

Rheological measurements of polymer melts for characterisation and modelling material behaviour.

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ABSTRACT

This report describes the advantages and disadvantages of the various techniques used either to identify qualitative differences in the flow behaviour of the materials or to obtain quantitative data on the materials for use in flow modelling. The techniques discussed include: shear viscosity, entrance pressure drop and extrudate swell measurements using a capillary extrusion rheometer, steady shear viscosity, normal force and stress relaxation measurements using a rotational rheometer, stress relaxation measurements using an extensional rheometer, and dynamic moduli measurements using an oscillatory rheometer. The determination of data for numerical modelling is discussed in the context of the requirements for fitting the data using a modified Wagner viscoelastic constitutive equation. The rheological, or flow, characterisation of two high density polyethylene melts that exhibited significant differences in their extrusion processing behaviour is presented. No one technique emerges as being most suitable for the characterisation of polymer melts: the suitability of the method depends on the need for the data. The use of several techniques to obtain a more complete description of a material's rheological properties can be used to assess the suitability of chosen rheological equations. Further work is required to assess the implications for flow modelling of the uncertainties in the values of the parameters of the Wagner model that were determined for the two HDPE materials.

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1 INTRODUCTION

This report describes the measurements that were made to characterise the viscoelastic behaviour of polymer melts. This work was undertaken as part of the MTS programme on processability, Project PMP5, Polymer Moulding Models: The Determination of the elasticity of polymer melts'.

The objectives for characterising materials are two-fold. Firstly, to qualitatively compare the flow behaviour of materials in order to rank their behaviour and obtain a better understanding of the relationships between rheological properties and processing behaviour. The reasons for this are to improve the processing of existing materials and to predict the processability of new or untried materials on the basis of rheological measurements that are easier, quicker and cheaper to carry out, need smaller sample sizes and need not interfere with production by avoiding or minimising the need for expensive processing trials. The second and perhaps more demanding objective in carrying out rheological measurements is to obtain quantitatively accurate data that can be used for modelling processing behaviour. Through the use of modelling techniques improvements in materials development, materials selection, process and product design and process optimisation can be achieved.

This report describes the various techniques that can be used to characterise the viscoelastic behaviour of polymer melts for both comparative purposes and for providing data for modelling. The rheological characterisation of polymer melts is illustrated by reference to two high density polyethylene melts that exhibited significant differences in their process behaviour, yet apparently little difference in their shear viscosities. The techniques discussed include shear viscosity, entrance pressure drop and extrudate swell measurements using a capillary extrusion rheometer, steady shear viscosity, normal force and stress relaxation measurements using a rotational rheometer, stress relaxation using an extensional rheometer and dynamic viscosity using an oscillatory rheometer. The provision of data for numerical modelling is discussed by illustration to fitting experimental data to a rheological viscoelastic constitutive equation (a modified Wagner model) that can be used for simulating the flow of polymer melts. The relative advantages and disadvantages of the various techniques for identifying qualitative differences in the behaviour of the materials and for obtaining quantitative data on the materials for use in numerical modelling are highlighted.

2. MATERIALS

The materials tested in this work were NCPE 3415 and NCPE 3416 (NPL reference: HFD000 and HFE000). Both were high density polyethylene materials primarily used for blow moulding applications. The published melt indexes of the materials are given in table 1 (1, 2). The polymer samples, received in granular form, were compression moulded into disc specimens for rotational and oscillatory rheometry testing.

Table 1: Melt index values for Neste NCPE 3415 and NCPE 3416

Melt index	NCPE 3415	NCPE 3416	Test method
MI ₂	0.1	0.2	ISO 1133, Cond 4
MI ₅	0.5	1.0	ISO 1133, Cond 18
MI ₂₁	15	25	ISO 1133, Cond 7

3 RHEOLOGICAL CHARACTERISATION

3.1 GENERAL: DATA REQUIREMENTS FOR FITTING TO A VISCOELASTIC MODEL

The viscoelastic constitutive model selected for extrudate swell modelling is a Wagner model modified to include a damping function (see Appendix 1 for details). The formulation has a discrete relaxation spectrum. The work reported below was based on the use of an 8-mode relaxation spectrum: that is 8 relaxation times. The damping function is necessary to introduce shear thinning behaviour and also limits the extensional viscosity behaviour of the material to more accurately represent the behaviour of polymers. The formulation of this model and the expressions that can be derived for the dynamic moduli, steady shear viscosity, step-strain and extensional behaviours are presented in Appendix 1.

3.2 OSCILLATORY RHEOMETRY: DYNAMIC VISCOSITY

The dynamic or oscillatory shear testing was carried out using two types of rotational rheometer, a Carri-med CSL 500 controlled stress rheometer and a Bohlin VORM controlled strain rheometer. The procedure for testing is described in detail in the draft standard *ISO-CD 6721-10 Plastics - Determination of dynamic mechanical properties, Part 10 Dynamic shear viscosity using a parallel plate oscillatory rheometer* (3). The technique is also described in references (4-6). The method is used to measure the shear storage modulus G' and the shear loss modulus G'' of the material. The properties G' and G'' are measures of the elastic and viscous responses of the material respectively. The shear loss modulus G'' is related to dynamic shear viscosity η' by the expression

$$G'' = \omega \eta$$

where ω is the angular frequency (rad/s) and η' is the dynamic viscosity. Also, the loss factor $\tan \delta$ is given by

$$\tan \delta = G'' / G'$$

The loss factor, also known as the loss tangent, is a measure of the relative viscous and elastic components of the flow. A lower value of $\tan \delta$ indicates that the flow is dominated more by elastic than by viscous behaviour.

An extensive international round robin on the measurement of the dynamic properties of polyethylene and polypropylene melts (7), based on the standard ISO-CD 6721-10 (3), indicated that the repeatability of measurements of G' and G'' was of the order of 4-8% and the reproducibility was of the order of 23-29% (95% confidence limits quoted). Recommendations for improved testing are reported therein.

Typical plots of the shear storage and loss moduli G' and G'' respectively and $\tan \delta$, in this case for NCPE 3415 and NCPE 3416, are presented in figure 1. At low frequencies the flow of NCPE 3415 was more elastic in its nature (lower $\tan \delta$) than NCPE 3416. It was noted that for these and other groups of similar materials (8) values of G' and G'' tended to converge at higher frequencies with the difference in values between the materials being of the order of the repeatability of measurements. Thus to distinguish between different grades of material these results indicate that it is preferable to characterise the material at lower rather than higher frequencies.

The G' and G'' experimental data for the HDPEs NCPE 3415 and 3416 at 190 °C were used to determine the discrete relaxation spectrum for the modified Wagner model, based on an 8-mode relaxation spectrum (9). The values of these parameters are required for modelling using the Wagner equation. The optimised spectrum, presented in Table 2, was used to back-

calculate G' and G'' values, figures 2 and 3. The calculated values were in excellent agreement with the raw data indicating the high level of accuracy of the optimisation procedure used. However, the extrapolated values of the back-calculated moduli beyond the frequency range of the experimental data exhibited trends that were suspect. The errors introduced in modelling due to using extrapolating data could be evaluated through flow simulation sensitivity analyses. These results indicate that for flow simulation exercises it would be desirable to obtain relaxation data over as wide a range of frequencies as possible. However, in practice it is not so easy to extend the range of frequencies used in the measurements. The upper frequency value is limited by the natural resonant frequency of the instrument, typically in the region of 300 rad/s (50 Hz). The lower limit is restricted often by degradation of the polymer or by the sensitivity of the instrument. On the aspect of degradation of the polymer during testing, the time taken, for example, to complete one oscillation at an angular frequency of 0.1 rad/s is 62.8 seconds (or 11 minutes at 0.01 rad/s) and in practice to make a single measurement the testing time can be several times this values. Therefore the testing time very rapidly increases as the frequency is decreased with the consequence that sample degradation may become significant. Identification of sample degradation and how to carry out measurements to minimise its effect on results is described in the draft standard ISO-CD 6721-10 (3). Assuming that the errors in the moduli G' and G'' are independent of angular frequency, as was approximately the case in the oscillatory round robin (7), then the errors in the calculated relaxation moduli g_i are equal to the errors in the moduli G' and G'' (see equations 3 and 4, Appendix 1).

Table 2: Relaxation times λ_i and moduli g_i obtained from complex moduli data G' and G'' for NCPE 3415 and NCPE 3416 at 190 °C : 8-mode relaxation spectrum (see Appendix 1 for definitions of λ_i and g_i).

NCPE 3415		NCPE 3416	
$0.2\lambda_i$, s	g_i , Pa	λ_i , s	g_i , Pa
0.000214	665000	0.00195	153000
0.00522	88500	0.00744	64800
0.0205	51900	0.0289	52400
0.0741	31900	0.116	27700
0.276	18400	0.476	13100
1.01	9970	2.00	4640
4.04	5440	9.00	1180
30.90	4200	32.00	1030

3.3 CAPILLARY EXTRUSION RHEOMETRY: SHEAR VISCOSITY, ENTRANCE PRESSURE DROP AND EXTRUDATE SWELL

The procedure for capillary extrusion testing to determine shear viscosity, entrance pressure drop and extrudate swell behaviour is covered by the standard ISO 11443: 1995 *Plastics - Determination of the fluidity of plastics using capillary and slit die rheometers* (10). An extensive international round robin on the measurement of shear viscosity and entrance pressure drop values was carried out using an unfilled polyethylene (PE) and a glass fibre filled polypropylene (GFPP) material (11). In summary, the repeatability of shear viscosity measurement was approximately 20 - 25% (95% confidence levels quoted). The repeatability

of extrusion pressure measurement was 20% for PE and 38% for GFPP, though for both materials the repeatability value was greatest when testing at lower pressure values. The reproducibility of shear viscosity measurement was approximately 28 - 35% and for entrance pressure drop was 50% for PE and 56% for GFPP. Recommendations for improved testing were presented (11).

