New Capabilities of Rheology for Polymer Compound Industry

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Summary: Recent developments in testing equipment are enabling a better exploitation of rheology as a tool for polymer compound industry.
After a short review of the novelties of recent equipment, some selected possibilities are shown in this paper, ranging from improved quality control of incoming and outcoming products, to recycling management, masterbatches characterization, and evaluation of dispersion effects on filled materials.

Keywords: capillary viscometers; compounding; masterbatches; quality control; rheology

Introduction

Rheology has always been considered a powerful tool to characterise polymer melt under real processing conditions. As a matter of fact, shear rates and shear stresses available in capillary rheometers (also called capillary viscometers) are of the same order of magnitude of those found in the most known processing technologies, such as extrusion and injection moulding.

This paper will show many possibilities offered by rheology in compounding. It will be demonstrated that modern rheological techniques may be used at different levels to suit specific requirements.

The novelties

<u>Melt Flow Tester</u>

The development of the traditional Melt Flow Rate (MFR from now on) tester was triggered by the use of an encoder, a device meant to follow continuously and with high precision the piston position. Apart from transforming the traditional weight-based test into a volume test, the new equipment features new tests such as the melt density, the thermal stability and the shear sensitivity.

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Melt density is obtained from the ratio of mass flow rate and volume flow rate. It is a valuable piece of information since it is not dependent on crystallinity.

Thermal stability, defined as the variation of the MFR per unit time, is a parameter revealing the changes undergone by the melt. It may be evaluated under standard conditions, such as those found in MFR tests, or, better, under more severe conditions, such as those experienced by materials in real processing.

Shear sensitivity is the ratio of MFRs obtained with two different loads. Usually they differ by a factor of 10. For simple polymers this parameter may be easily related to the broadness of the molecular weight distribution.

It may be worthwhile mentioning that in each run we may have, depending on the material, up to 40 experimental data, and the broadness of their dispersion, expressed as standard deviation, may be taken as a quick and easy indicator of homogeneity of a given polymeric material. This is a fully new information whose potential is still to be exploited.

Capillary Viscometer

A development of capillary viscometers was the introduction of a twin-bore instrument instead of the traditional single-bore, fig. 1.

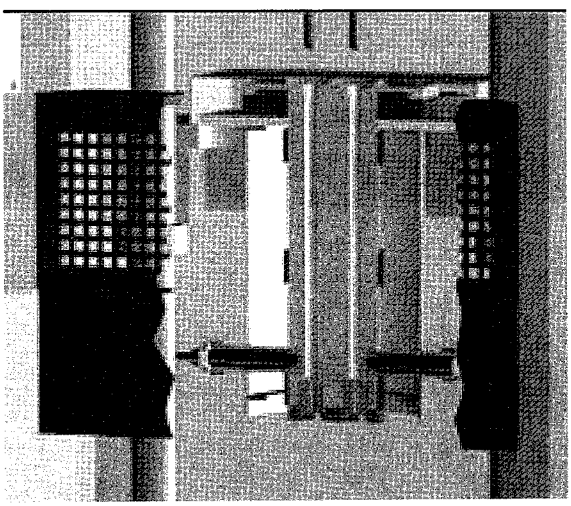

Figure1. Detail of a twin bore capillary viscometer.

Running tests with two dies of different lengths and the same diameter allows performing automatically the Bagley and Rabinowitsch corrections.[1,2] Fig.2 shows an example of rheological curve, before and after doing the corrections: the rather relevant differences on the viscosity values from the two capillaries, are strongly reduced after the corrections.

