

Round robin for parallel plate oscillatory rheometry using polyethylene and polypropylene melts

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ABSTRACT

The results of an extensive round robin on the measurement of dynamic rheological properties of a high density polyethylene melt and a polypropylene melt are reported. The round robin was based on the use of the draft standard 'ISO-CD 6721-10 Plastics, Determination of dynamic mechanical properties, Part 10: Complex shear viscosity using a parallel plate oscillatory rheometer'. Time sweep and strain sweep measurements were carried out to determine the duration of thermal stability of the sample and the limiting strain value for linear viscoelasticity measurements. Measurements to determine the frequency response of the materials were carried out and repeatability and reproducibility values at selected frequencies were determined for the storage modulus G' and loss modulus G'' . A precision statement for inclusion in the standard has been proposed.

In summary, the repeatability of measurements for the HDPE and PP materials was in the range 4 - 8%, and the reproducibility was in the range 21 - 32% (95% confidence levels quoted). These findings have significant implications for testing using this method, whether comparing data obtained on the same instrument for quality control applications, comparing data obtained on the same material but using different instruments, or using data for predictive modelling.

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1 INTRODUCTION

This work has been undertaken as part of the Department of Trade and Industry Electrical Engineering Division's (EED) programme on processability, Projects 4 and 5 on the determination of the viscosity of polymers as a function of cure, temperature and pressure, and the determination of the elasticity of polymer melts respectively. These projects are two of a wider range of projects on the processability of materials funded by the EED.

The standard 'ISO 6721-10 Plastics, Determination of dynamic mechanical properties, Part 10: Complex shear viscosity using a parallel plate oscillatory rheometer' (1)¹ is currently under development. The aim of this round robin is, in part, to provide a precision statement for inclusion into the standard and to provide input into the development of the procedure of the testing method.

The standard ASTM D4440-93 Rheological measurement of polymer melts using dynamic mechanical procedures (2) has no precision or bias statement. Samurkas and Rogers (3) carried out a round robin study on a hygroscopic material, poly-ε-caprolactam/polypropylene blend, and concluded that there was need to improve the standardisation of the testing methodology. More recently repeatability measurements have been carried out by Bafna et al (4) and reproducibility measurements by Gahleitner et al (5). In the latter, standard deviations varied with angular frequency and temperature. The standard deviation for G' increased and for the loss factor $\tan \delta$ it decreased with increasing frequency. However, the standard deviation for G'' was relatively insensitive to angular frequency. Standard deviation values were in the ranges 6 - 35% for G' , 5 - 20% for G'' and 6 - 35% for $\tan \delta$. Again inadequate specification of the measuring procedure was highlighted as a probable source of error causing the high standard deviation values.

2 ISO STANDARD

2.1 SPECIFICATION OF STANDARD

The round robin was based on the working draft ISO-CD 6721-10: Plastics - Determination of dynamic mechanical properties, Part 10: Complex shear viscosity using a parallel plate oscillatory rheometer (1). The latest version of the draft international standard ISO-DIS 6721-10 specifies the following for the measurement of the dynamic properties of polymer melts.

Torque measurement:	$\pm 2\% \text{ fsd}^2$
Angular displacement:	$\pm 20 \times 10^{-6} \text{ rad}^3$
Plate diameter:	$\pm 0.01 \text{ mm}$
Plate gap:	$\pm 0.01 \text{ mm}$
Non-alignment of plates:	$\pm 0.01 \text{ mm}$
Angular frequency:	$\pm 2\% \text{ absolute.}$
Temperature θ :	$\pm 0.5^\circ\text{C for } \theta \leq 200^\circ\text{C}$

¹The standard covers the measurement of both the real and loss components of viscosity despite the inference of the title. The author anticipates that the title will be changed at the next stage of the standard's development to reflect more accurately the purpose of the standard.

² The working draft ISO-CD 6721-10 specified $\pm 2\%$ of absolute, but has since been changed to $\pm 2\%$ of full scale deflection.

