

High rate extensional rheometry of polymer melts

Martin Rides and Crispin Allen

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Martin Rides and Crispin Allen
NPL Materials Centre
National Physical Laboratory
Teddington, Middlesex
United Kingdom
TW11 0LW

ABSTRACT

The NPL extensional rheometer has been developed further to test polymer melts at high strain rates. Results of extensional viscosity measurements up to nominal strain rates of 100 s^{-1} for several polyethylene melts are reported. Repeatability of the results is demonstrated to be good, even at the highest rate. The materials exhibit significant differences in their behaviour, particularly in their additional strain hardening to failure. Sources of error due to the acceleration of the motor and the differences observed between the set and measured strain rates have been investigated, and the magnitude of these errors estimated. The effect of these errors on the measurement of tensile stress growth coefficient values (transient extensional viscosities) has been determined using an analysis of measurement uncertainties. This showed that the errors increased significantly as strain rate increased, and also for increasing strains above a value of approximately 1.

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National Physical Laboratory
Teddington, Middlesex, UK, TW11 0LW

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on measurements related to the processability of materials

Approved on behalf of Managing Director, NPL
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1. INTRODUCTION

In many plastics-forming processes the polymer melt undergoes significant extensional or stretching flow, for example in blow moulding, vacuum forming, film extrusion 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 moulded product, for example due to the stresses generated by the extensional deformation that are subsequently frozen into the product. However, established rheological techniques predominantly characterize the behaviour of polymers in shear and it can prove difficult to relate the behaviour measured in shear with that observed in processing where the deformation is predominantly extensional, for example in blow moulding. An ability to characterize their behaviour more appropriately will have benefits in materials development and in process and product design.

The techniques most suitable for characterizing the extensional flow behaviour of polymer melts are converging flow methods, which use capillary extrusion rheometry data, and stretching flow methods. These techniques have been the focus of recent research and were critically reviewed [1, 2]. The converging flow approach can be used to obtain qualitative data on the extensional flow behaviour of materials [3], but to obtain reliable quantitative data then the stretching flow methods should be used [4,5].

However, stretching techniques available for the characterisation of the extensional flow behaviour of polymers are very limited in number, and those that do exist are generally not suited to testing at high strain rates. Instruments are generally limited to a maximum strain rate of $\approx 1 \text{ s}^{-1}$ [1, 5].

To address the measurement of polymer melts at high strain rates the NPL extensional rheometer was developed further. This report describes that instrument and discusses various measurement issues that were identified. It presents results demonstrating the use of the instrument in characterizing the flow properties of three polymers that exhibit significant differences in their extensional flow behaviour: a high density polyethylene (HDPE), a low density polyethylene (LDPE) and a linear low density polyethylene (LLDPE).

2. HIGH RATE EXTENSIONAL RHEOMETER

An instrument for measuring the extensional viscoelasticity of polymer melts has been developed to operate at high 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 used were either approximately 20 mm or 80 mm in length. The rotating clamp, by winding up the specimen, controlled the rate at which the specimen was stretched. In using a rotating clamp, measurements at constant strain rate can be obtained simply by using a constant rotation speed. More importantly, the use of a rotating clamp results in an instrument that is not limited in its maximum strain capability. For an instrument that uses translating clamps the maximum strain that can be achieved is limited by the dimensions of the instrument.

The fixed clamp was used to measure the tensile force developed in the specimen during stretching. This clamp was mounted on a leaf spring, the displacement of which was measured using a non-contacting optical transducer. The force was then calculated from the force - displacement characteristics of the leaf spring, determined through calibration.

The specimens were fixed to the clamps using an epoxy adhesive. After loading a specimen into the instrument, the specimen and clamps were then 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 has a maximum operating temperature of 250 °C, limited by the maximum operating temperature of the silicone oil used. By using a larger diameter winding drum and short specimen lengths, high strain rates up to $\approx 100 \text{ s}^{-1}$ have been achieved using this instrument. Further developments of the data logging facilities were necessary to allow for the capture of data at high sampling rates up to 2000 per second.

Transient extensional viscosity values are presented, according to nomenclature convention, as tensile stress growth coefficient values [6]. For full details of the measurement principle, nomenclature and for details of the analysis of the experimental data see reference [4].

3. RESULTS

Three polyethylenes exhibiting significant differences in their extensional flow behaviour were investigated in this work: a high density polyethylene (HDPE), a low density polyethylene (LDPE) and a linear low density polyethylene (LLDPE). The NPL references for these materials are:

HDPE	HFU000
LDPE	HGE000
LLDPE	HGF000

Initial testing was undertaken to assess the performance of the instrument modified for high rate testing, and is reported in the following sections.

3.1 Instrument acceleration

To obtain true tensile stress growth coefficient data one should have constant rate deformation of the specimen from the start of the test. For very high rate testing in particular this is not practical due to the inertia of the instrument and the very short test durations. The performance of the motor over the first revolution was predicted using the specification data for the drive motor and was also measured in calibration tests to determine its true response, Figure 2. The specification for the acceleration of the servo motor was 250 rev/s^2 . Higher accelerations were theoretically possible using the motor, but were not achievable whilst keeping the motor under programmed control. The results demonstrated that the motor's performance was slightly worse than that predicted, presumably due to the added inertia elements of the specimen, drum and drum support. For tests at strain rates up to approximately 50 s^{-1} the error in time (and thus average rotation speed) taken to complete one revolution from a standing start was less than approximately 5%. For the second rotation from start-up the error between the set and measured speeds was negligible.

In the more extreme case of testing at 100 s^{-1} , for tests up to a strain of 4 the predicted error in the time taken was approximately 30%. For shorter tests up to a strain of 3 this value increased to approximately 35%. These values fall below 10% for tests at a strain rate of approximately 50 s^{-1} . The strain at which the velocity reaches the set value for a test at 100 s^{-1} is estimated to be approximately 1.6, and 0.4 at 50 s^{-1} . Thus, as specimens normally failed at greater strain values than these, the strain rates at failure were equivalent to those set. Also, as a first approximation, only correction for the strain/time error need be applied for tests above approximately 50 s^{-1} as the magnitude of the errors are considered not to be too significant below that strain rate. For strain rates greater than 50 s^{-1} the magnitude of the

correction can be estimated using linear interpretation of the above information.

3.2 Measurement of strain rate using a video camera

It is desirable to check that the specimens deform as anticipated, given the set speeds of the instrument. For this purpose a video camera was used to visualise and hence measure the diameter of the specimen during testing. This information permitted the strains in the specimen during testing to be determined, and hence also the strain rates. This has demonstrated that the instrument performs well, with measured strain rates being approximately 95% of the set strain rates over a range up to 25 s^{-1} , Figure 3. Evaluation at higher strain rates was not possible as a shorter sample length of 20 mm length is used and it was not physically possible to get the camera into a suitable position to record the test.