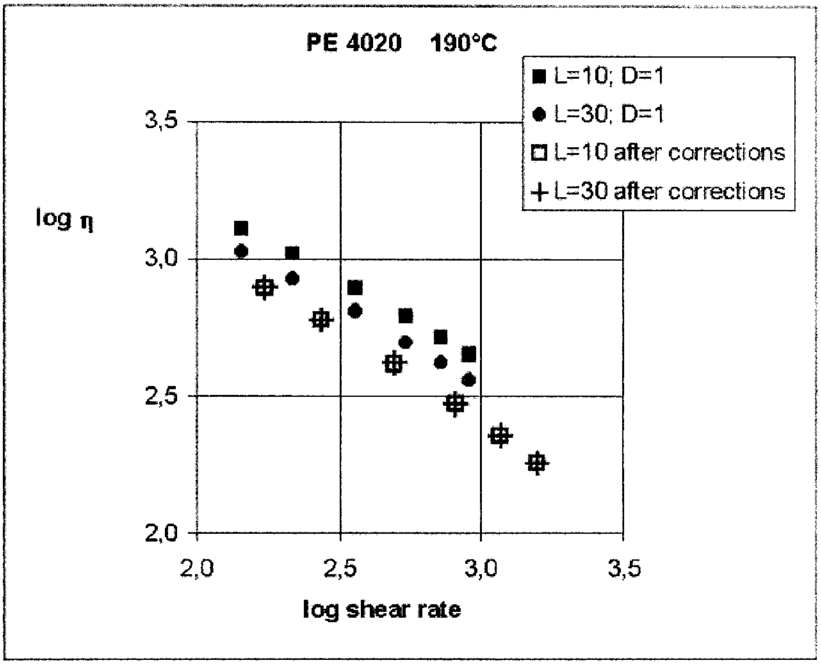

Figure 2. Shear viscosity (the unit for η is Pa·s) vs shear rate (1/s). The application of Rabinowitsch and Bagley corrections brings the two uncorrected curves (filled symbols) into one curve. Using a twin bore equipment, the correction task is optimized and automatically performed.

Actually, running tests on the same material under identical conditions offers the highest precision for the Bagley correction.

The new equipment may prove also extremely useful to detect slip wall effects, which may be very important when dealing with polymers containing additives or lubricants, and sometimes with pigmented polymers. Slip wall tests are performed using capillaries with different diameters and the same length (the opposite of what done with the Bagley test). Then, by plotting the throughput as a function of the reciprocal of L/D (at constant shear rate), the extrapolation at 1/(L/D) = 0 provides a measurement of this effect. Again, as for the Bagley correction, the quality of the answer is optimized with the twin bore equipment, since the test is run on the same batch of material and under the same test conditions.

Finally, the twin bore capillary rheometer offers an easy way to evaluate the elongational viscosity, i.e. the viscosity under tensile stress. To this purpose a method proposed years ago by Cogswell[3] may be used, which requires the Bagley pressure as a basic data. The availability of the Bagley pressure makes the evaluation of the elongational viscosity a matter of simple calculation which can be automatically performed from the equipment computer. Fig. 3 shows an example of evaluation of the elongational viscosity as a function of the elongational rate.

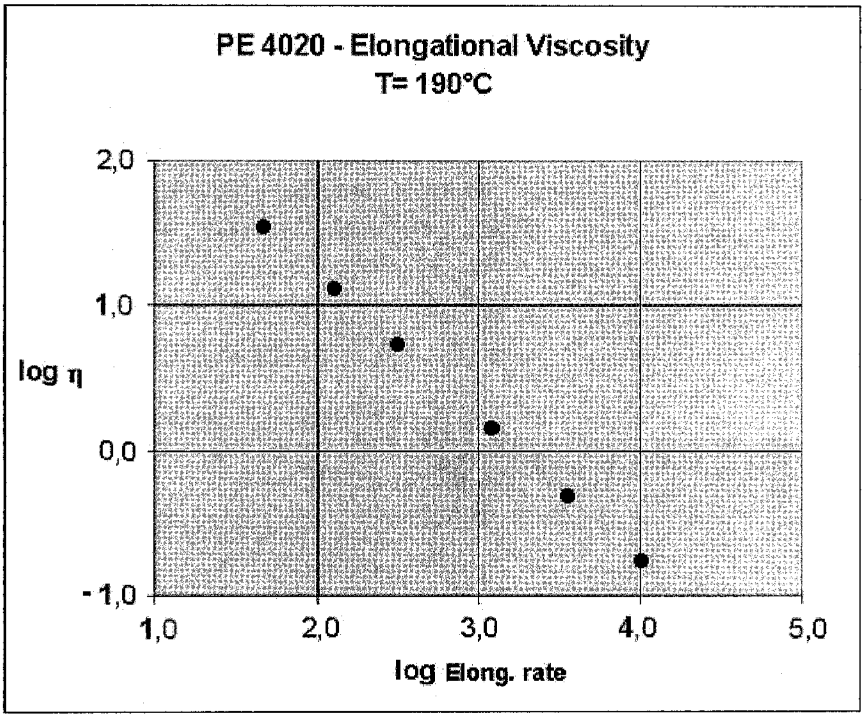

Figure 3. An example of elongational viscosity, obtained by a twin bore capillary viscometer. The plot shows elongational viscosity (the unit for η is Pa·s) vs elongational rate (1/s).

Application of rheology to polymer compounding

The application of the rheological information obtained from new equipment will be now considered in compounding industry.

a) Quality Control (QC from now on) of incoming materials

On the light of the above improvements in rheological equipment, it may be considered to extend the use of the MFR, on a routine basis, to perform other tests. In particular, the broadness of a single MFR run (the standard deviation of the test), may be used as an indicator for the homogeneity of the material (the broader the MFR, the poorer the homogeneity), and the thermal stability test as an indicator for stability. This data is available at no extra cost, since it is obtained automatically for each run.

The stability test may also be run under different conditions from the standard MFR, i.e. at temperatures a little bit higher than the nominal temperatures used when processing; this will give a more realistic information, which may sometimes explain faults experienced in processing.

