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ORIGINAL CONTRIBUTION

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Sources of error and other difficulties in extensional rheometry revisited: commenting and complementing a recent paper by T. Schweizer

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Abstract In a recent paper by T. Schweizer (Schweizer 2000) a large collection of experimental difficulties associated with the measurement of uniaxial extensional properties of polymer melts in the Rheometrics RME extensional rheometer is described. The work covers topics such as sample preparation for different types of polymers (sensitive or not to moisture) supplied in different shapes (pellets or powder), the necessary corrections to the tensile force, and the ever-present problem of determining the true strain rates of the experiments. The aim of the present paper is to complement and expand the work of Schweizer by pointing out other experimental problems that are the cause of errors in extensional rheometry of polymer melts. The present analysis, however, is not exclusively dedicated to the RME, unlike that of Schweizer, being directed instead to a general class of apparatus that work according to the principle of stretching a constant length sample between pairs of counter-rotating rollers; for example, all the data shown was obtained with our own extensional rheometer (Maia et al. 1999). This work will focus on the importance of the correct choice of the supporting media used for sample heating and support, the importance of end-effects, and the influence that the griping surfaces can have in such measurements.

Key words Extensional rheometry · Polymer melts · Experimental problems · Error sources

Introduction

Usually, when studies on uniaxial extension of polymer melts are performed, the main concern is the achievement of the largest possible deformation with a homogeneous stretching of the sample at the highest deformation rate possible. Therefore, it is necessary to ensure that the correct experimental conditions are achieved.

Schweizer (2000) recently published a paper in which some of the problems related to extensional viscosity measurements are discussed. The work is focused on the well-known Rheometrics RME, and intends to be a guide for its users in obtaining good results. As such, its first topic is sample preparation. The author describes the necessary procedures in order to obtain good samples for testing in the RME. Care has to be taken with materials that are sensitive to moisture, especially if in powder form, due to the possibility of sintering when the material is dried in an oven. Details are also given on the necessary steps for placing correctly and adjusting the samples in the RME.

Two other major aspects focused in Schweizer's work are the control of the measured force curve and the determination and meaning of the true strain rate. In the case of the measured force, it is stated that if it shows spikes or discontinuities this is evidence of a bad experiment. Another important aspect related to the force measurement is the value of the residual force observed at the end of the test. In fact, in some cases a correction to the actual measured force is necessary because this indicates that the sample was not completely relaxed at the beginning of the experiment and, as shown in the paper, a small value for the force correction can have a large impact in the calculated viscosity curve and give rise to artificial strain hardening.

Regarding the effective strain rates attained during extension, Schweizer shows that the true value and meaning of the strain rate attained during the process is one of the most important factors in such measurements. It is by now well established that the simple use of the nominal strain rate (given by the set linear velocity at the periphery of the clamp divided by the length of the sample) does not correctly describe a uniaxial flow experiment for the RME-type of instruments. Along with end effects related to non-pure extension in the region close to the clamps, there are problems related to non-complete transfer of the linear velocity of the clamps to the sample due to lack of grip (coming from the nature of its surface). Consequently, as is shown for the RME, the errors in the calculation of the cross-section can be very large when using the nominal value and evidently propagate in the calculation of the elongational viscosity. Therefore, the true strain rate should always be evaluated, which can be done by some kind of visualization technique. In the case of Schweizer's experiments, this is performed with a particle-tracking scheme, making use of markers that are sprinkled on the surface of the sample. When the true value (as determined by the particle-tracking scheme) is not constant in time, an average value is used.

Although very thorough and complete regarding the topics it aimed to cover, Schweizer's analysis left out some major potential sources of error in extensional rheometry of polymer melts, namely the case of the importance of end-effects, grip between the sample and the rollers, and supporting and heating media, gaps that the present work aims to help bridge.

The first of the above-mentioned effects has been partially addressed by a number of authors in the past. For example, Vinogradov et al. (1970) and Cogswell (1972) state that specimens must have an aspect ratio larger than 10 in order for end-effects to become negligible. Münstedt (1975) also stated that if an experimental method is to be reliable, then it must be independent of geometry, and presented results for different L/D ratios.

