the extensional flow properties of polymer melts using stretching flow methods, NPL Measurement Good Practice Guide No.18, May 1999.
5. Rides, M., Allen, C.R.G., and Chakravorty, S., Intercomparison of extensional flow characterization techniques for polymer melts: tensile stretching and converging flow methods, NPL Report CMMT(A)171, April 1999.
6. Dealy, J.M., *J Rheol.*, 39(1) January/February 1995, pp253-265.
7. Rides, M., Allen, C.R.G., and Dawson, A., Improved testing using the melt flow rate instrument – multi-rate and extensional flow measurements, NPL Report MATC(A)28, June 2001
8. Rides, M., Allen, C.R.G., Low rate extensional rheometry of polymer melts, NPL Report MATC(A)114, July 2002.

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