The testing reported here was performed using a C.B.E RACER capillary extrusion rheometer with dies of 10, 20, 30 and 40 mm length and 2 mm diameter. Typical Bagley plots (10) for polymer melts are shown in figures 4 and 5. Variation in behaviour between the two materials was more apparent when using shorter dies. For example, over the range of shear rates used in the testing the 5 mm length die yielded an average difference in extrusion pressure between NCPE 3415 and NCPE 3416 of 25% whereas the 20 mm length die yielded a difference of 16%.

The difference in shear viscosities between the two materials decreased as shear rate increased. At the lowest shear rate of 62.5 s^{-1} there was a 15% difference in values and at the highest shear rate of 625 s^{-1} there was a 5% difference, figure 6. These difference are less than the 95% confidence limits established in the round robin (11). A larger difference in behaviour between the two materials was observed in the entrance pressure drop values, figure 7, determined by extrapolating the best-fit straight lines of the Bagley plots (figures 4 and 5) to the y-axis (ie equivalent to a die length of zero). However, as noted above in reference to the round robin, the scatter for entrance pressure drop measurement was higher than for shear viscosity measurements. The difference in entrance pressure drop values between the two materials was on average 41%. This greater effect on entrance pressure drop values than shear viscosity values explains the observation made above that the use of shorter dies yielded greater differences between the materials.

The measurement of extrudate swell is reported in detail in reference 13. The results of a limited international round robin based on the standard ISO 11443: 1995 *Plastics - Determination of the fluidity of plastics using capillary and slit die rheometers* (10) indicated a large variation in measured values (12). This reflects the difficulty in using this method to obtain reproducible results, although the repeatability of measurements can be good (13). The difference in extrudate swell behaviour of the two HDPE materials is clearly shown in figure 8, with up to a factor of approximately 2 difference in measured values. NCPE 3415 has the higher extrudate swell. The percentage extrudate swell is calculated as the $100\% \times [\text{extrudate diameter} - \text{die diameter}] / \text{die diameter}$.

3.4 STEADY SHEAR ROTATION: SHEAR VISCOSITY AND NORMAL STRESS DIFFERENCE

Steady shear viscosity and the first normal stress difference were measured using a rotational rheometer with a cone and plate geometry, figure 9. Again it was observed that the difference in measured properties decreased as the testing rate (in this case shear rate) increased. The measurement of both parameters was limited to maximum shear rates of approximately 2 s^{-1} due to the onset of distortion of the sample at its outer edge. A slight distortion of the outer edge of the sample has a significant effect on the measured values as the viscosity is inversely proportional to the radius raised to the power three. Consequently results above 2 s^{-1} are considered to be low for this reason. In practice, shear viscosity values could be measured at much lower shear rates than the first normal stress difference N_1 due to the range of the normal force transducer which was limited to operation over only two decades of force. For measurement of the normal stress difference it was important to ensure that the compressive force generated on the sample during loading was allowed to relax to a small value. In practice it was allowed to relax to below 10% of the full scale of the instrument. Relaxation significantly below this value would have been preferable but the time taken would have increased significantly and with the potential consequence of

degradation of the sample. In summary, the measurement of the first normal force was relatively unsatisfactory with reliable values obtained over a very restricted shear rate range only.

The predictions of the Wagner model with damping function were compared with the shear viscosity and normal stress difference (N_1) results, figures 10 and 11, using the discrete relaxation spectrum data presented in table 2 and a range of values for the damping coefficient k . Normal stress difference values were calculated numerically using the Polyflow simulation package. These plots indicate the difficulty in fitting a model to experimental data. Steady shear rotational results obtained at shear rates above 2 s^{-1} are underlined to indicate that melt fracture occurred. For NCPE 3415 a value of 0.3 gave a good fit at low rates, but at higher rates a value of 0.6 gave a better fit, figure 10. For NCPE 3416 the fit of the model was better with a single value of approximately 0.5 giving the best fit to all the shear viscosity data. It is emphasised that there is no a priori reason why the material behaviour should fit the constitutive equation which is simply a mathematical representation of an idealised material behaviour. The inability to fit the model to the full shear rate range in the case of NCPE 3415 has obvious implications for modelling of the flow of that material. The effect of the uncertainties in the parameters of the Wagner equation on modelling of flow behaviour needs to be assessed through sensitivity studies.

3.5 STRESS RELAXATION

Stress relaxation measurements in shear were made using a Bohlin controlled stress VORM rotational rheometer. Step strain measurements up to 12% strain were made using the instruments stress relaxation testing mode, figures 12 and 13. The independence of the relaxation modulus values to the initial strain clearly indicates that the material response was in the linear viscoelastic regime. The predicted linear viscoelastic behaviour, based on the Wagner model and the discrete relaxation spectrum values presented in table 2, were lower than the measured values for both NCPE 3415 and NCPE 3416. This again shows the difficulty in fitting a single model to data derived from various sources. To obtain stress relaxation results at higher initial strains (ie non-linear viscoelastic behaviour) the flow-relaxation mode of operation of the rheometer had to be used. This however did not produce the same modulus values at low strain values that were within the linear viscoelastic regime. In using the flow-relaxation mode with longer strain times the initial relaxation moduli at short times were approximately 80% higher. Further investigation of the use of the flow-relaxation mode is required to confirm the validity, or otherwise, of the measurements. Nevertheless damping coefficient values were calculated using the suspect flow-relaxation data and gave values of 0.46 for NCPE 3415 and 0.49 for NCPE 3416. Stress relaxation measurements performed by Cambridge University using a Rheometrics RDSII rheometer yielded values for the damping coefficient of $k = 0.27$ for NCPE 3415 and 0.24 for NCPE 3416 (14). Shear viscosity values were calculated using this range of damping coefficient values and are presented in figures 10 and 11 for comparison with experimental data (see section 3.4).

Further characterisation of the NCPE materials was carried out by stress relaxation testing in extension using a novel extensional rheometer that is described in detail by Rides et al (15). The extensional stress relaxation results are compared with shear stress relaxation results in figure 14. The materials had higher relaxation modulus values in extension than in shear and in particular the measurements indicated that they were strain thinning in shear (non-linear viscoelastic behaviour) yet tension thickening in extension. It is this tension thickening behaviour in extension that is critical to the processability of materials in many processes, for example blow moulding, film blowing and thermoforming that require stable stretching flows. For further details of the extensional stress relaxation testing see Rides et al (15).

4 DISCUSSION

Various techniques can be used to characterise the viscoelastic behaviour of polymer melts including their purely viscous response, eg steady shear viscosity. The question of which is the preferred technique to use should always be addressed by the industrialist wanting to understand better the materials that they are processing. The preferred technique obviously depends on the need for the data, and the advantages and disadvantages of the various techniques must be viewed in that light. The advantages and disadvantages can be summarised primarily as the repeatability, reproducibility and accuracy of the technique, the degree of difficulty and complexity of the test, the cost of the equipment and of carrying out the measurements and the appropriateness of the data to the need. Data that are required for processing purposes should preferably, one might consider, be data obtained at high rates and large strains as manufacturing processes, eg injection moulding, extrusion and blow moulding tend to be high rate and large strain processes. However, suitable measurement techniques, for example shear viscosity measurements using a capillary extrusion rheometer, tend not to distinguish well between similar grades of material. Entrance pressure drop or extrudate swell measurements using capillary extrusion rheometers appear to be more sensitive to material variations, but are principally qualitative measurements and tend to be less repeatable and reproducible. Thus, although the differences are larger the uncertainties in the measurements are also larger. Low frequency oscillatory rheometry measurements appear to be most sensitive in distinguishing between various grades of material and are relatively repeatable and reproducible. However, the difficulty is then to relate the low rate, low strain measurement behaviour to the high rate, high strain behaviour occurring in processing. Such correlations can be made yet their universal applicability cannot be guaranteed and should not be expected.

The reason for the greater sensitivity of low strain, low rate techniques to differences in materials compared with high strain, high rate techniques is because they probe the molecular structure of the material to a greater extent. They are thus more sensitive to differences in molecular structure. The significant difference observed in, for example, the extrudate swell behaviour of the two NCPE grades but not in their shear viscosity values is considered to be due to the extensional flow nature of the swelling process. The extensional flow behaviour is affected more by differences in the molecular structure of the material than is shear flow behaviour. Hence, results obtained using low strain, low rate techniques are better than those obtained using high strain, high rate techniques, such as capillary extrusion rheometry, for correlating with behaviour in processing where there is a significant extensional flow component.

In determining the values of the parameters to fit the Wagner model the choice of technique is more limited by the requirements of that model. The relaxation spectrum is determined from dynamic moduli that are easily and relatively accurately obtainable. The value of the damping coefficient can be determined from fitting the model to steady shear viscosity, first normal stress difference or shear stress relaxation data. Difficulties relating to the measurement of normal stress difference and stress relaxation are described above. Nevertheless, non-linear stress relaxation measurements in shear are, in principal, an easy method for determining the value of the damping coefficient. However, the fitting of the model to steady shear viscosity values is perhaps a better and more challenging demonstration of the suitability of the model as data can be obtained over a much wider range of rates by using both rotational and capillary extrusion techniques. By using more than one approach to determining the value of the damping parameter then the confidence in that value can be assessed.

In summary, there is no single answer to the question of which technique is best as many factors that are presented above need to be taken into account.

5 CONCLUSIONS

The more significant conclusions resulting from the work presented in this report for the project on characterisation of the viscoelastic behaviour of polymer melts are as follows.

Differences in the behaviour of the materials were most clearly apparent when testing at low strains and strain rates.

In using a capillary extrusion rheometer there was a greater difference in the behaviour of different material when using entrance pressure drop measurements rather than shear viscosity measurements. Differences in shear viscosity values were small and of the order of the repeatability of the measurements.