Non-uniformities in temperature and deformation throughout the whole specimen also constitute another potential error source (Dealy 1978; Laun and Münstedt 1976). Both factors are connected since a non-homogeneous temperature field can promote the appearance of favored failure spots (due to the variations in resistance to stretching that are induced). Therefore, good temperature control must exist in order to obtain precise measurements, some solutions having been proposed in order to reduce temperature variations in the sample. For example, the use of glass covers in the heating bath (Meissner et al. 1981) and/or of a double-layer heating apparatus (Muller and Froelich 1985; Münstedt 1975, 1979), with an inner and an outer oil bath, reportedly improves temperature uniformity (in these cases silicone oils are the most commonly used), as does the use of heated air chambers (the RME works according to this principle).

Previously to Schweizer, Rides et al. (1996) have also provided a thorough review on the problems associated with the measurement of extensional viscoelasticity of polymer melts and pointed out other factors capable (in principle) of introducing large errors in the determination of the extensional characteristics of polymer melts. Among these are the effects connected with gravity, inertia and viscous or frictional drag of the sample, instrument friction, and inertia and interfacial tension. While in most of these cases those errors were found to be negligible in practice (see, for example Laun and Münstedt 1978), such is not the case for gravitational effects. These can be overcome by employing heating baths that serve also as means of supporting the sample or by using an inert gas cushion. In the former case, a careful choice of the characteristics of the supporting media must be made. In order to eliminate buoyancy effects and sagging of the sample, the density of the liquid must be matched to that of the polymeric sample, at the test temperature. Also, the liquid must be able to attain high enough temperatures to melt the sample, without inducing degradation. The best-known example of the latter is that of the gas cushion of the RME (Meissner and Hostettler 1994). The cushion is generated by compressed gas flowing through a flat metal frit where the sample rests and the gas temperature is made equal to the test temperature. In these cases, however, problems can arise when the sample becomes sufficiently small, which causes it to vibrate or stick on the supporting table, as is acknowledged by Schweizer.

In view of the above discussion, the aim of the present paper is to complement and expand the work of Schweizer by pointing out other experimental problems that are the cause of errors in extensional rheometry of polymer melts with Meissner-type instruments. The work will focus on the importance of the correct choice of the supporting media used for sample heating and support, the importance of end-effects, and the influence that the griping surfaces can have in such measurements.

Experimental

Description of the experimental apparatus

The instrument used for the experiments reported in the present paper is a modified TA Instruments Weissenberg Rheogoniometer, which will be referred to as MRR (Modified Rotational Rheometer). This is a prototype uniaxial extensional rheometer that works under the principle first proposed by Meissner (1969, 1972), and is already described elsewhere (Maia et al. 1999). According to the classification proposed by Rides et al. (1996) this is a Type 2 instrument, and it is composed of a fixed clamp and a rotating clamp with two rotating elements. A large range of rotational speeds is available from the motor of the Weissenberg. There is also the possibility of changing one of the transmission gears of the MRR, in order to achieve different transmission ratios and, consequently, different strain rates for the same rotational speed of the motor. The measured axial forces can vary from 8.2×10^{-4} N up to about 15 N, with different resolutions for different torsion bars. True strain rates are obtained by measuring the radius evolution of the sample with the help of a digital video camera and an image analysis software package.

Achievable strain rates depend on the material being tested but can be as low as 10^{-3} s^{-1} or as high as 10 s^{-1}. Hencky strains of up to 7 have been achieved for highly elastic materials, such as LDPE. Also, one feature of this instrument is its fast data acquisition rate that, in the first seconds of the experiments, can be as high as 200 points per second.

The rollers are interchangeable, thus allowing for different surface finishes to be used. At present there are three different types of rollers: smooth, toothed, and grinded. Toothed rollers are approximately 0.2 mm deep, the pitch being 0.6 mm. Grinded rollers were obtained by cold deformation, the resulting surface being composed of small pyramid-like grooves of 1.5 mm square sides and 0.4 mm in height.

High temperatures are achieved in the instrument by immersing the sample, the rollers and the clamp in a heating bath of a fluid with a density roughly matching that of the polymer (up to 300 °C may be reached, depending on the thermal stability of the oil used). The bath is 28 mm deep, it is heated from below and, as such, there will always exist a temperature gradient along its depth. This has been measured, the temperature decreasing by about 3% between the bottom and the surface of the bath. Since the typical sample width is between 1.5 and 2.5 mm, the temperature differences between the bottom and the top of the sample are smaller than 1.0 °C for all but the highest temperatures achievable. In order to minimize further the problems associated with temperature gradients, the temperature is always controlled by a thermocouple placed at mid-sample depth, which guarantees thermal stability of the sample to between ±0.5 °C.