All strain rates quoted below are nominal strain rates, without correction for acceleration and other effects. The implications of these errors for determination of extensional viscosity values are considered later.

3.3 Extensional viscosity results for the three polyethylenes

Results of testing of three polyethylenes clearly demonstrated the high rate capability of the instrument. For the HDPE (HFU000) strain rates up to 100 s^{-1} were achieved with test times less than 0.1 s, Figures 4 and 5. It is noted that strains are the natural logarithm of the extension ratio and thus a strain rate of 100 s^{-1} is significantly greater than that of 10 s^{-1} in terms of the rate of deformation occurring: a strain rate of 1 s^{-1} corresponds to stretching the sample 2.7 times its length per second, a rate of 10 s^{-1} corresponds to 22000 times its length per second, and 100 s^{-1} to 2.7×10^{43} times its length per second, though in practice the times for which these latter deformation rates occur is significantly shorter than one second and thus the total strains are also significantly shorter.

The repeatability of results is shown to be quite good, even at the highest strain rate of 100 s^{-1} , Figure 6. Several repeat tests overlap well, even to the extent of the oscillations in the data introduced due to the resonating force sensor.

It was noted that the oscillatory waveform evident in some of the results is particularly pronounced at a test rate of 40 s^{-1} , Figures 5 to 7. This was considered to be due to the fact that the resonant frequency of the load measuring system, which is approximately 40 Hz, corresponds to the effective rate of loading at this strain rate. The resonating appears to be less pronounced at 100 s^{-1} . Data obtained in the presence of resonance was in agreement with data obtained using a longer specimen for which resonance was not a problem, Figure 6. The main cause for concern with the resonance is in its effect on the accuracy of the values obtained at short time scales that are comparable with the period of oscillation of the resonance, Figure 6. Resonance of the force sensor is considered difficult to overcome due to the need for a sensor of low force capability, and thus low stiffness. However, the use of specimens of longer length may provide a means to minimise the effect.

For the LLDPE (HGF000), which has little chain branching, there appears to be some, albeit limited, additional strain hardening at strain rates above 10 s^{-1} , Figures 8 and 9. For both the HDPE (HFU000) and LDPE (HGE000) there appears to be greater additional strain hardening at very high strain rates compared with intermediate and lower rates, Figures 5 and 11 respectively. For LDPE (HGE000) the additional strain hardening is greatest of the three materials as would be expected for a LDPE having a greater degree of chain branching.

The use of the short length specimens of ≈ 20 mm is shown not to be problematic at strains in excess of 0.5 at 25 s^{-1} , 0.2 at 10 s^{-1} and 0.05 at 1 s^{-1} , Figures 4, 6, 8 and 10. Below these values the results differ more markedly but may be due to the very short times (and low forces) that they correspond to (<0.05 s). It is accepted that at times less than 0.01 s the scatter in results increases, presumably due to the acceleration of the instrument, Figure 5. Although not conclusive, but most clearly shown by HGF000 and HGE000, Figures 9 and 11, an examination of the viscosity versus time curves shows that at times less than 0.01 s the lowest value extensional viscosity data corresponds to that obtained at the highest rates. This is consistent with the effects of the initial acceleration of the drum in that the forces generated will be lower as the strains are lower than expected. As a consequence the derived extensional viscosity values will also be lower. On this basis, when examining viscosity versus time plots it is more appropriate to assume that, at short times, the data obtained at the lower strain rates are more reliable.¹

3.4 Assessment of uncertainties in extensional viscosity testing

As demonstrated previously [7], the uncertainties in extensional viscosity determination grow rapidly at large strains primarily due to the rapid decrease in cross-sectional area of the specimen with a resultant rapid decrease in the measured force. At high strain rates acceleration issues also become significant, as discussed above. Due to the acceleration behaviour of the instrument the strain achieved in a given time is less than that that would be achieved if an instantaneous acceleration were assumed. Furthermore, the difference in the measured to set strain rates, as observed using the video camera, has an effect on the accuracy of the derived results. An analysis of the uncertainties in extensional testing, details of which are presented elsewhere [7], was used to estimate the uncertainties in testing for the HDPE (HFU000) at 1 s^{-1} , 25.5 s^{-1} and 100 s^{-1} , taking into account these additional errors, Figures 12 to 14. The errors in the strain rate due to the acceleration of the drum and the visual observations has been accounted for by assigning a 7%, 15% or 40% error to the angular speed of the drum for set strain rates of 1 s^{-1} , 25.5 s^{-1} and 100 s^{-1} respectively. The contribution due to the visual observations was set at 5%, the remainder being due to the acceleration of the drum. The plots, Figures 12 to 14, show the measured tensile stress growth coefficient data along with calculated values, assuming a power law fit, and 95% confidence limits to the calculated data. The results show a rapid increase in the uncertainties as strains increases beyond a value of approximately 1, with the effect becoming more significant at higher strain rates. The 95% confidence limits to the data are not true confidence limits because the errors due to the acceleration and strain rates are systematic. The effect of both the acceleration phase and the error in strain rates observed using the video camera would be to result in lower transient stress growth coefficient values being determined than actual. Thus the upper 95% limit gives an indication of the maximum shift in data that would be necessary to correct for these effects, rather than due to random uncertainties in the various parameters.

4. DISCUSSION AND CONCLUSIONS

High strain rate testing puts particularly strenuous demands on extensional measurement instrumentation in terms of the high speeds required and very short test durations. The

¹ Tensile stress growth coefficient versus time plots are found useful as data obtained at different strain rates tend to form a master curve, with departure from that master curve occurring at high strains due to additional strain hardening.

combination of these factors requires very high acceleration rates, which were achieved in this work using a servo motor. However, above a strain rate of approximately 50 s^{-1} the error in the strain rate became a more significant factor affecting the accuracy of the results. At a set strain rate of 100 s^{-1} the error in the strain at a nominal strain of 4 was of the order of 30%. However, the strain rate at the point of specimen failure was as programmed: the motor's acceleration phase having been completed by then. Thus, as a first approximation, only correction for the actual strain achieved is required. Visual determination of the strain rates occurring during testing, at strain rates up to 25 s^{-1} , were within approximately 5% of the set value thus giving increased confidence in the instrument and procedures.

When testing at high rates, although resonance of the load sensor resulted in data having an oscillatory waveform superimposed, the data still agreed with data obtained using a longer specimen for which resonance was not a problem.