³ The working draft ISO-CD 6721-10 specified a value of $5 \times 10^{-3} \text{ rad}$ in error which would have resulted in significant measurement uncertainty. The value has been reduced to $20 \times 10^{-6} \text{ rad}$ following the October 1995 meeting of the committee responsible for the development of the standard ISO/TC61/WG2/SC5.

$$\begin{aligned} &\pm 1.0\text{ }^{\circ}\text{C for } 200\text{ }^{\circ}\text{C} < \theta \leq 300\text{ }^{\circ}\text{C} \\ &\pm 1.5\text{ }^{\circ}\text{C for } \theta > 300\text{ }^{\circ}\text{C} \end{aligned}$$

2.2 UNCERTAINTY LIMITS OF TESTING

The uncertainties in the determination of the storage modulus G' and loss modulus G'' were calculated using expressions presented in appendix 1 where the moduli were given by:

$$G' = \frac{32 d T_o \cos \delta}{\theta_o \pi D^4}$$

$$G'' = \frac{32 d T_o \sin \delta}{\theta_o \pi D^4}$$

where d is the plate gap, T_o the torque amplitude, δ the loss angle, θ_o the angular displacement amplitude and D the plate diameter. The fractional uncertainties of each of these parameters were determined using the tolerances specified in the standard (see section 2.1 but assuming the error in torque measurement to be 2% absolute) and the values of each of the parameters as specified below.

For testing using 25 mm diameter plates with a gap of 1.5 mm and 5% strain at the plate edge and based on the assumptions given below, then the uncertainties in the measurement of G' and G'' are given in Table 1.

Table 1. Estimate of the uncertainties of the measurement of the storage modulus G' and loss modulus G'' .

Temperature dependence of viscosity of the material, %/ $^{\circ}\text{C}$	Temperature error, $\pm\text{ }^{\circ}\text{C}$	Uncertainty in G' and G'' measurement, %
0	-	5.5
1	0.5	5.6
1	1.0	5.6
3	1.0	6.3

Obviously the uncertainties in measurement of G' and G'' are related to the temperature dependence of the material being tested. For the HDPE and PP samples used in this round robin it was estimated, based on temperature sweep data, that the temperature dependence of the moduli was approximately 1 %/ $^{\circ}\text{C}$.

Furthermore it was estimated that the error in the determination of the loss angle δ was of the order of 0.2° when testing a Newtonian fluid (ie $\delta = 90^{\circ}$) and 0.5° when testing a metal sample (ie $\delta = 0^{\circ}$). The effect of this error on the determination of G' or G'' depends on the value of δ and cannot be simply and accurately expressed as a percentage value. However, as an indicator, for an error in δ of 0.5° the errors associated with $\cos \delta$ and $\sin \delta$ would be of the order of $< 3\%$ over the range $17^{\circ} < \delta < 73^{\circ}$, see table 2. A value of 3% has been used in calculating the uncertainty values presented in table 1. However, for small or large values

of δ (tending to 0° or 90° respectively) the error associated with $\sin \delta$ and $\cos \delta$ respectively will be large. For small values of δ the error associated with $\cos \delta$ will be small, and for large values of δ the error associated with $\sin \delta$ will be small. Therefore the effect of errors in δ on the measurement uncertainties in G' and G'' may vary considerably depending on the material tested and the measurement conditions used.

Table 2: Range of values for the loss angle δ , in degrees, for which the percentage error in $\cos \delta$ or $\sin \delta$ does not exceed the stated value, given the error in the measurement of the loss angle.