Materials

The uniaxial extension experiments at room temperature were performed using a polyisobutylene, BASF Oppanol B15, since this is a well characterized (see, for example Meissner 1985 and Padmanabhan et al. 1996) and simple to use material. According to the manufacturer, the average molecular weight is 85,000 and its density is 0.93 g cm^{-3} (23 °C).

The experiments shown at high temperature correspond to a 50/50 w/w blend of High Impact Polystyrene (HIPS) and a general-purpose polystyrene (GPPS), both supplied by ELF, and were performed at 150 °C.

Sample preparation

PIB samples for the elongational experiments were prepared by slow extrusion (up to 30 min per cylindrical rod 8–10 cm long and 3–4 mm thick for PIB and 1–2.5 mm thick for the HIPS/GPPS blend), either through a small orifice, using a weight loaded piston in order to produce cylindrical samples with good surface finish and constant diameter (PIB), or through a capillary rheometer (HIPS/GPPS blend). Special attention was taken to reject samples with enclosed air bubbles. Before any experiment started, any sagging the samples exhibited was removed, the samples then being allowed to relax for a few minutes further, either at room temperature (PIB) or at 150 °C (HIPS/GPPS blend).

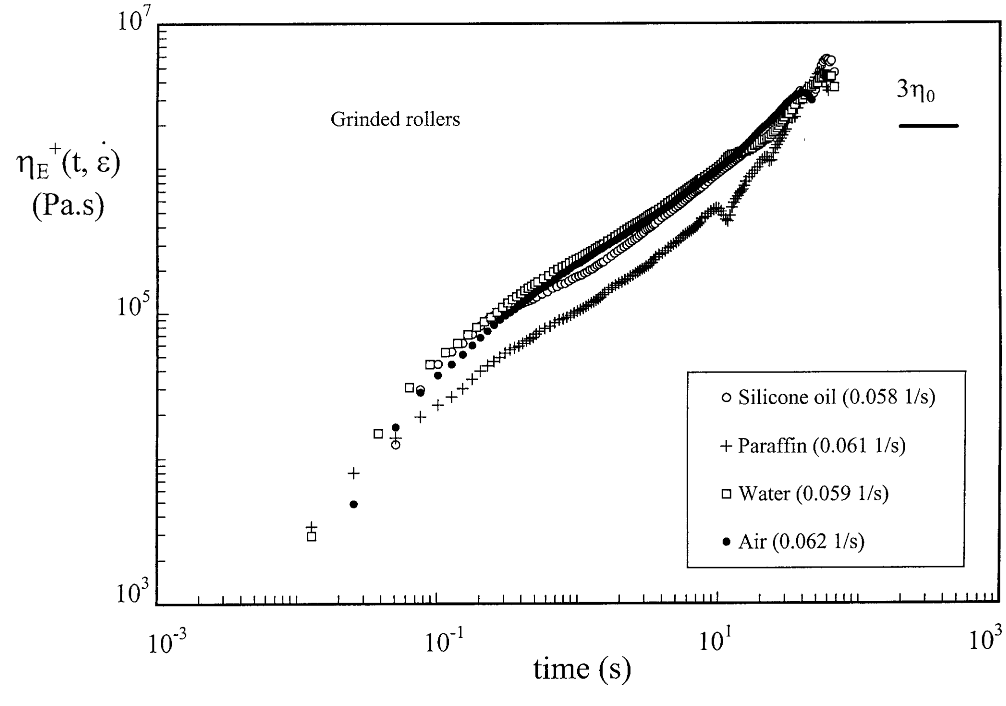


Fig. 1 Influence of the supporting medium for PIB Oppanol B15