The use of different length specimens had negligible effect on the magnitude of the extensional viscosity values measured, with good agreement being obtained over a range of strain rates. Using short specimens is essential in order to obtain high strain rate data.

Repeatability of testing even at 100 s^{-1} was good. The feature of the extensional behaviour that is hardest to achieve repeatably is the point of failure of the specimen. It is reasonable to assume that where repeat testing is carried out the highest strain to failure is the most reliable: any premature failures being due to inhomogeneities in the specimens.

An analysis of the uncertainties, taking into account the errors due to the instrument's acceleration behaviour and the observed discrepancy between the set and measured strain rates, has indicated the potential magnitude of the effect of these factors on the determined tensile stress growth coefficient values. At 100 s^{-1} the effect becomes quite significant at high strain values.

The three polyethylenes qualitatively differed most significantly in their additional hardening behaviour. The LLDPE exhibited little additional strain hardening, whereas the LDPE exhibited very significant additional strain hardening, and is a reflection of the degree of chain branching of these materials.

5. ACKNOWLEDGEMENTS

The work was carried out as part of a project on viscoelastic measurement techniques for polymer melts (MPM 1.2, milestone 12). This project is part of a programme of underpinning research financed by the Engineering Industries Directorate (EID) of the Department of Trade and Industry on measurements related to the processability of materials.

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Ref: MATC(A)71_high rate extension_6dec01_v#4.doc

FIGURES

Figure 1: High rate extensional rheometer for testing molten polymers.

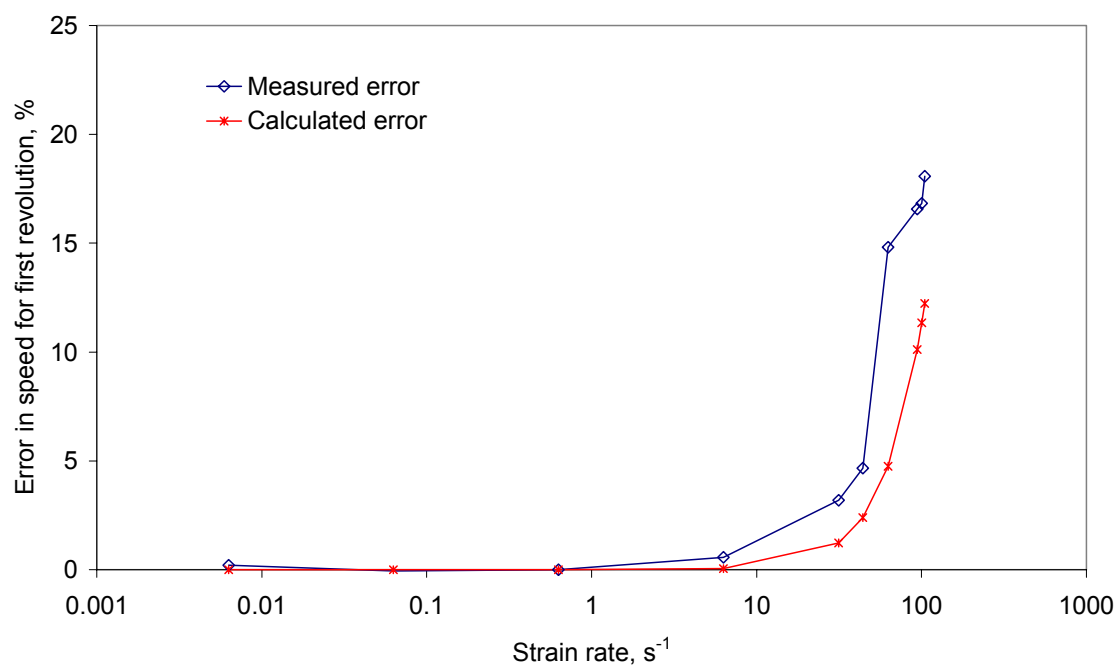


Figure 2: Error in rotation speed due to drum acceleration (using specimen length of ≈ 20 mm and drum radius of 40 mm).

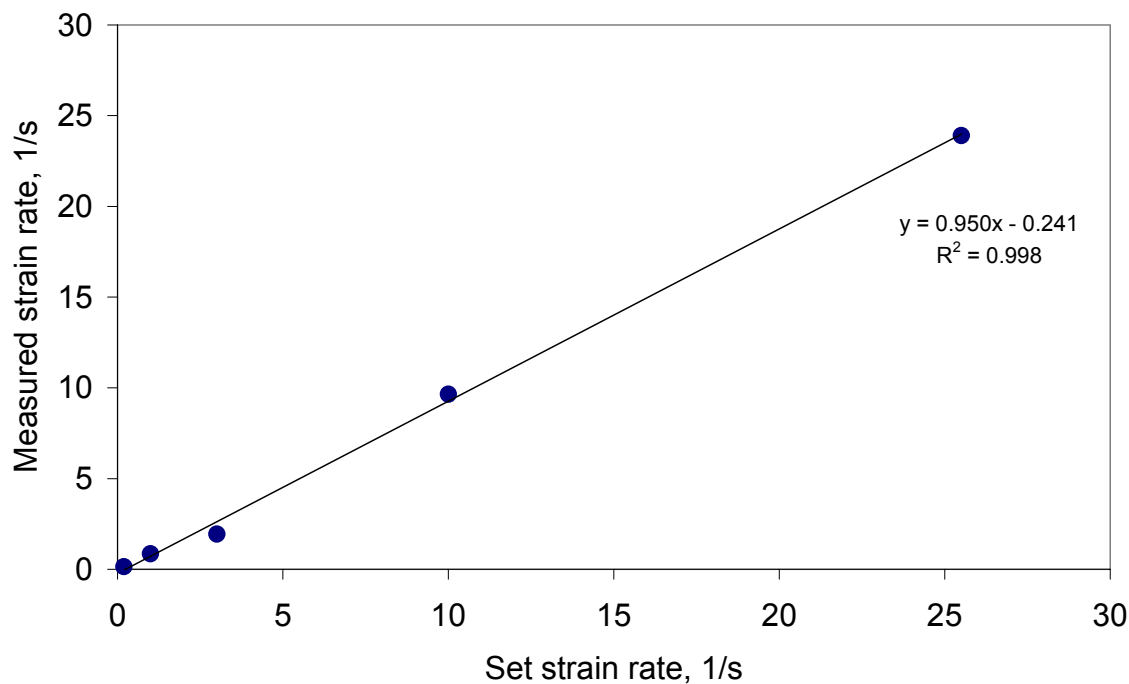


Figure 3: Comparison of set with optically measured values of strain rate for the extensional rheometer, the measured values being determined using a video camera.