In using oscillatory measurements to identify differences in the viscoelastic behaviour of materials it was preferable to use the loss factor ($\tan \delta$) and moduli G' and G'' values at low frequencies. As the frequency increased the difference in behaviour between the materials decreased.

Steady shear testing using a rotational rheometer to measure shear viscosity and the first normal stress difference proved to be unsatisfactory at higher rates due to the occurrence of melt distortion.

Determination of the discrete relaxation spectrum for the Wagner model can be accurately carried out. However, significant uncertainty lies in the accuracy of extrapolating dynamic moduli (G' and G'') values using the Wagner model to outside the frequency range over which the raw data was obtained. There are experimental difficulties that limit the frequency range over which G' and G'' measurements can easily and accurately be made.

Difficulties in determining the values of the parameters for the Wagner model have been illustrated. The sensitivity of the predictions of flow modelling to the uncertainties in the values of the parameters for the Wagner model needs to be assessed.

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APPENDIX 1: MODIFIED WAGNER CONSTITUTIVE MODEL

The modified Wagner constitutive model is given by the integral equation

$$\tau(t) = \int_{-\infty}^t \sum_i \frac{g_i}{\lambda_i} e^{-(t-t')/\lambda_i} h(I_1, I_2) C^{-1}(t, t') dt' \quad (1)$$

where

$$h(I_1, I_2) = e^{-k[\beta I_1 + (1-\beta)I_2 - 3]^{0.5}} \quad (2)$$

where τ is the stress tensor, g_i and λ_i are the discrete relaxation spectrum moduli and times respectively, k is a damping coefficient that controls the strain thinning and extensional viscosity behaviour, β is an additional damping coefficient for extensional flow but does not have an effect in simple shear or planar extensional flow, t and t' are the present and past times, C^{-1} is the Finger strain tensor that describes the deformation of the fluid and I_1 and I_2 are the first and second invariant of the Finger tensor. For further details see Ahmed et al¹. The following terms can be derived using the Wagner model, where ω is the angular frequency (rad/s), $\dot{\gamma}$ is the shear rate, γ is the shear strain and other terms are as previously defined. These expressions were used to fit the experimental data presented in the report.

Shear storage modulus G' :

$$G' = \sum_i \frac{g_i \omega^2 \lambda_i^2}{(1 + \omega^2 \lambda_i^2)} \quad (3)$$

Shear loss modulus G'' :

$$G'' = \sum_i \frac{g_i \omega \lambda_i}{(1 + \omega^2 \lambda_i^2)} \quad (4)$$

Steady shear viscosity:

$$\eta_s = \sum_i \frac{g_i \lambda_i}{(1 + k \lambda_i \dot{\gamma})^2} \quad (5)$$

¹R Ahmed, R.F. Liang and M.R. Mackley, The experimental observation and numerical prediction of planar entry flow and die swell for molten polyethylenes, J. Non-Newtonian Fluid Mech., 59(1995) 129-153.

Shear relaxation moduli G following step strain:

Linear viscoelastic modulus (small strain):

$$G(\gamma_o, t) = \sum_i g_i e^{-t/\lambda_i} \quad (6)$$

Non-linear viscoelastic modulus (large strain):

$$\frac{G(\gamma, t)}{G(\gamma_o, t)} = e^{-k\gamma} \quad (7)$$

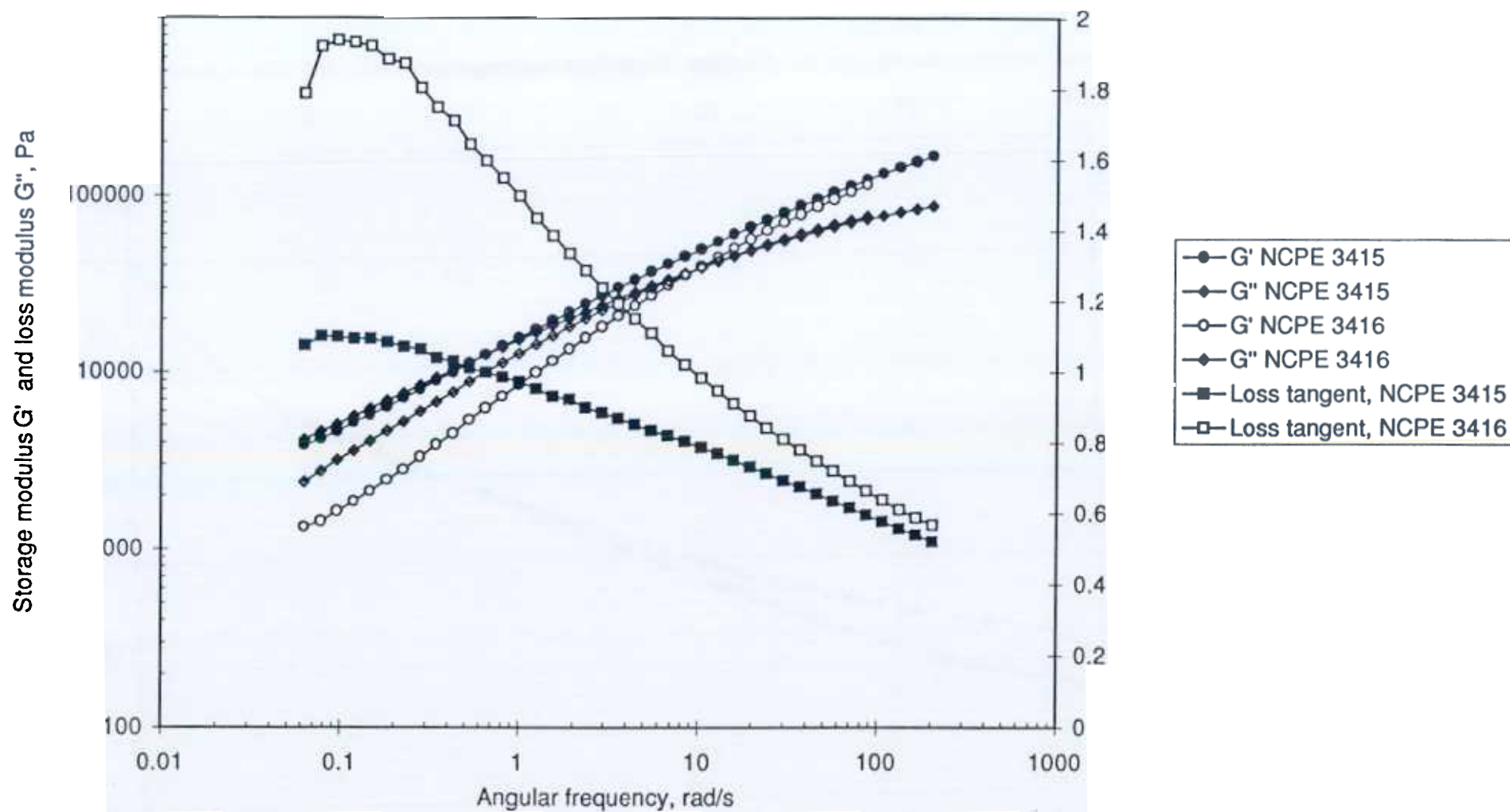


Figure 1: Dynamic moduli and loss tangent data for HDPE NCPE 3415 and NCPE 3416 obtained using an oscillatory rheometer at 190 °C.

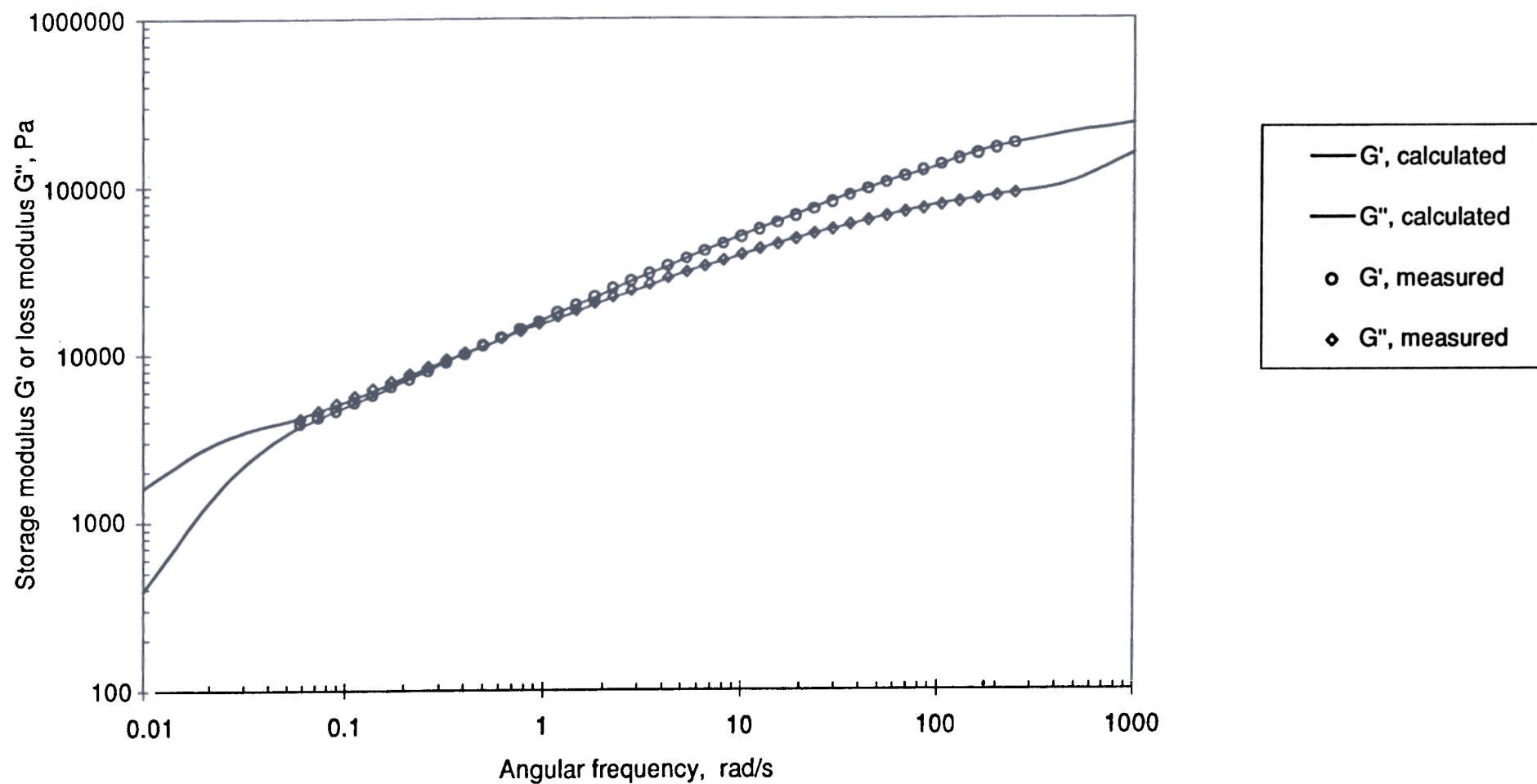


Figure 2: Fit of the Wagner model to the dynamic moduli data for NCPE 3415 at 190 °C using an 8-mode discrete relaxation spectrum.