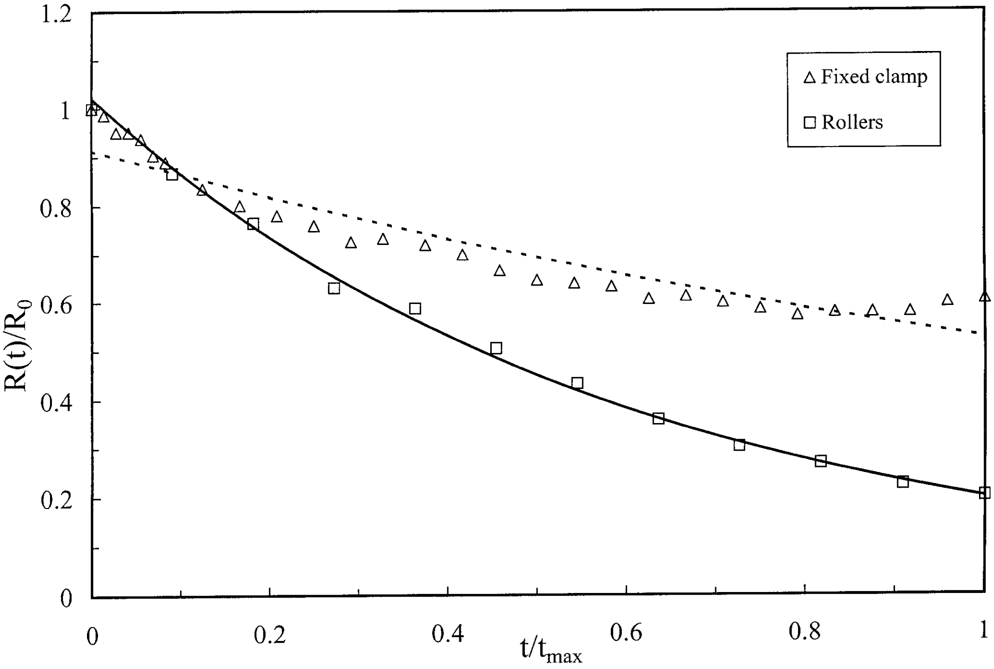


Fig. 2 Evolution of the measured radius of the samples in time for PIB Oppanol B15. Data were taken in two distinct points on the sample, next to the rollers and next to the fixed clamp lines represent the best exponential fit to the data

The cross-sectional shape of the sample may be an important factor in extensional rheometry of polymer melts due to the end-effects that arise from having samples with different cross-sections. Rectangular cross-sections have the advantage of easier clamping and lower distortion when clamped, whereas circular ones allow for easier visualization of the cross-section. For example, in our instrument the rollers are vertical and, therefore, samples with rectangular cross-section would have to be clamped with the longest side of the cross section on the vertical, which would make an accurate measurement of the true strain rate at high temperatures (where an oil bath is used, see below) extremely difficult. As such, all the samples used in this work were of circular cross-section, end-effects being avoided by strict compliance to the recommendations of Vinogradov et al. (1970) and Cogswell (1972); L/D ratios varying between 11 and 15 for PIB and between 15 and 30 for the HIPS/GPPS blend were used (sample length is kept constant at 42 mm) – see section on end-effects below.