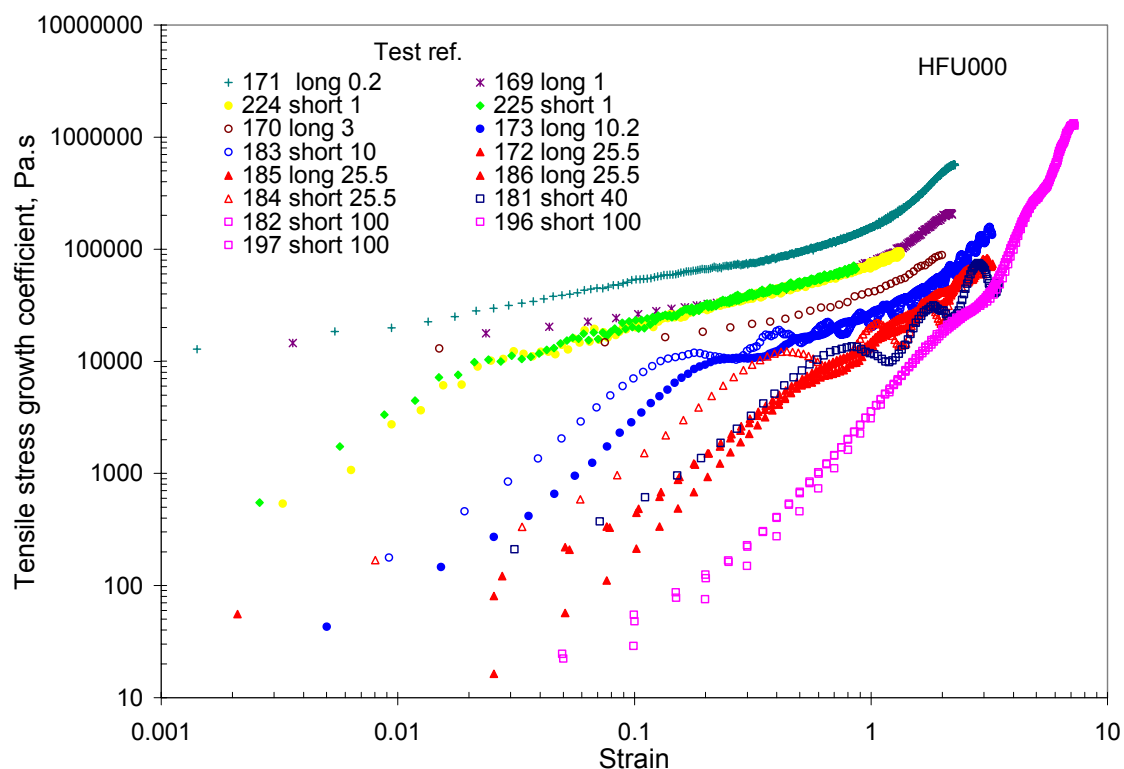


Figure 4: Extensional viscosity data as a function of strain for a HDPE (HFU000) at 150 °C. The legend presents: test reference, specimen length (long or short) and strain rate (s^{-1}).

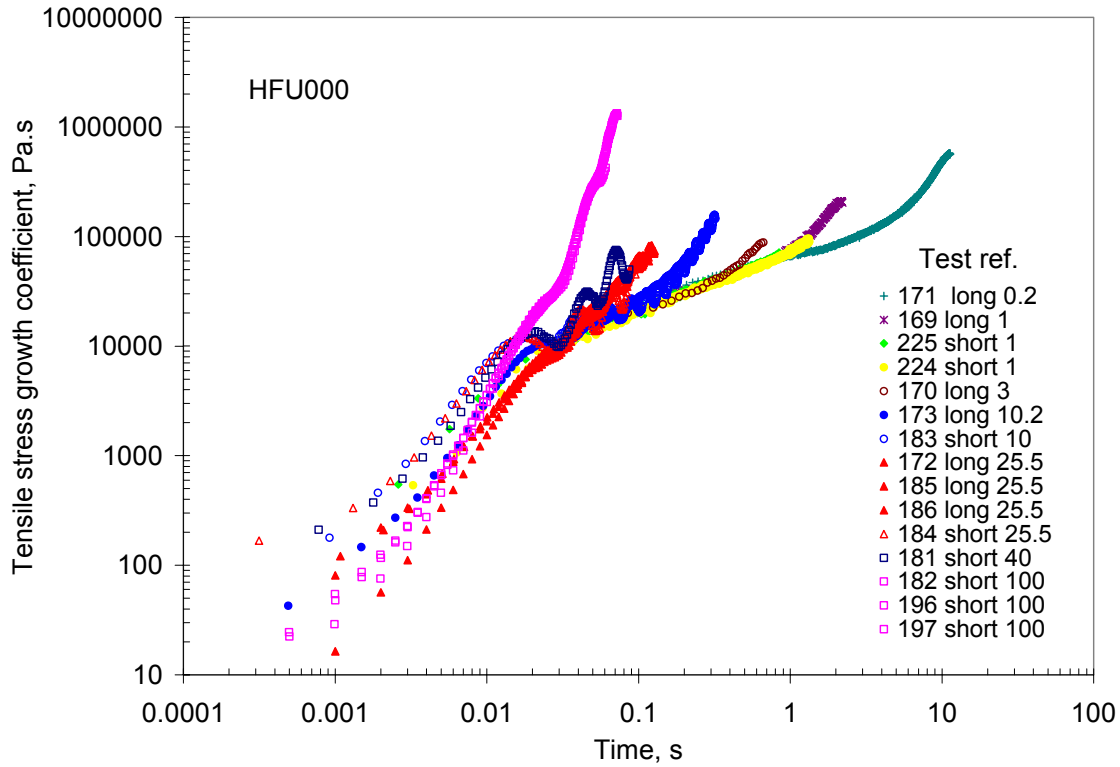


Figure 5: Extensional viscosity data as a function of time for a HDPE (HFU000) at 150 °C. The legend presents: test reference, specimen length (long or short) and strain rate (s^{-1}).