The capillary viscometer may also be used on a routine basis, since modern equipment is now friendly and faster. A quickly increasing number of industries is appreciating the potential of such approach which relies on the evaluation of the full curve instead of a single point.

In particular, they appreciate the possibility of making sound comparisons (i.e. comparisons among 'true curves') of different lots of a given material or of competitor materials over a broad range of shear rates.

The Bagley function too, far from being only an annoying duty, may be used as a new quality indicator for a given polymer. This would easily extend the QC without spending further experimental time.

In some cases the melt strength or the drawdown have also begun to be used as indicators for homogeneity.

This duty, which may be performed as a routine test, relies on the strong sensitivity of the stretching test (see Figures 4 and 5) to reveal inhomogeneous domains in a given material or irregular polymer-filler adhesion.

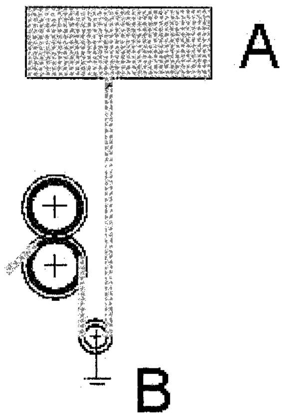

Figure 4. Sketch of a stretching unit (or drawing unit), which may be located below the viscometer to measure the force-elongation curve ('the stretching behaviour') of a polymer melt (A: viscometer, B: load transducer).

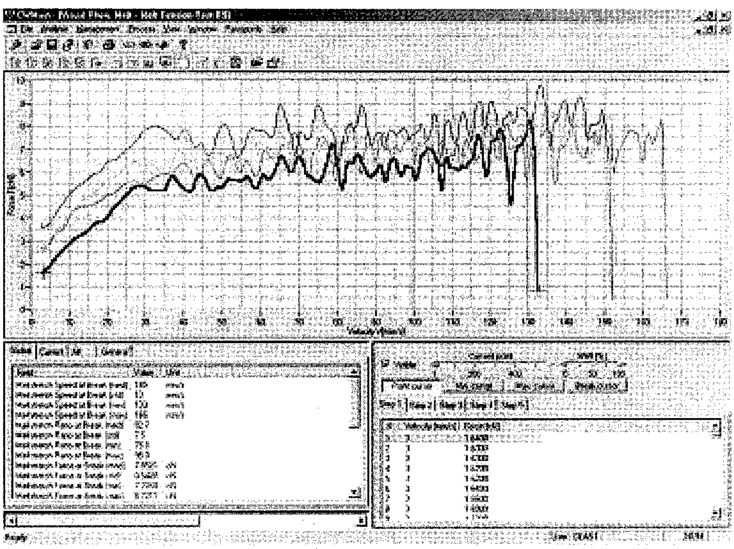

Figure 5. Example of the output of stretching tests on carbon filled polyethylene. The dispersion quality is revealed by differences in the stretching curves: poor dispersion is usually associated with low values of the force and elongation at break.

b) Quality Control of outcoming materials (after compounding). Beyond the above mentioned possibilities, are of particular interest: the thermal stability (e.g. for flame retardant compounds), the melt density (as representative of the actual filler/reinforcement content) and the melt strength (as indicator of anomalies).

c) For recycling and reusing of materials, rheological equipment may help to widen the possible (even beyond standard characterization) knowledge of the incoming recycled/reused materials. Here are some possibilities offered by rheological tools on incoming materials:

- the MFR Test allows the evaluation of the basic quality, even with very fluid materials; may easily reveal material defects (through visual inspection of the molten strand)
- the melt density may indicate the presence of foreign substances in the recycled material or may be used to evaluate the filler amount
- the Thermal Stability Test may reveal critical aspects of recycled material (e. g., materials too unstable to be re-processed) or may be used to optimize new formulations of the recycled material

d) Finally, rheological tools may be used to test the quality of masterbatches. Usually masterbatches are very fluid, beyond the capability of manual standard MFR equipment. New graders provide an easy solution, being able to measure MFR up to 900 g/10 min.
Melt Strength testing is often the right technique to reveal possible defects in a compound, such as poor dispersion of an additive or a filler.

Conclusions

Rheological testing by capillary viscometers is not only showing an improvement in the experimental precision, but also an increase in output information and user friendliness. As a consequence, the application of rheology to polymer compounding is going to be a little easier and more fruitful than in the past.

[1] Rabinowitsch B., *Z. Physik. Chem.*, A145 (1) **1929**, pp. 1-26
[2] Bagley E.B., *J. Applied Physics*, 28 (5) **1957**, pp. 624-627
[3] F. N. Cogswell, *Polym. Eng. And Science* 12 (1) **1972**, pp. 64-73.