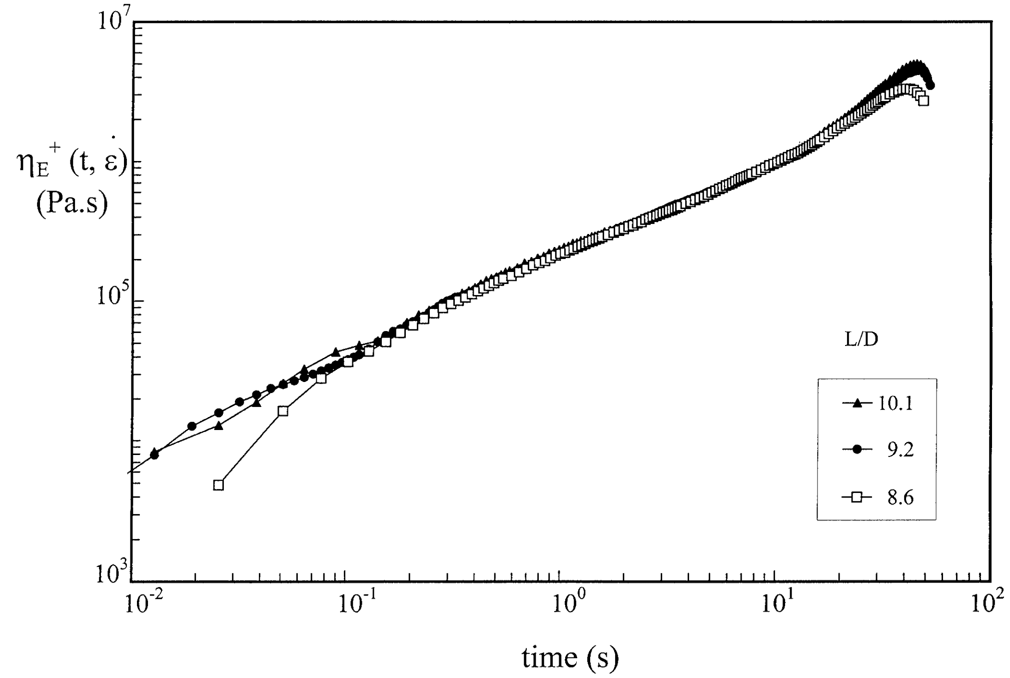


Fig. 3 Influence of L/D ratios on result reproducibility for PIB Oppanol B15

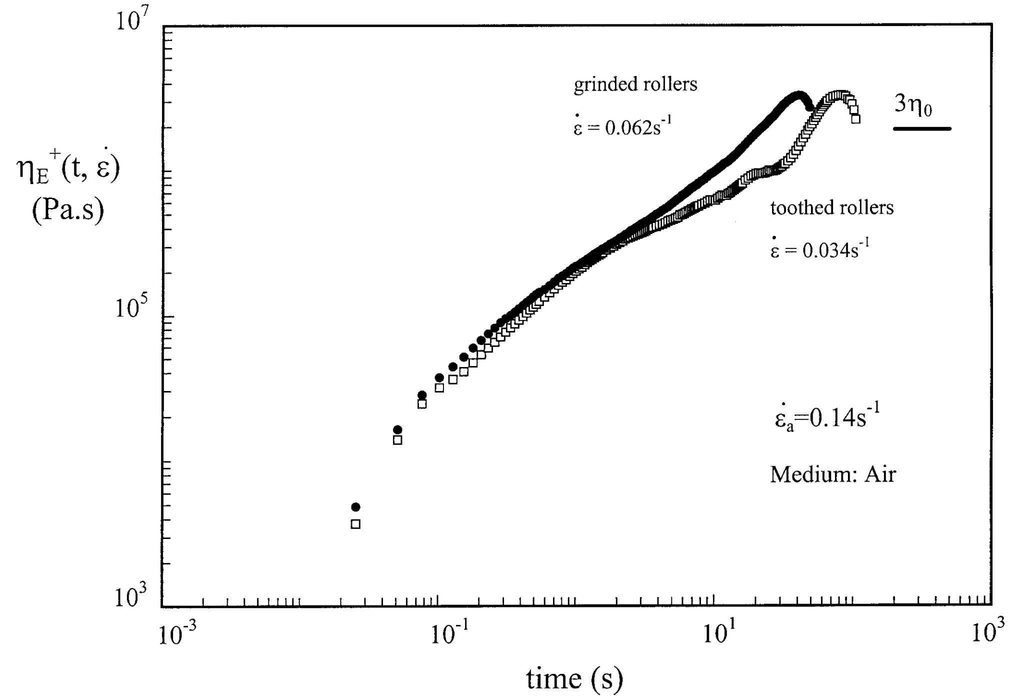


Fig. 4 Influence of the surface of the clamps for PIB Oppanol B15

Results

Influence of the supporting medium

In the RME, the use of a cushion of an inert gas prevents interaction between the sample and the supporting medium from occurring. In order to avoid the drawbacks mentioned earlier regarding the use of an inert gas cushion, a number of researchers have resorted instead to the use of heating baths when developing their instruments (as mentioned before, this is also the present case).

In order to demonstrate the importance of a correct choice for the supporting bath (which also serves as heat transfer medium), PIB samples immersed in several fluids were tested, the results being shown in Fig. 1. The fluids used were water, silicone oil ($\rho = 0.97$ g cm^{-3}), a commercial paraffin oil ($\rho = 0.85$ g cm^{-3}), and air (all the experiments were performed using the same rotational speed for the rollers). It is apparent that the experiment performed using paraffin oil shows a behavior distinct from the remainder, the transient stress being lower than for the other cases. This is possibly due to a lubrication phenomenon occurring in the surface of the rollers that may promote slippage since it appears, from the observed oscillations, that there is a stick-slip regime (another possibility, namely that of PIB swelling when immersed in paraffin oil was tested for and discarded). This example clearly shows the importance of using a liquid of adequate molecular structure and density as the heating medium, so that no interactions occur between the sample and the bath.