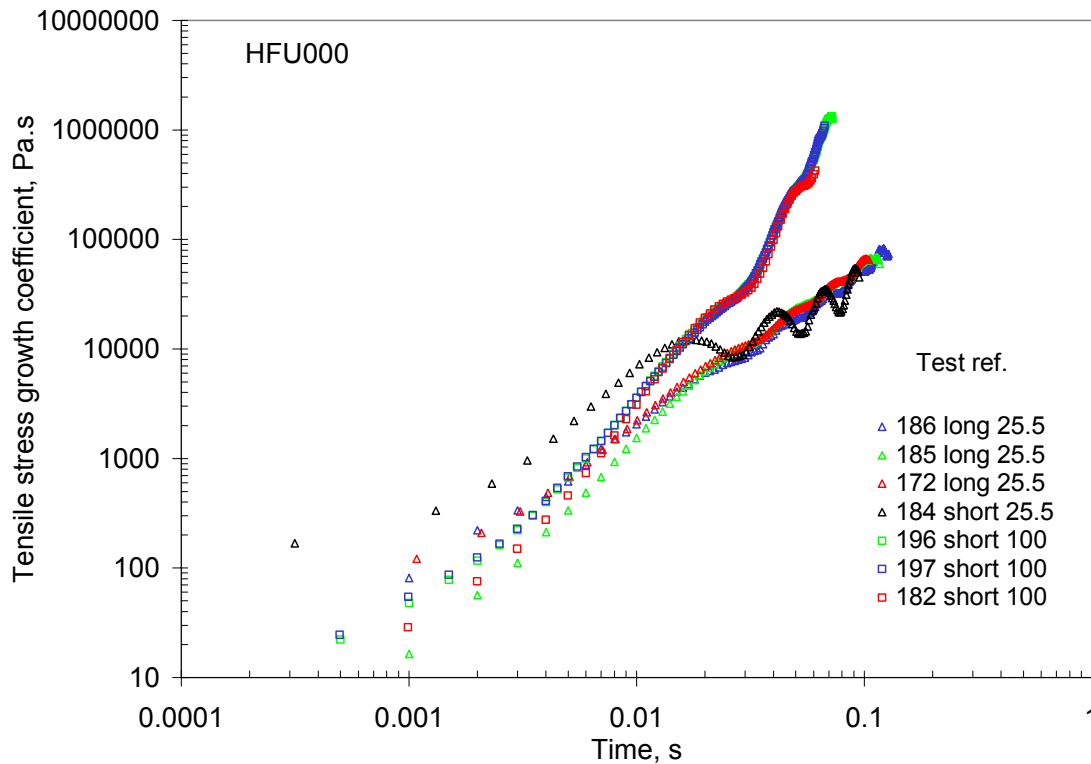


Figure 6: Measurements demonstrating the repeatability of extensional viscosity data, presented as a function of time for a HDPE (HFU000) at 150 °C. The legend presents: test reference, specimen length (long or short) and strain rate (s^{-1}).

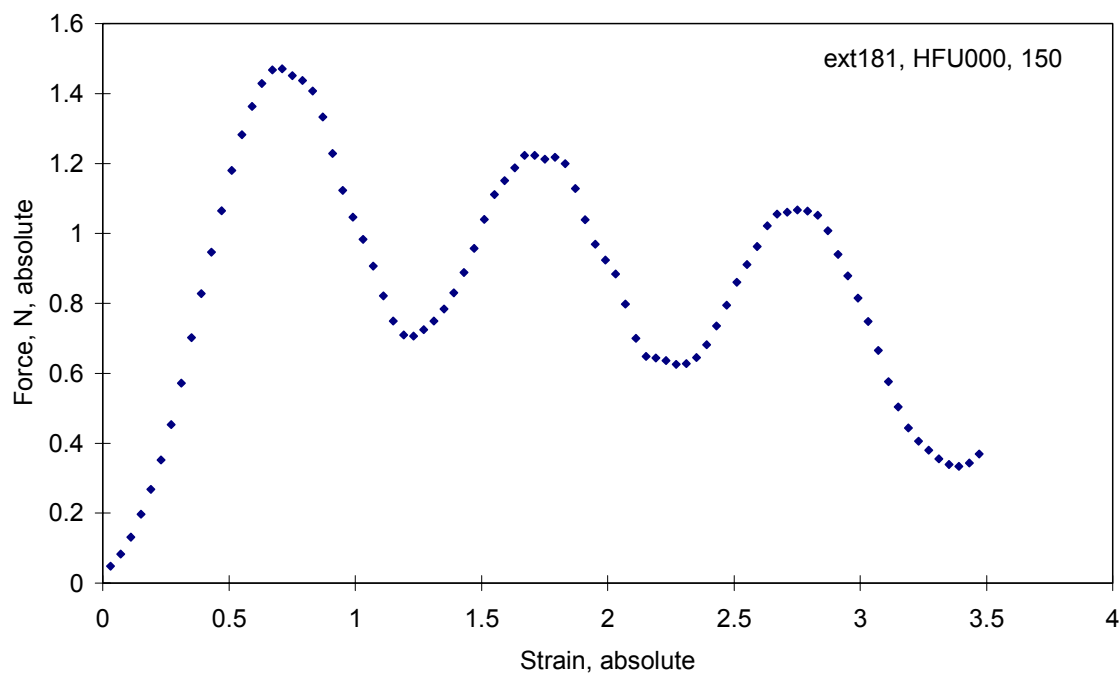


Figure 7: Resonance of the force measuring system as observed when measuring the extensional viscosity of a HDPE (HFU000) at 150 °C. Strain rate = 40 s^{-1} , thus a strain of 1 corresponds to a time interval of 0.025 s seconds.