Percentage error in $\cos \delta$ or $\sin \delta$	Error in measurement of loss angle, δ			
	$\pm 0.1^\circ$	$\pm 0.2^\circ$	$\pm 0.5^\circ$	$\pm 1.0^\circ$
1%	$\delta = 10 - 80^\circ$	20 - 70	42 - 48	-*
2%	5 - 85	10 - 80	24 - 76	41 - 49
3%	4 - 86	7 - 83	17 - 73	31 - 59
5%	2 - 88	4 - 86	10 - 80	20 - 70
10%	1 - 89	2 - 88	5 - 85	10 - 80

* indicates that for the given error in measurement of the loss angle δ no value of δ had a percentage error for $\cos \delta$ or $\sin \delta$ that was lower than 1%.

In determining the uncertainty values in measurements of G' and G'' it was also assumed that:

- the effect of a 2% error in the determination of angular frequency had a 2% effect on the measured values of G' or G'' - ie that $\log(G')$ and $\log(G'')$ are linear relations of $\log(\text{angular frequency})$ with a slope of 1,
- degradation of the sample had a 2% effect on measured values of G' and G'' ,
- and the error due to non-linear viscoelastic behaviour (related to determining the limiting strain for linear viscoelastic measurements) had a 3% effect on measured values.

These uncertainties do not take into account errors due to sample inertia, and the instrument-related factors of non-parallelism and non-axial alignment of the plates, edge effects, machine inertia and machine compliance. These factors will all increase the level of uncertainty in the measurements.

3 EXPERIMENTAL TECHNIQUES

3.1 PARTICIPANTS

The participant in the round robin were:

BASF, Germany,
BP Chemicals Ltd UK,
EniChem Mantova Research Centre, Italy
Himont, Italy
ICI Materials, UK

Kobe Steel Europe Ltd, UK
 National Physical Laboratory, UK
 PCD Polymere Ges.m.b.H, Austria
 Solvay, USA
 TA Instruments, UK

3.2 TEST MATERIALS

Two materials were selected for testing in the round robin, an unfilled high density polyethylene (HDPE: material A, NPL reference HFU000) and an unfilled polypropylene (PP: material C, NPL reference HFV000). Both materials were commercially available. Plate samples of the HDPE were produced by compression moulding, and plate samples of the PP by injection moulding. All samples were supplied to the participants by the National Physical Laboratory (NPL). The HDPE (material A, NPL ref HFU000) was the same as that used in a round robin on capillary extrusion rheometry (6).

3.3 PROCEDURE

Ten laboratories participated in the round robin using the instruments listed in table 3. Instructions detailing the testing procedure to be used and specifying the results and testing information to be provided by the participating laboratory was sent to all participants along with moulded plate samples of the two materials.

Table 3: Instrument and plate diameter used by each of the laboratories indicated by reference number.

Laboratory reference no.	Instrument	Plate diameter
3	Rheometrics RDS II	25
6	Rheometrics RDA II	40
8	Bohlin VORM	25
11	Rheometrics RMS-800	25
16i	Rheometrics DSR 200	25
16j	Rheometrics RDS II	25
17	Rheometrics RDS II	25
19	Rheometrics RMS-800	25
20	Bohlin CSM	25
27	Rheometrics RDA II	25
28	TA Instruments CSL ² 500	40

The laboratory references 16i and 16j indicate the same laboratory but different instruments.

4 RESULTS

4.1 GENERAL

Results are presented of time sweeps, strain sweep and frequency sweeps carried out on the two materials (7). Analysis of the frequency sweep results was carried out in accordance with (8) and is summarised in appendix 2. Also, further analysis has been carried out by fitting a 4th-order polynomial to the log(modulus, Pa) versus log (angular frequency, rad.s⁻¹) data to obtain an overall statistical fit of the data. This data fitting exercise involved the use of a significantly greater number of data that were obtained by a greater number of laboratories and over a wider frequency range than was analyzed according to (8).