Influence of end-effects

The location of the section where the diameter is measured is of great importance because the existence of a fixed clamp leads to inevitable end effects. For example, Fig. 2 shows the radius evolution in the vicinity of the fixed clamp and of the rollers for PIB in air. Whereas a good description is found near the rollers (and, in fact, throughout most of the sample) showing that, at that point, the deformation is purely extensional, the data taken in the vicinity, i.e., within approximately 1 mm or less, of the fixed clamp cannot be fitted with an exponential function. In fact, the radius actually increases at long times (as a result of the elastic recoil when the sample becomes sufficiently thin at very long times), which is a clear indication that, near the clamp, the deformation is not purely extensional and is probably not even extension-dominated.

Although most of the sample is undergoing true (and well defined) extensional flow, the portion that is undergoing mixed flow may influence the data enough to compromise the accuracy of the results, a result that may be further influenced by the shape of the cross-section of the sample (see section on sample preparation). For example, Fig. 3 shows the effect of growing L/D ratio on the results for PIB in air, at 0.065 s^{-1}, it being

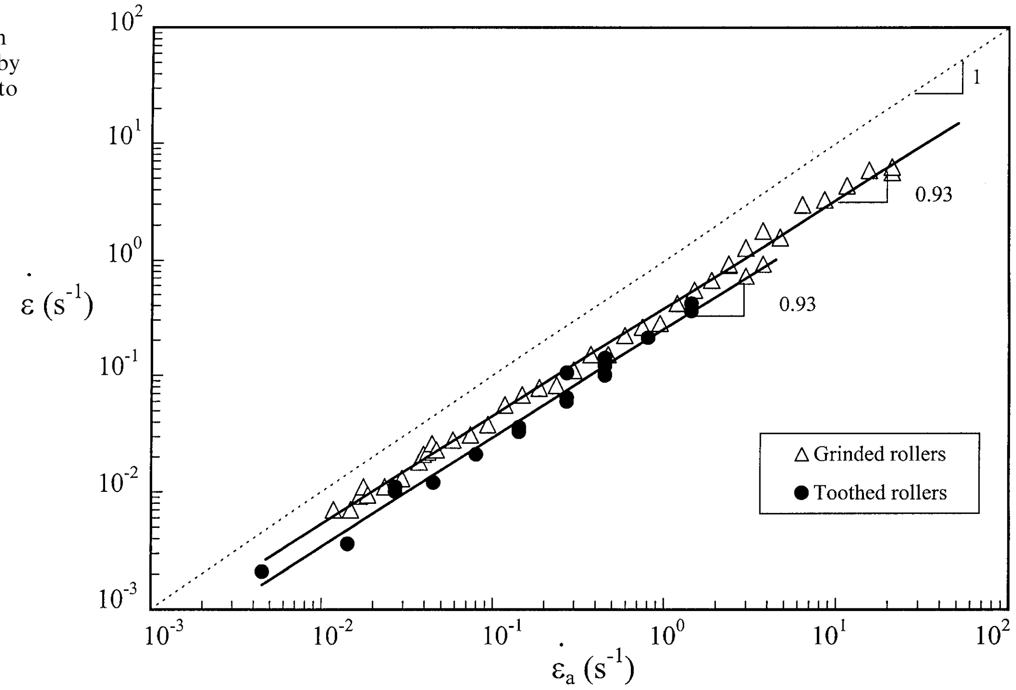


Fig. 5 Dependence of the true strain rate on the apparent strain rate. True strain rates are found by fitting the radius evolution next to the rollers; the apparent value is calculated through the set linear velocity of the rollers

apparent that, in this particular case, the importance of end-effects can be neglected for L/D ratios in excess of approximately 9. As such, it is proposed that, instead of assuming a minimum L/D ratio (as originally proposed by Vinogradov et al. and by Cogswell), preliminary tests be performed for samples with increasing aspect ratios until the error induced by the end-effects is small enough as not to affect the reproducibility of the experiments. It may even be the case that the characteristics of the material allow for L/D ratios lower than 10 to be used.