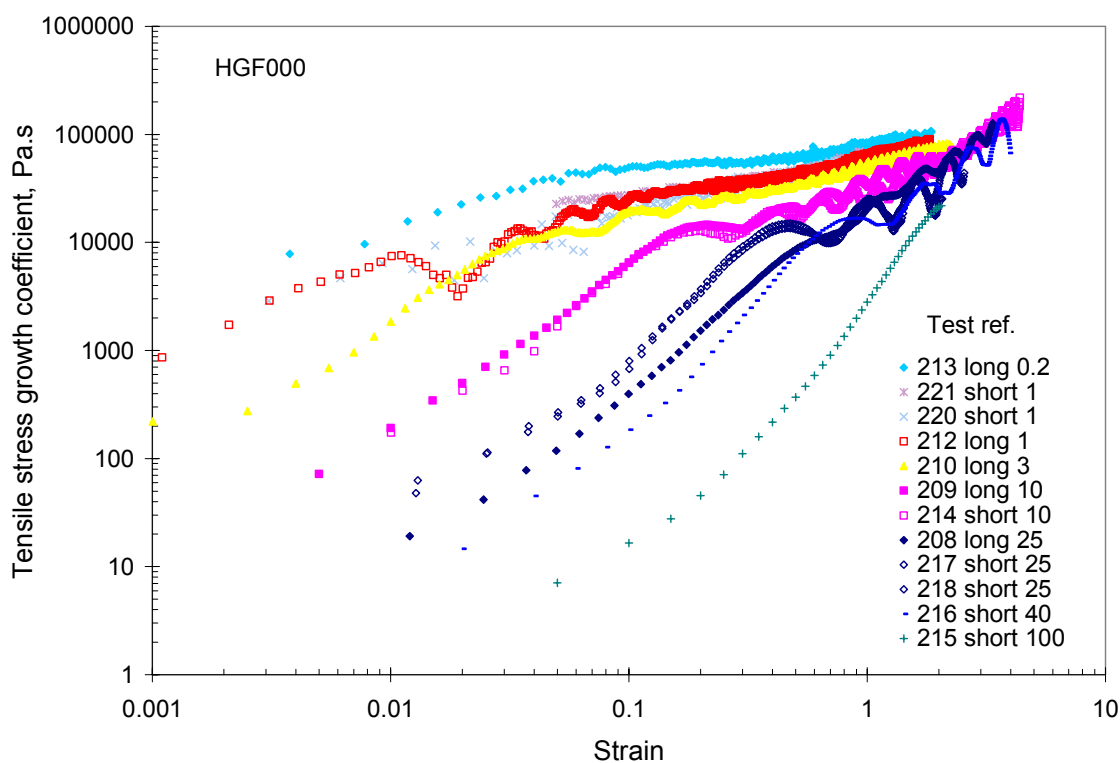


Figure 8: Extensional viscosity data as a function of strain for a LLDPE (HGF000) at 150 °C. The legend presents: test reference, specimen length (long or short) and strain rate (s^{-1}).

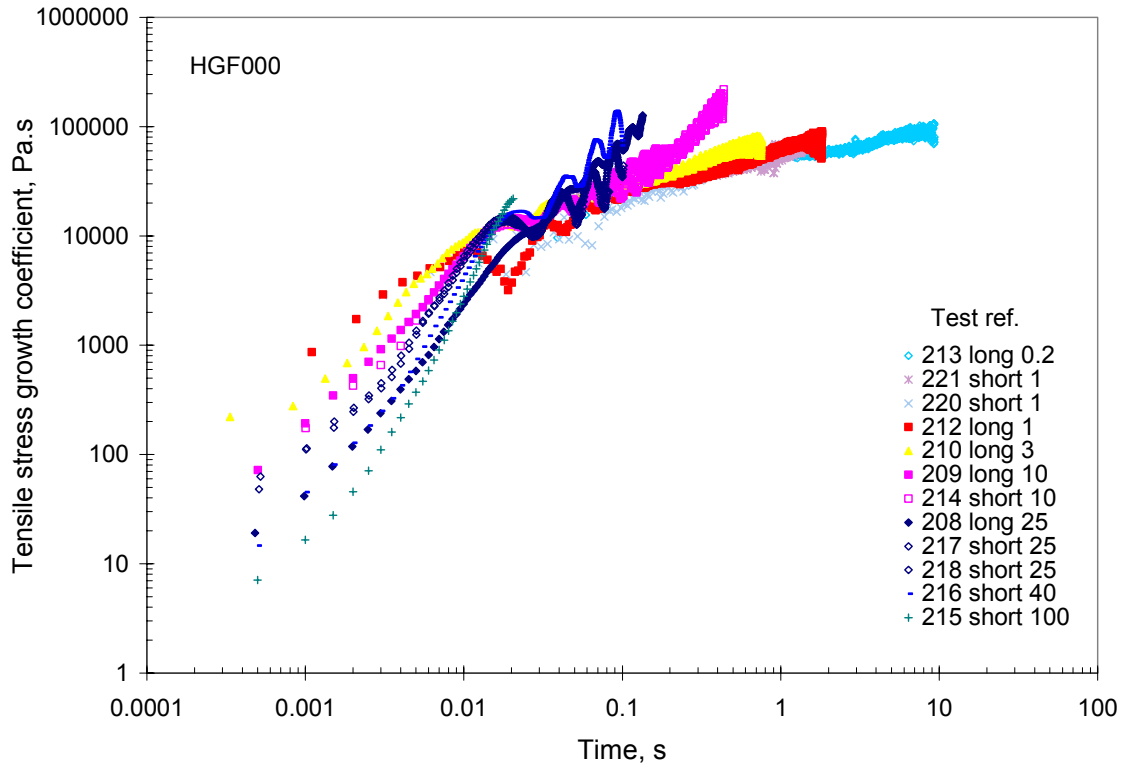


Figure 9: Extensional viscosity data as a function of time for a LLDPE (HGF000) at 150 °C. The legend presents: test reference, specimen length (long or short) and strain rate (s^{-1}).