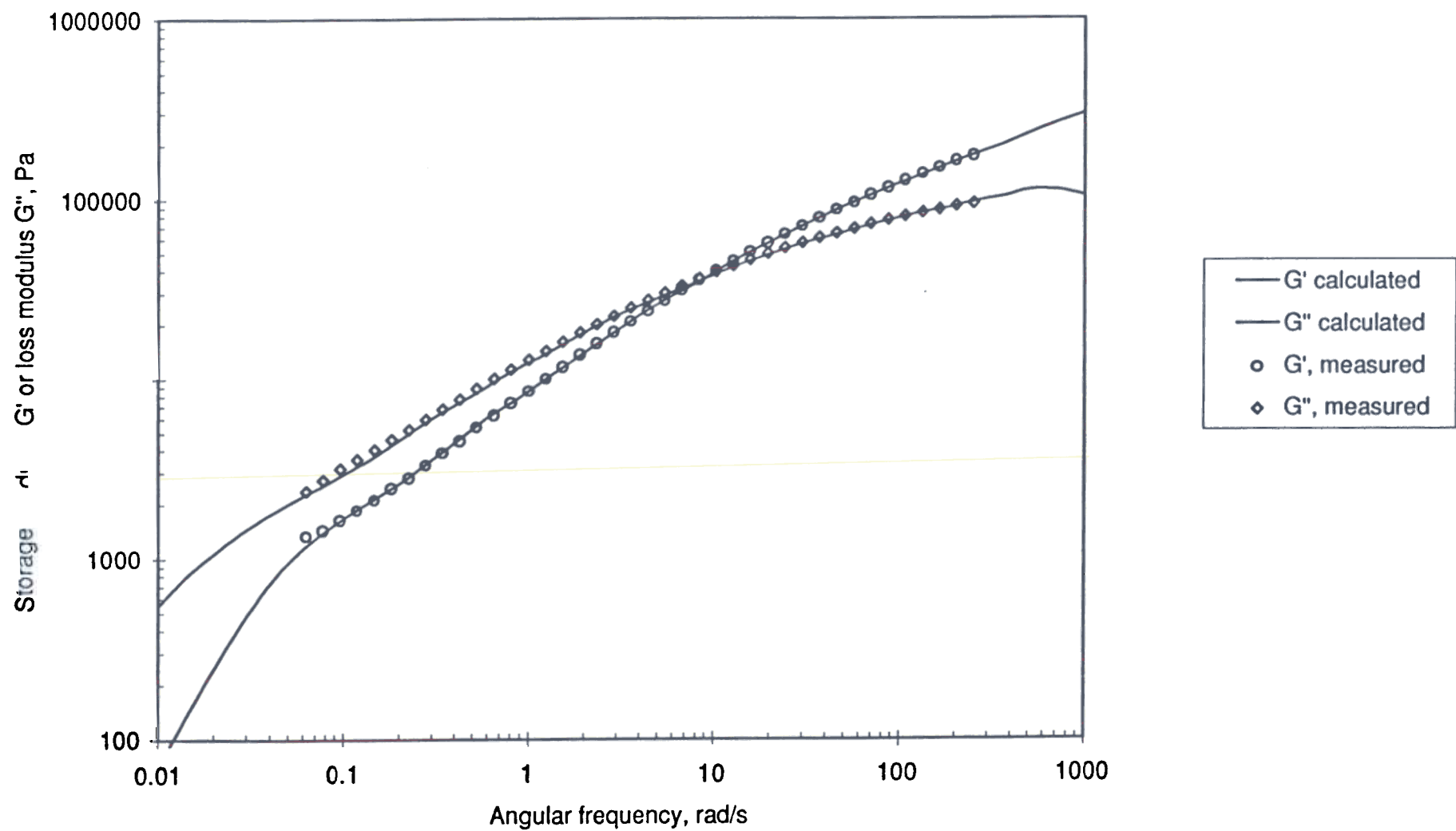


Figure 3: Fit of the Wagner model to the dynamic moduli data for NCPE 3416 at 190 °C using an 8-mode discrete relaxation spectrum.

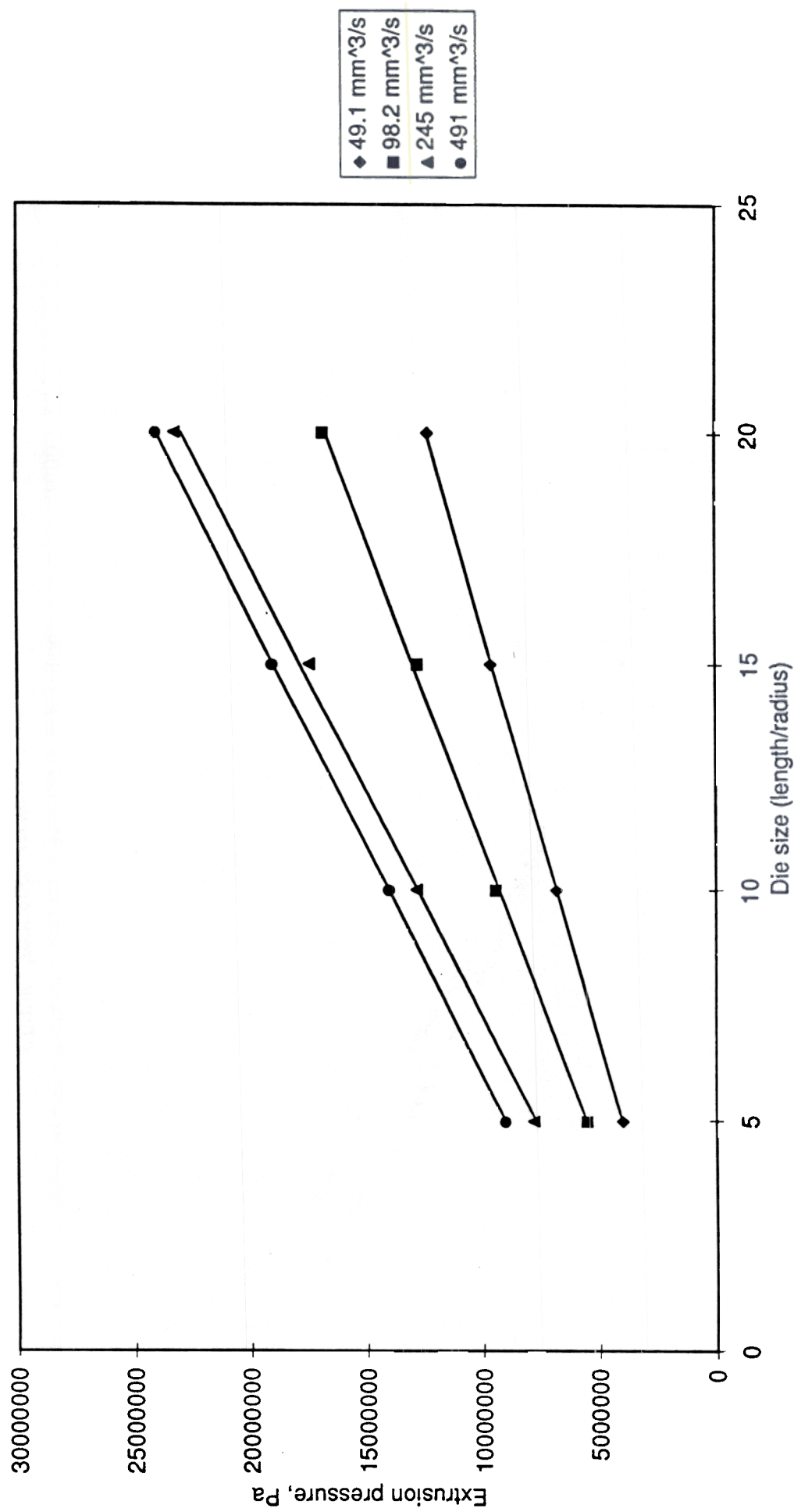


Figure 4: Bagley plot obtained from capillary extrusion rheometry of NCPE 3415 at 190 °C (legend gives flow rates).