Strain rate measurement

The determination of the true value for the strain rate is perhaps the single most influential factor in obtaining

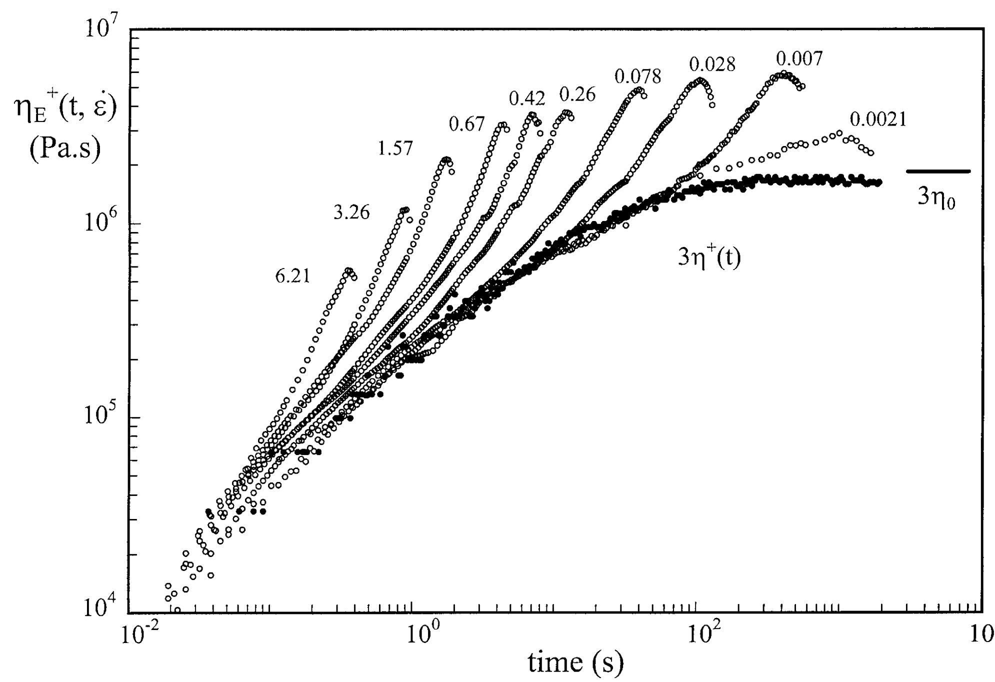
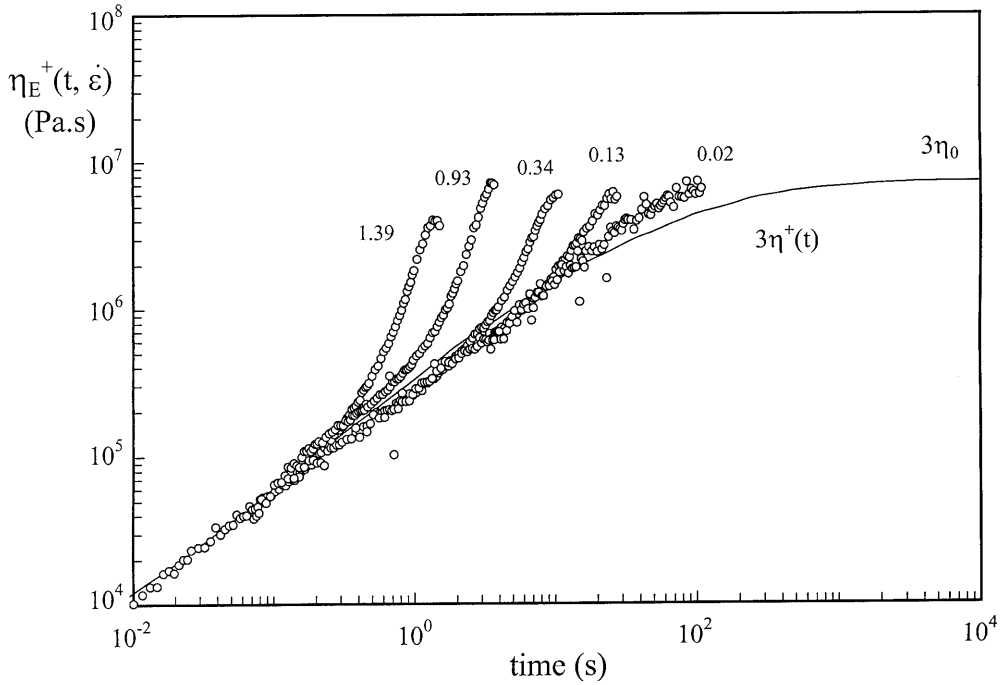