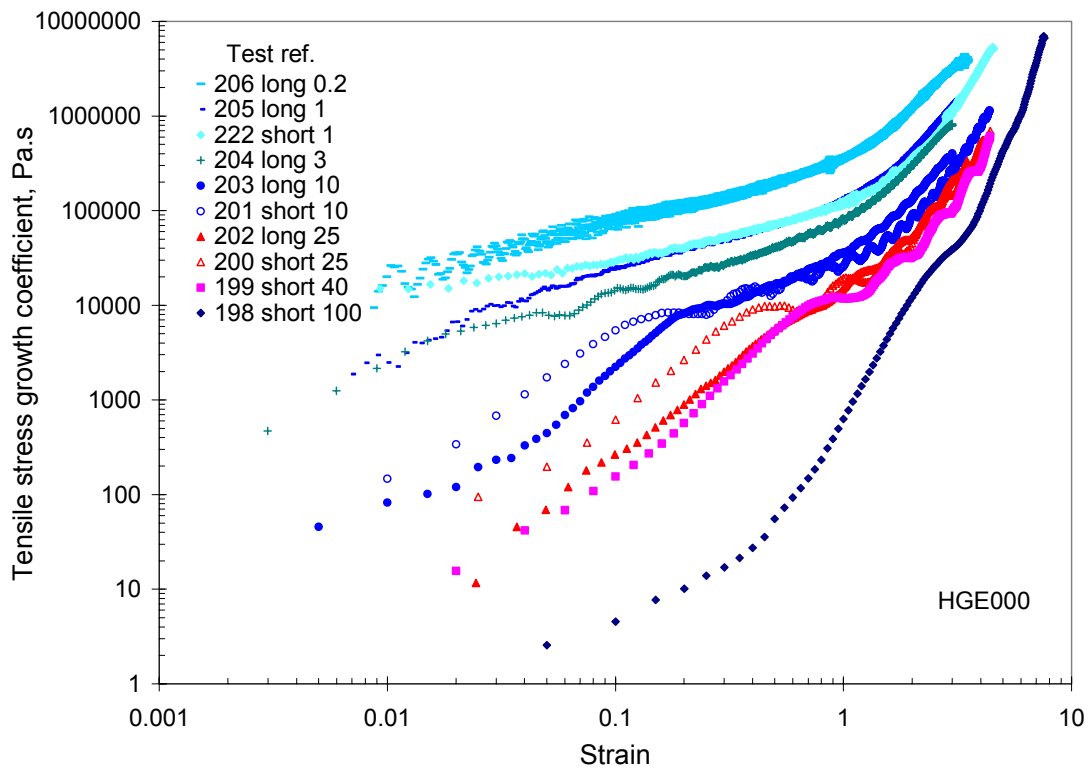


Figure 10: Extensional viscosity data as a function of strain for a LDPE (HGE000) at 150 °C. The legend presents: test reference, specimen length (long or short) and strain rate (s^{-1}).

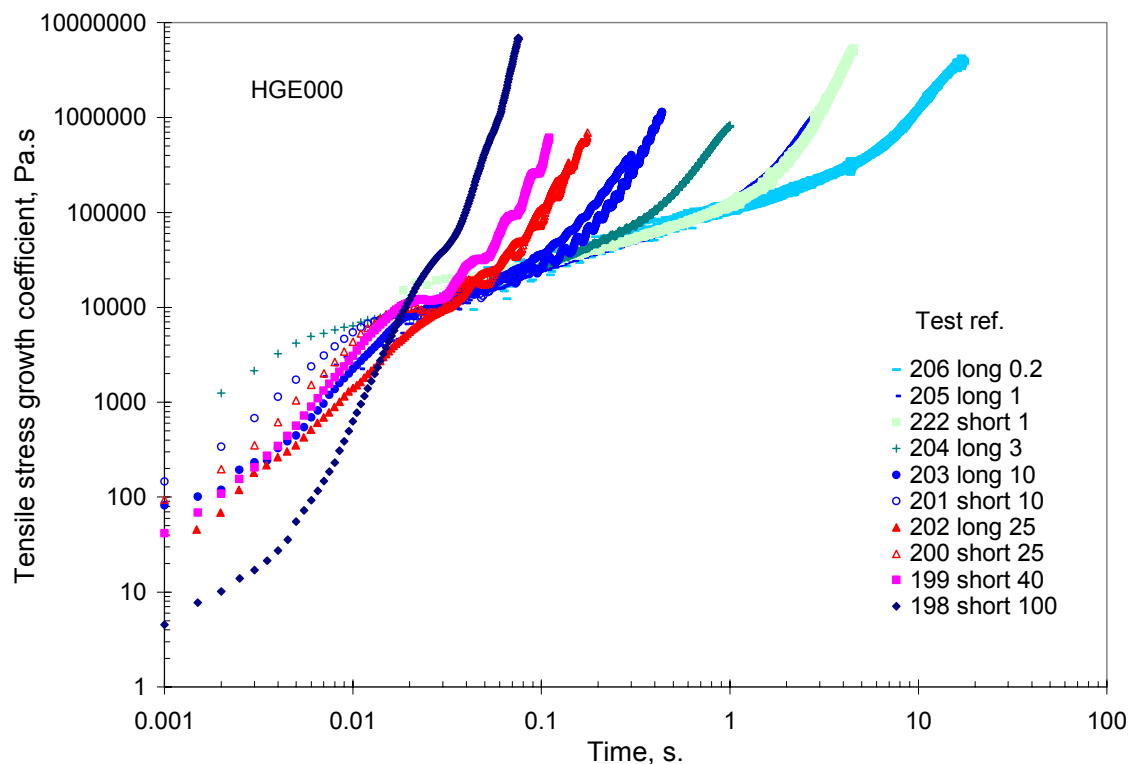


Figure 11: Extensional viscosity data as a function of time for a LDPE (HGE000) at 150 °C. The legend presents: test reference, specimen length (long or short) and strain rate (s⁻¹).

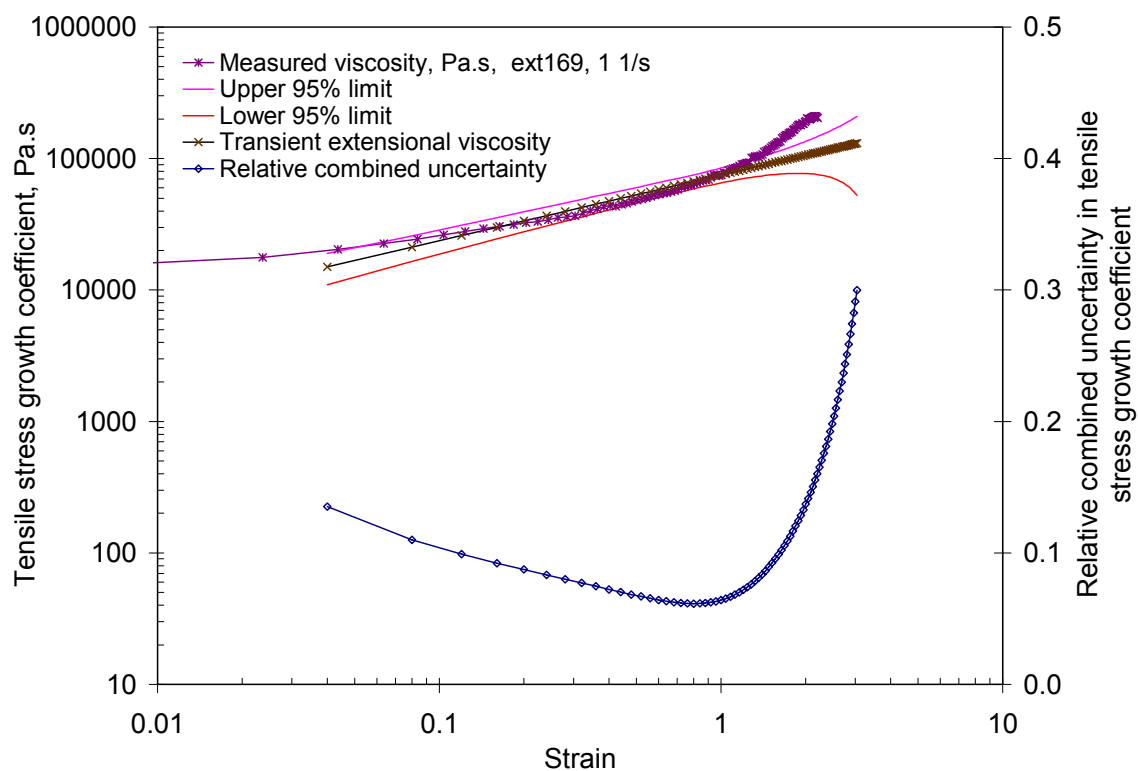


Figure 12: Assessment of the uncertainties in extensional viscosity – HFU000 at 1 s⁻¹ (test ref ext169).