4.2 TIME SWEEP

Time sweeps were carried out to determine the duration of thermal stability, or maximum permissible test duration. That is the time for which testing can continue prior to degradation of the sample having a significant affect on the results. The term 'degradation' is used to indicate a variation with time of the properties of the material from their original values that may result from mechanisms such as oxidation and further cross-linking of the polymer. The duration of thermal stability is defined, by the standard, as the time taken from the start of the test to that at which the measured values have changed from the initial values by $\pm 2\%$. Testing should then be carried out in a time less than the duration of thermal stability to ensure that the effects of degradation are known to be less than the specified amount of $\pm 2\%$.

Time sweeps were carried out on the two materials by each of the laboratories. Results for HDPE are compared in figures 1 and 2 for the storage modulus G' and loss modulus G'' respectively, and for PP in figures 3 and 4. The time axis gives elapsed time from the start of the test and does not take into account the time taken to reach temperature equilibrium. The variation between laboratories in the magnitude of the values of each of G' and G'' was due to the different angular frequencies used in testing.

For HDPE the results all exhibited a similar trend in behaviour of increasing moduli values with time, with the rate of increase becoming greater at longer times, figures 1 and 2. The majority of results indicated that there was sufficient time to carry out frequency sweep testing prior to degradation effects being greater than 2%. The use of an air atmosphere as opposed to a nitrogen atmosphere had no significant effect on the results for this material: testing by laboratory 8 was carried out in an air atmosphere. In all cases the effect of degradation was more significant in the G' values than in G'' values.

For PP the results exhibited the opposite trend of decreasing moduli with time, figure 3 and 4. However there was little apparent difference in the behaviour of the storage and loss moduli. The most significant effect was due to the use of a nitrogen atmosphere which was necessary in testing this material. When testing in an air atmosphere, laboratory 8, degradation effects were immediately apparent in the moduli values. When testing using a nitrogen atmosphere sufficiently long testing times without excessive degradation effects could be obtained to carry out frequency sweep measurements.

4.3 STRAIN SWEEP

Strain sweep measurements were carried out to determine the maximum strain that could be applied so that frequency sweep measurements could be carried out in the linear viscoelastic region, figures 5 - 8. If the measurements of moduli are not made within the

linear viscoelastic region then the assumptions made in the analysis of the raw data to determine G' and G'' values are not valid and consequently the results would be invalid. The limiting strain value was taken to be that at which the modulus value changed by $\pm 3\%$ from its linear viscoelastic "plateau" value at low strain.

The differences in the magnitude of the moduli values obtained were due to the different frequencies used in testing, ranging from 0.1 to 100 rad.s^{-1} .

Visual examination of the results for both HDPE and PP indicated that the limiting strain values were approximately similar for the measurement of both G' and G'' , figures 7 - 10. More detailed analysis of the results, by calculating the strain corresponding to a 3% variation from the initial moduli value, indicated that there was a trend of decreasing limiting strain value with increasing frequency for both materials, figures 9 and 10. The limiting strain values were, on average, 50 - 60% higher for G'' than for G' . However, the scatter in results was high due to the difficulty in determining the initial strain value and also to the lack of sufficient data to more accurately determine the strain value corresponding to a 3% change in modulus.

4.4 DYNAMIC PROPERTIES MEASUREMENT

The storage modulus G' and loss modulus G'' were measured over a range of frequencies by each laboratory, including repeat measurements. Values of G' and G'' at angular frequencies of 1, 10 and 100 rad.s^{-1} have been determined for each set of measurements made by each laboratory and analyzed as detailed in Appendix 2 to yield values for the repeatability limit r and reproducibility limit R . The values of r and R are calculated as 2.8 times the standard deviation within a laboratory S_r and between laboratories S_R . The repeatability and reproducibility limits therefore represent 95% confidence levels for the measurements (see section 6 and appendix 2). These results are presented for HDPE in table 4 for G' and table 5 for G'' , and for PP in table 6 for G' and table 7 for G'' . Each table presents values for measurements at each of the angular frequencies 1, 10 and 100 rad.s^{-1} . It is noted that the number of repeats carried out by some laboratories was small and that this may have a detrimental effect on the accuracy of the mean and standard deviation values calculated (9).