Fig. 6 Flow curves for PIB Oppanol B15 at 23 °C. The numbers next to the flow curves represent the true strain rates (in s^{-1})

Fig. 7 Flow curves for HIPS/GPPS blend at 150 °C. The numbers next to the flow curves represent the true strain rates (in s^{-1})



good quality data in extensional rheometry of polymer melts. In his work, Schweizer states that in the RME the problem of evaluating the true strain rate can be solved using a particle-tracking program. In the present case, however, the strain rate is determined from the measurement of the evolution of the sample radius throughout the experiment using image analysis software. This has led to good results, (provided, of course, that the sample is correctly loaded and initial sagging is avoided) with good exponential fits to the measured data, as can be seen in Fig. 2.

A major problem, however, and one that was not addressed by Schweizer, is the influence of the griping surface on the true strain rate. Problems related with the grip of the rollers can lead to significant deviations from the set (nominal) strain rate, due to the existence of end effects in the nip of the rollers, where it is recognized that the extensional deformation is propagated via a shear deformation of the outer layers. For example, Fig. 4 presents the results for two sets of experiments performed using both toothed and grinded rollers, again for PIB in air (smooth rollers were not used in the particular case of PIB since the samples stuck to the surface). Although the rotation speed was the same for both experiments, toothed rollers provided worse traction than grinded ones, which is not unsurprising since the latter have a rougher surface finish. This becomes evident when the values for the "apparent" strain rate calculated by the angular speed of the rollers (denoted by $\dot{\varepsilon}_a$) are compared with the real values, $\dot{\varepsilon}$, determined for each experiment by fitting the radius evolution data to an exponential.

A correction factor needs, therefore, to be introduced in order to describe the dependence of the true strain rate on the calculated value, i.e., on the value calculated from the rotation of the rollers. For the particular case of Oppanol B15, for example, Fig. 5 shows that the relation between the true strain rate and the calculated strain rate is well described by a "power-law" equation of index 0.93.

Flow curves

Only once all the possible error sources are taken into account and corrected for, is it possible to measure correctly the behavior of polymer melts in uniaxial extension, as is shown in the examples of Figs 6 and 7.

The flow curves for Oppanol B15 are presented in Fig. 6 and, as can be observed, a characterization over a very wide range of strain rates (covering more than three decades of true strain rate) was achieved. There is good agreement in the linear viscoelastic region, with the material showing an expected strain hardening behavior for higher accumulated strains. Furthermore, this data is in agreement with the results found in the literature for this particular material (for example, Meissner 1985; Padmanabhan et al. 1996). It should be noted that all the curves shown in the figure are represented until the point of rupture, which is considered to be the point where a substantial sudden decrease in the measured tensile stress is observed.

Finally, Fig. 7 shows the example of the HIPS/GPPS blend, i.e., results at high temperature, and, again, the results are of good overall quality, a wide range of strain rates having also been achieved (although not as wide as for PIB since the rapid movement of the rollers disturbs the both oil and masks the true signal at high strains, when the sample has become very thin).

Conclusions

The aim of this paper was to complement and expand the results of a recent paper by Schweizer (Schweizer 2000), which was intended to be applicable only to the Rheometrics RME. The main conclusions from our study are that:

1. The correct choice of supporting medium is very important as, in addition to possible buoyancy problems, liquid-induced slippage at the rollers can have a major influence in the measured force curves.
2. End-effects must be taken into account by performing experiments with samples of varying L/D ratios, so as to ensure that the influence of the end-effects on the data is negligible. This also means that the location where the strain rate is determined is very important for this type of extensional rheometers.
3. The true strain rates of the process can be very different from those calculated from the angular speed of the pulling rollers. Thus, it is of paramount importance that the true strain rates are measured in-line, whether by particle tracking or via the monitoring of radius evolution.
4. In order to achieve as high strain rates as possible, the grip of the sample must also be as high as possible, since the extensional deformation is propagated from the pulling elements via a shear deformation of the outer layers of the sample. In general, this can be achieved by changing the surface finish of the pulling elements.

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