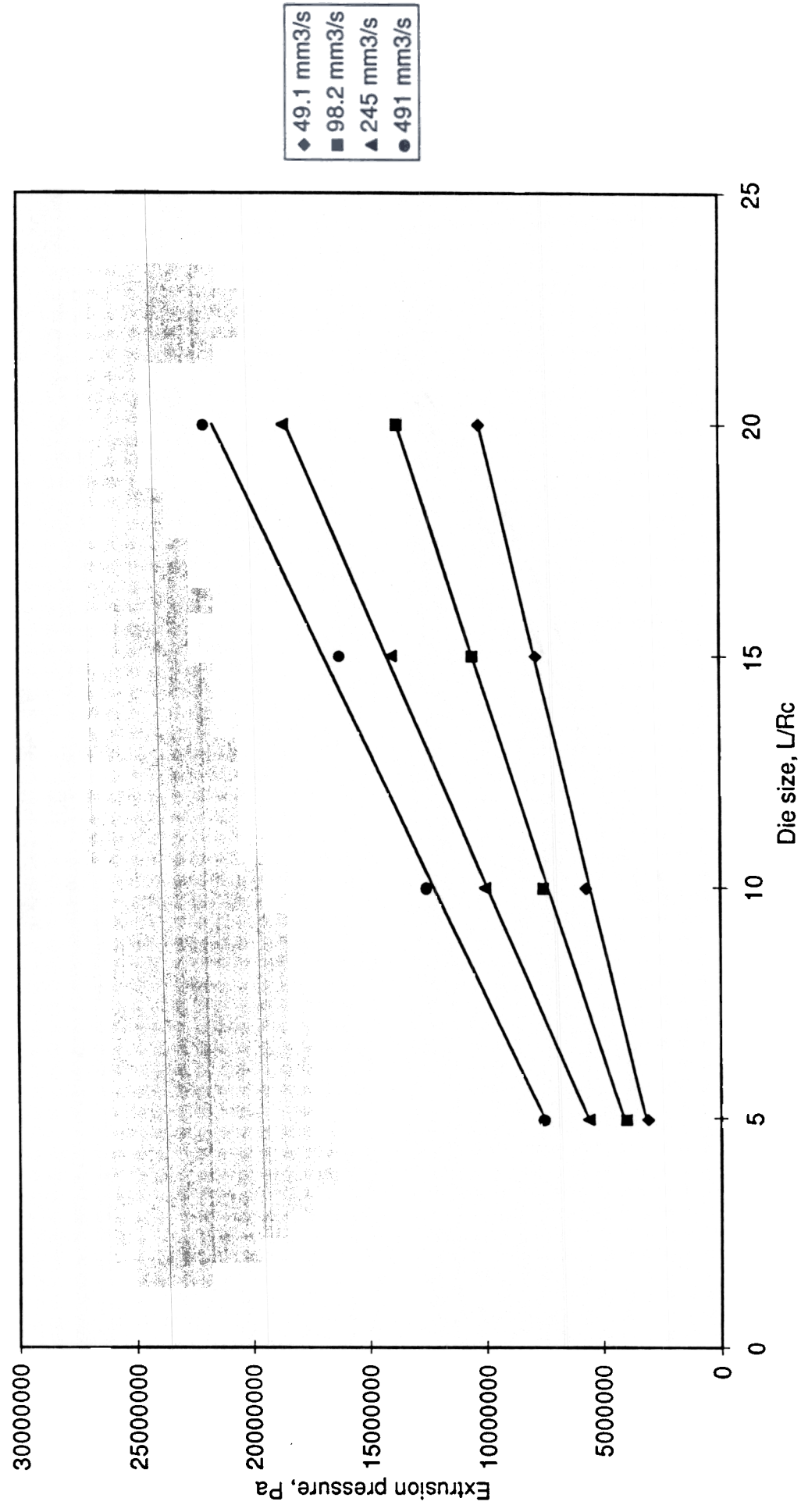
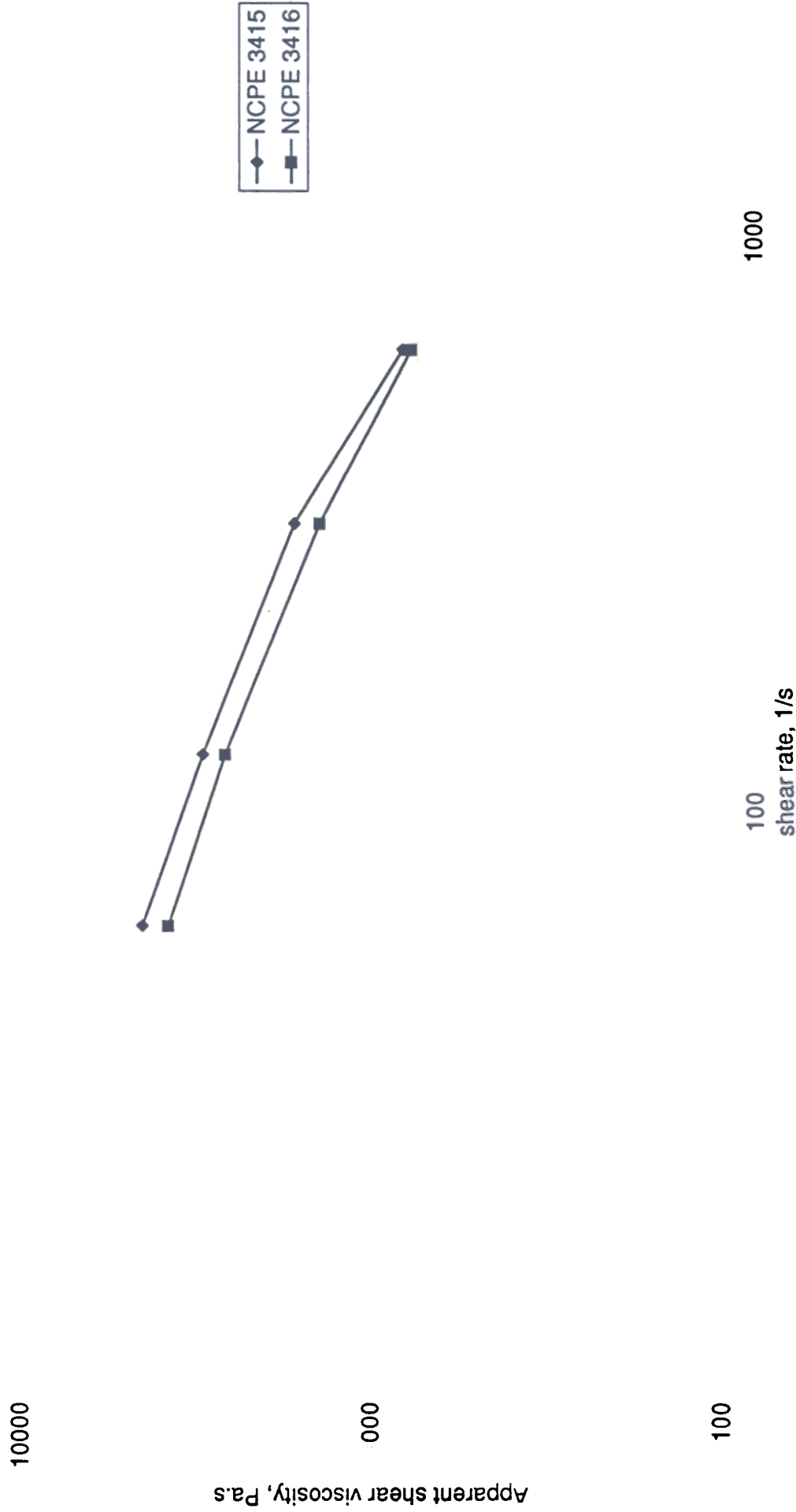


Figure 5: Bagley plot obtained from capillary extrusion rheometry of NCPE 3416 at 190 °C (legend gives flow rates).



Shear viscosity of NCPE 3415 and NCPE 3416 at 190 °C measured using a capillary extrusion rheometer