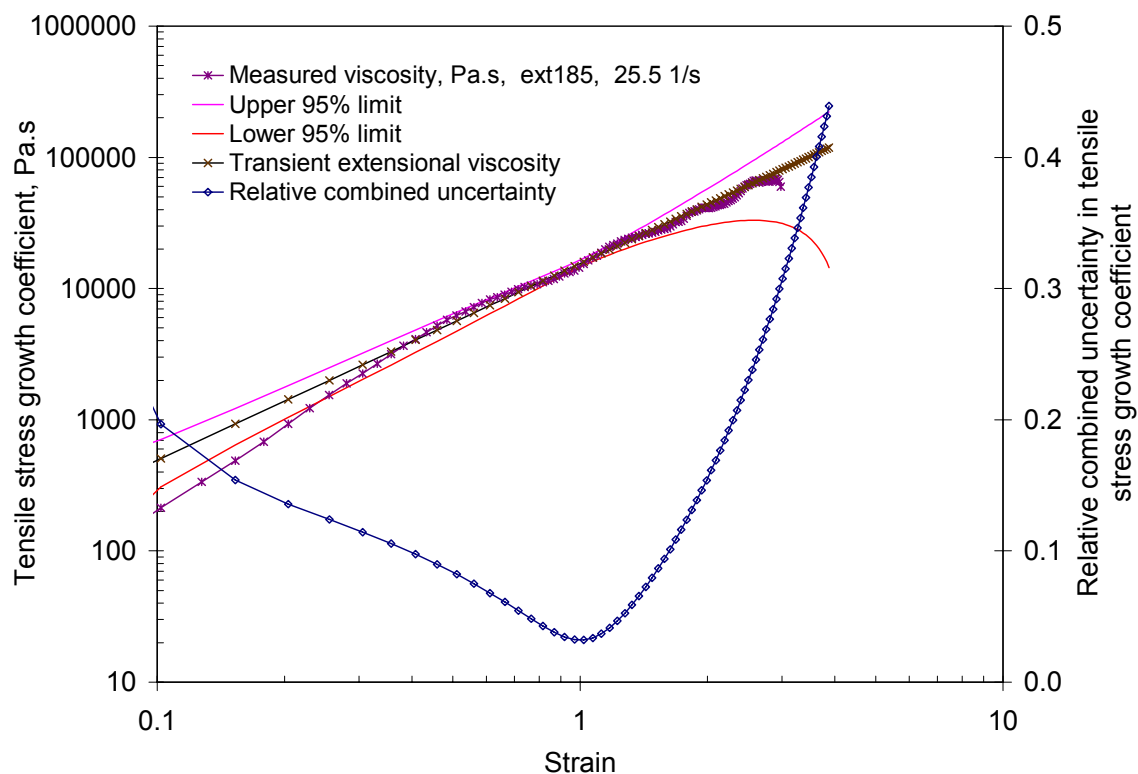


Figure 13: Assessment of the uncertainties in extensional viscosity when testing at high rates – HFU000 at 25.5 s^{-1} (test ref ext185).

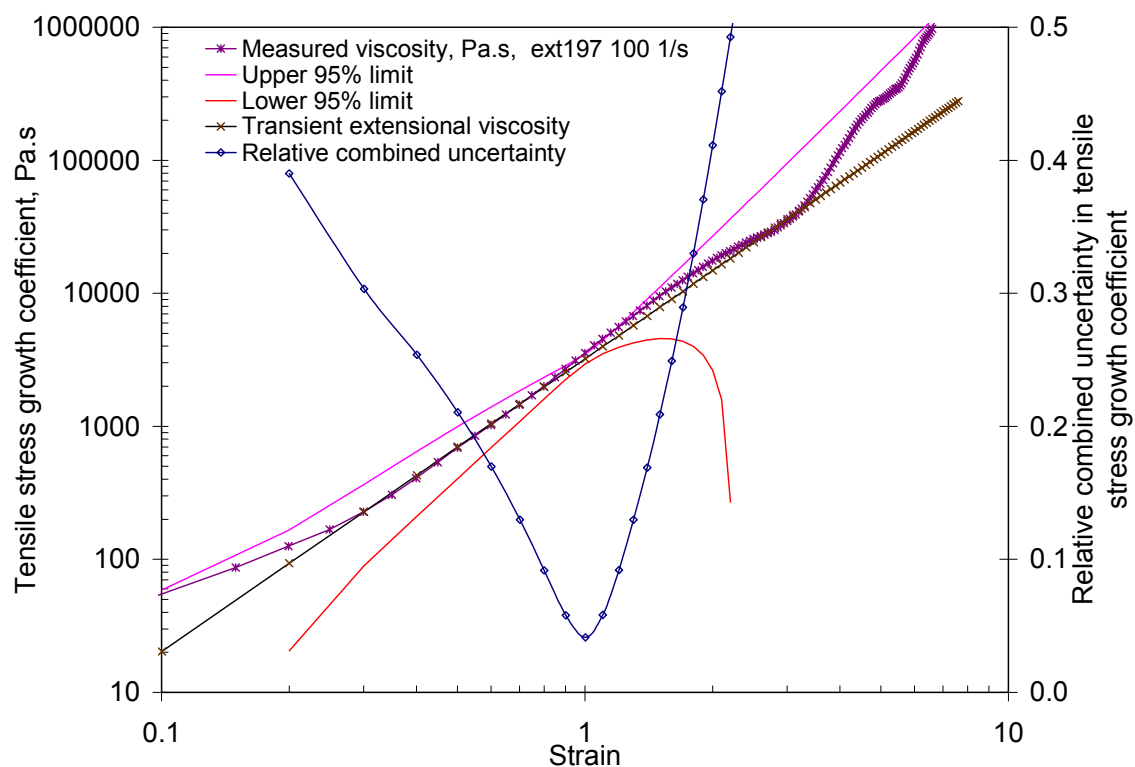


Figure 14: Assessment of the uncertainties in extensional viscosity when testing at high rates – HFU000 at 100 s^{-1} (test ref ext197).