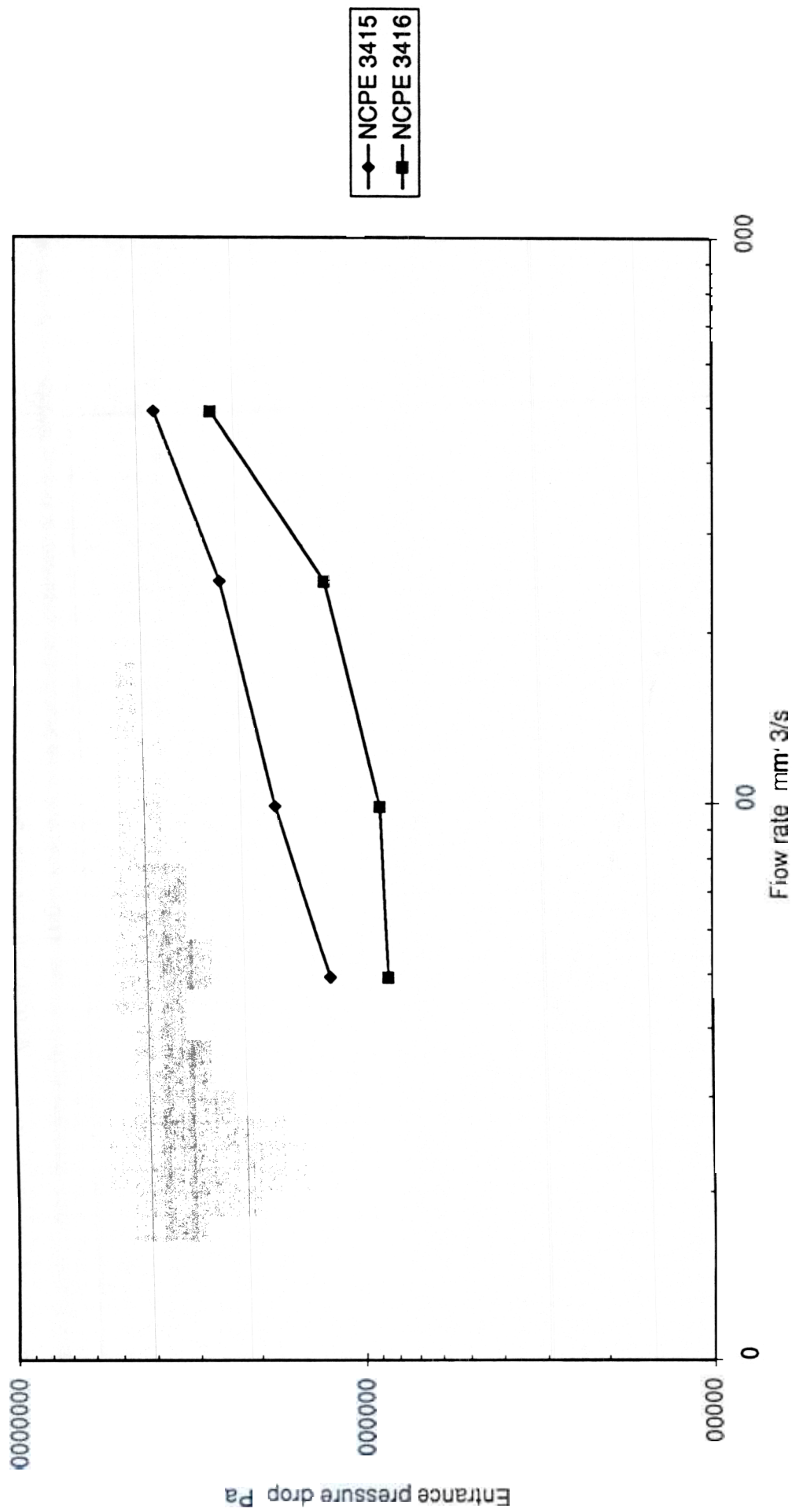


Figure 7: Entrance pressure drop values for NCPE 34 and NCPE 3415 90 °C measured using capillary extrusion rheometer

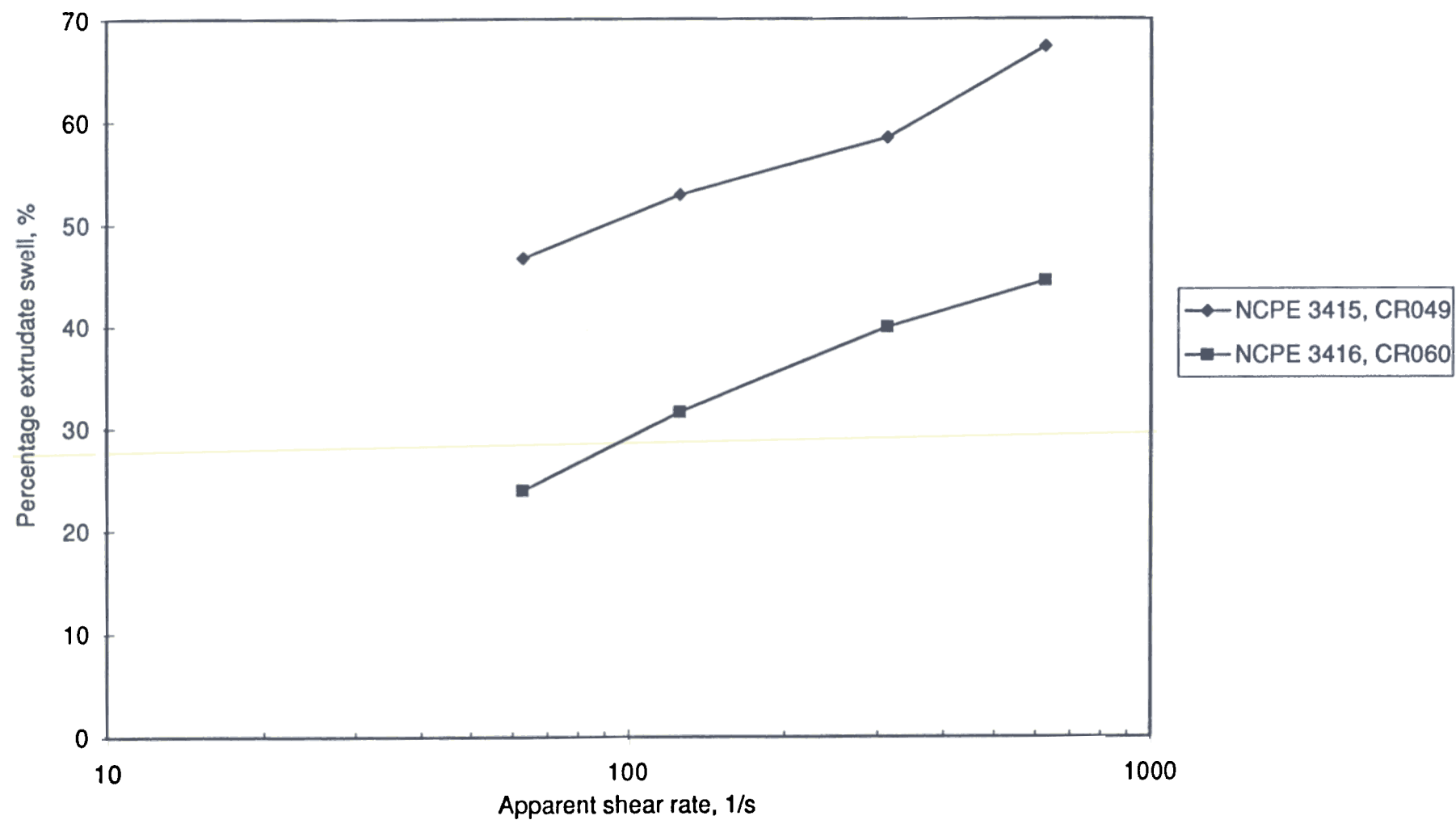


Figure 8: Extrudate swell measurements for NCPE 3415 and NCPE 3416 at 190 °C measured using a capillary extrusion rheometer.

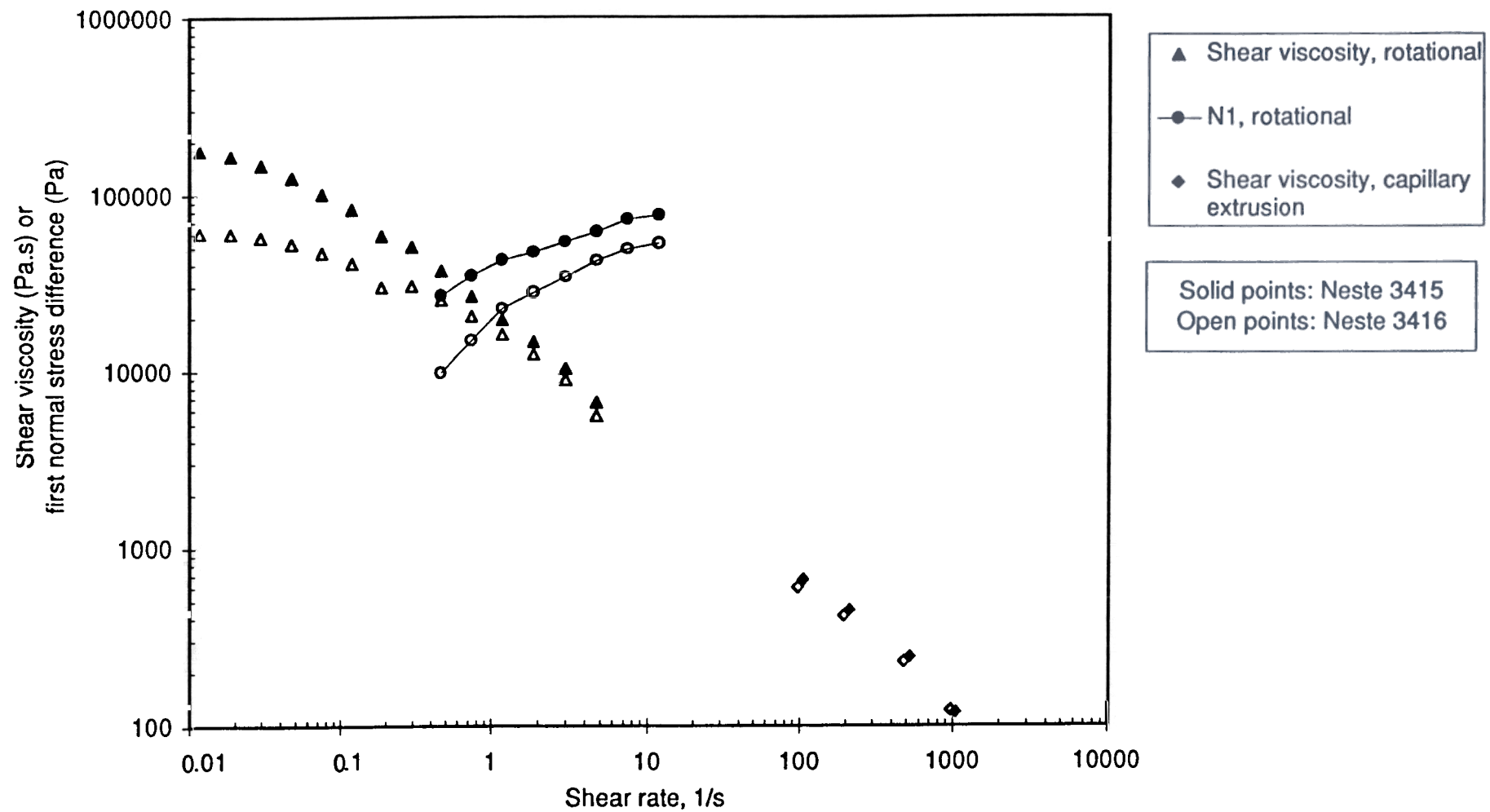
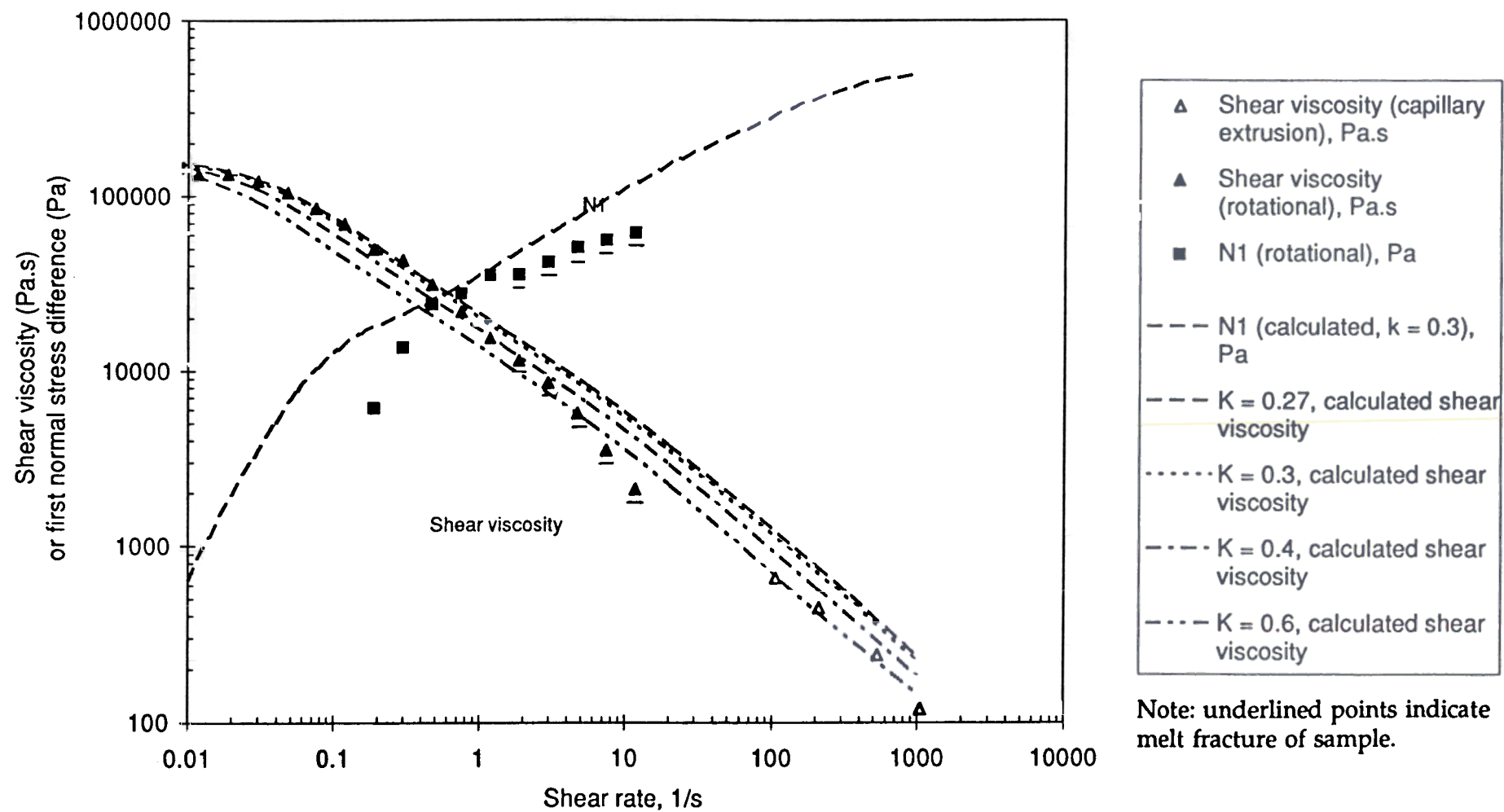


Figure 9: Comparison of the steady shear behaviour of NCPE 3415 and NCPE 3416 using low shear rate rotational rheometry and high shear rate capillary extrusion rheometry.



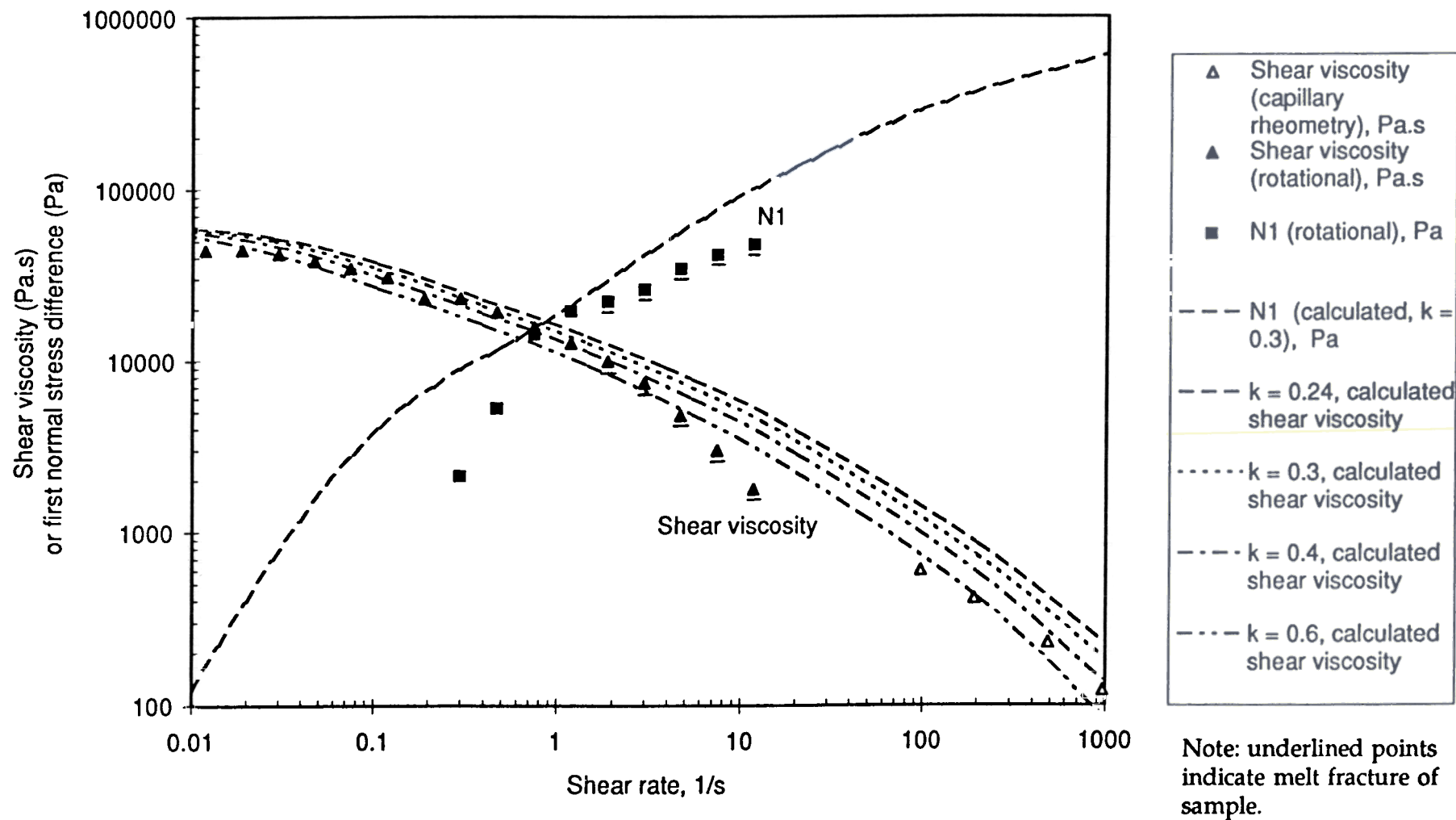


Figure 11: Fit of the modified Wagner model to the steady shear viscosity and first normal stress difference data for NCPE 3416 at 190 °C

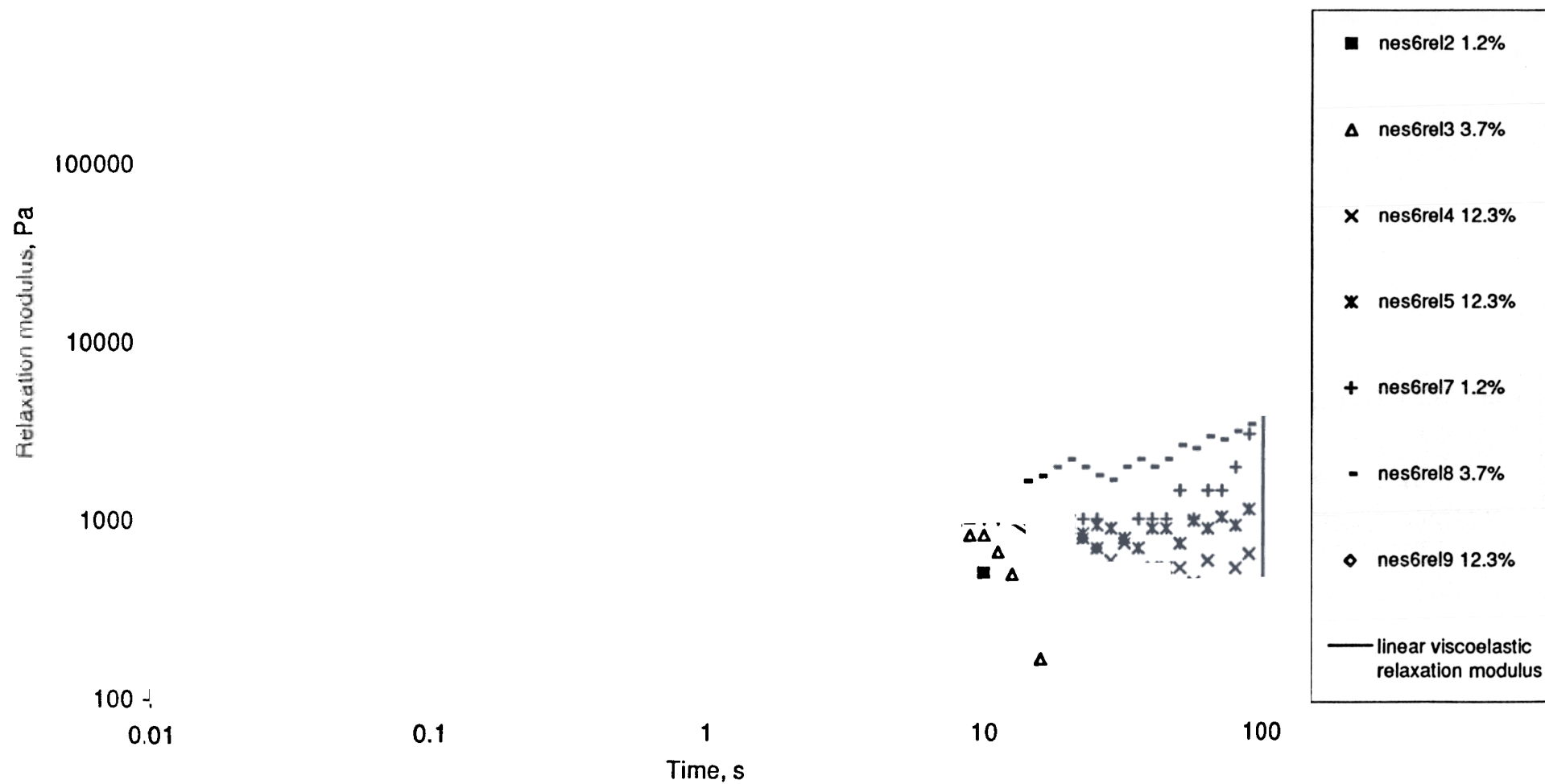


Figure 13: Fit of the modified Wagner model to linear viscoelastic stress relaxation data for NCPE 3416 at 190 °C, with the experiments carried out using initial strains from 1.2 to 12.3%.

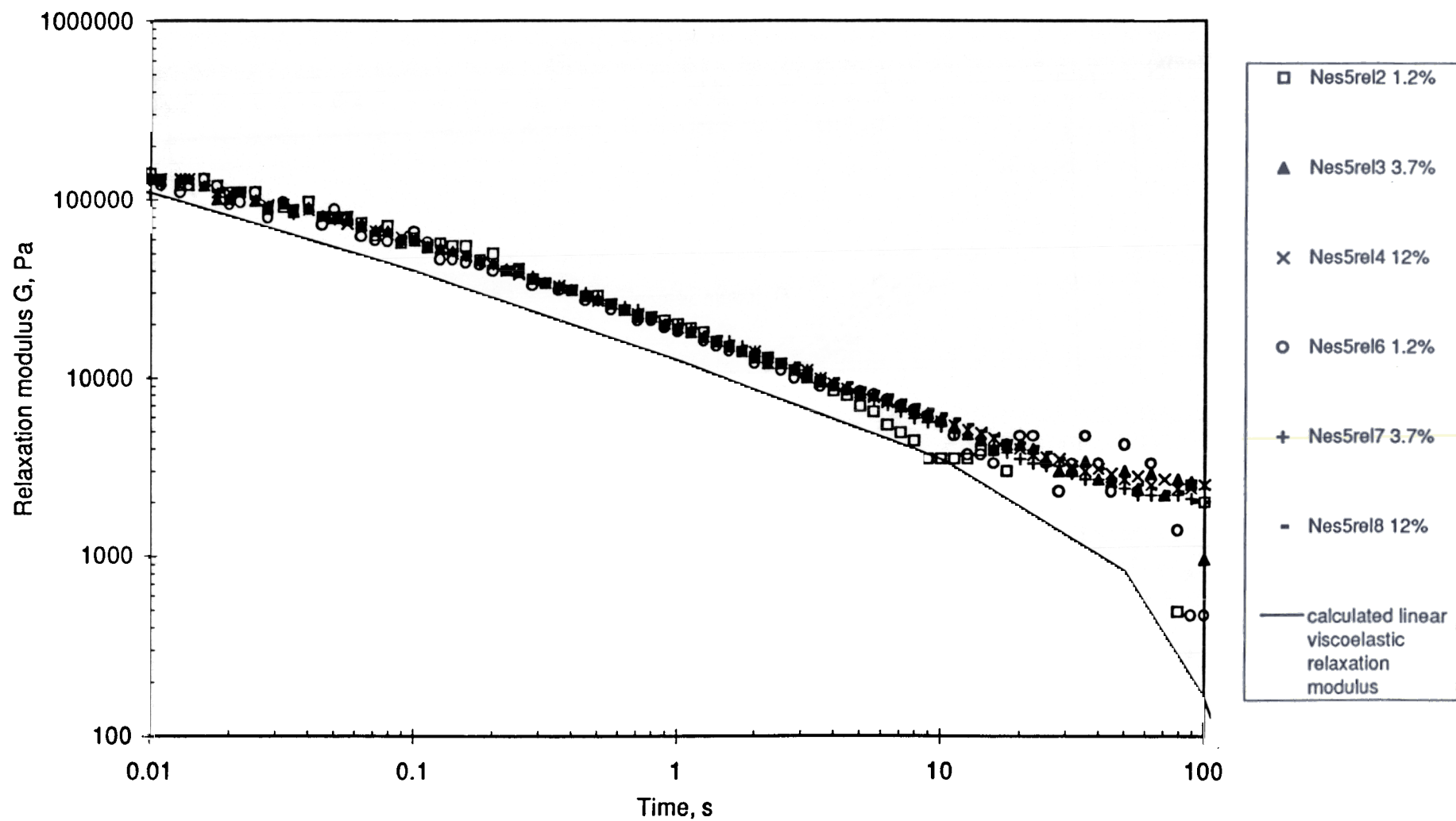


Figure 12: Fit of the modified Wagner model to linear viscoelastic stress relaxation data for NCPE 3415 at 190 °C, with the experiments carried out using initial strains from 1.2 to 12%.

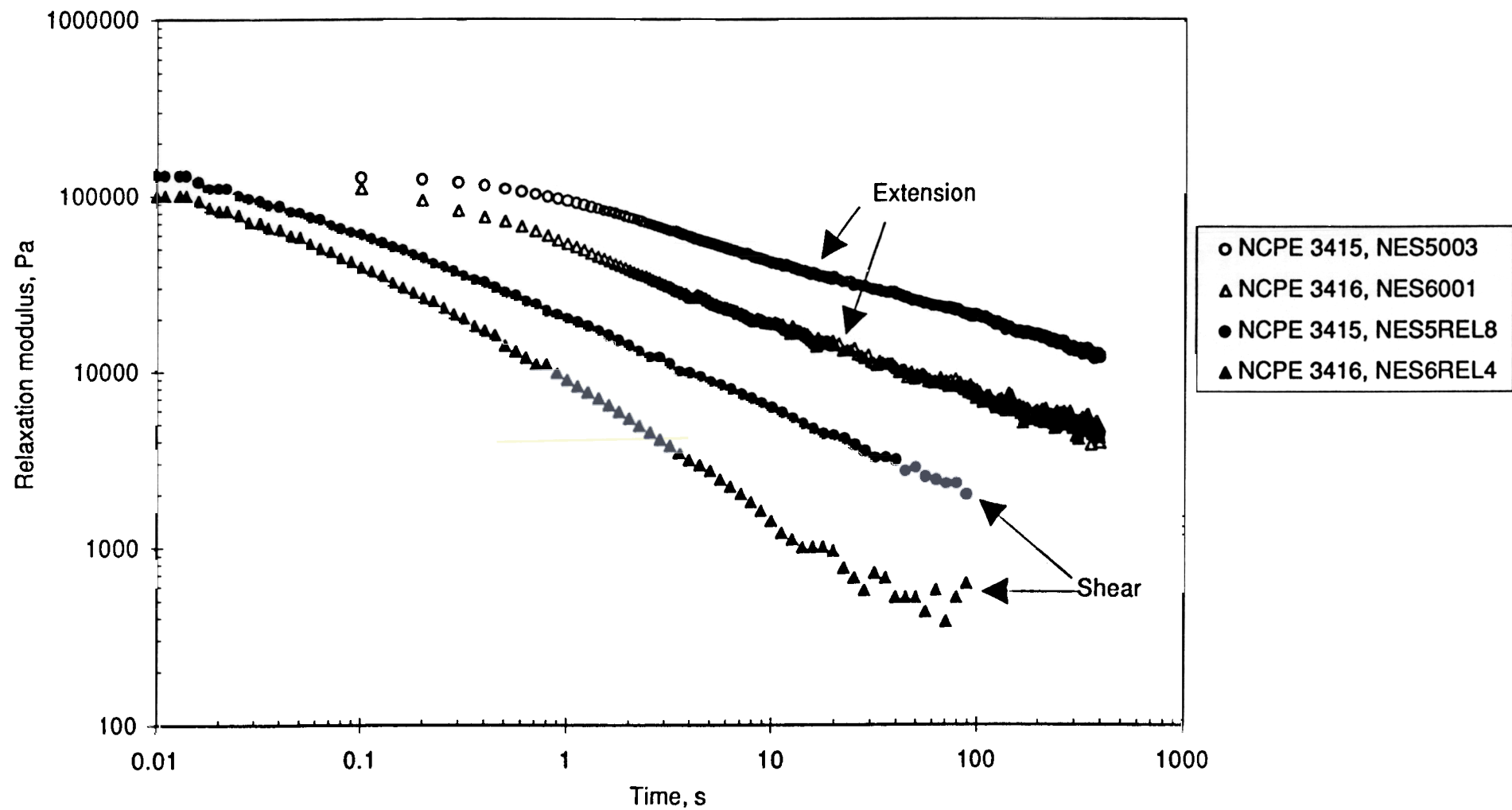


Figure 14: Comparison of linear viscoelastic shear and extensional stress relaxation behaviours for NCPE 3415 and NCPE 3416 at 190 °C.