The repeatability levels r varied in the range 3.7 - 8.4% for HDPE and 6.6 - 9.4% for PP with the values for PP being, on average, 50% higher than for HDPE. On the basis of these results the magnitude of r was independent of angular frequency.

The reproducibility levels R varied in the range 21 - 27% for HDPE and 25 - 32% for PP with the values for PP being, on average, 10 - 20% higher than for HDPE. The magnitude of R decreased slightly with increasing angular frequency.

Removal of the most outlying results (laboratory 8 results only) for HDPE reduced the reproducibility levels by approximately 40%, for example from a value of 20% to 12%. However it had negligible effect on the repeatability levels.

Removal of the most outlying results (laboratory 6 results only) for PP reduced the reproducibility levels by approximately 15%, for example from 20% to 17%, but had negligible effect on the repeatability levels.

The moduli of HDPE were typically a factor of x2 higher than PP at equivalent angular frequencies although this difference increased to approximately a factor of x4 for G' at low angular frequency.

The G' and G'' data obtained from all the laboratories were fitted using a polynomial of the form

$$G = a + b\omega + c\omega^2 + d\omega^3 + e\omega^4$$

where G is the logarithm of the storage or loss modulus, a , b , c , d and e are constants determined from the curve fitting process and ω is the logarithm of the angular frequency. Logarithm values have been used so as not to distort the weighting of the data points which cover two to three decades in value. The results of this fitting exercise to G' and G'' data obtained over a much wider angular frequency range and also by additional laboratories are given in tables 4 - 7. The values calculated for the standard deviation from the fit of this model to the data agree with the standard deviations for reproducibility S_R calculated from the reduced sets of data at 1, 10 and 100 rad.s^{-1} to approximately 10%.

5 DISCUSSION

5.1 TIME SWEEP

As described in section 4.1, time sweeps were carried out to determine the duration of thermal stability, ie the maximum permissible test duration, prior to degradation having a significant affect on results. The standard specified that a 2% variation due to degradation was permitted. Subsequent testing is then carried out in a time less than the duration of thermal stability to ensure that the effects of degradation are known to be less than the specified amount.

The primary source of difficulty in determining the duration of thermal stability was due to the determination of the initial modulus value - the base line from which the time at which the modulus values have increased or decreased by the permitted value of 2% is determined. In testing, initial values often exhibited a higher apparent degree of scatter than values measured at a latter time. This is probably due to the sample undergoing some form of settling. Settling may also contribute to the behaviour at longer times and its effect may be inseparable from degradation effects. The uncertainty in the first measurements therefore made it difficult to accurately determine the initial modulus and therefore to calculate the permitted time for testing. This uncertainty could result in significant errors in the determination of the duration of thermal stability. It is suggested that for results exhibiting a high degree of scatter it may be preferable to fit a suitable function to the data and determine values of the initial moduli by extrapolation of the data to either zero or short times, the latter being relevant when plotting the data using a logarithmic time axis.

The results also indicate that it is not sufficient to use just one of the parameters G' or G'' to determine the duration of thermal stability. Changes were significantly greater for G' than for G'' in testing HDPE, but there was no significant difference between results for G' and G'' for PP. Thus both G' and G'' should be assessed for changes and the shortest time prior to a 2% change in values should be used as the duration of thermal stability.

On a point of good testing practice, the dwell time - the time from loading to the commencement of the test as is necessary to obtain thermal equilibrium - should ideally be small compared with the duration of thermal stability so that small changes in the dwell time used in subsequent testing do not significantly affect the maximum permitted duration of the test.

It was considered not suitable to assess the effect of angular frequency of measurement on the determination of the duration of thermal stability from these results. This would be best determined by the use of a single instrument using identical loading and thermal equilibrating procedures but different angular frequencies of testing.

5.2 STRAIN SWEEP

Strain sweeps were carried out to determine the maximum strains that could be applied such that the measurement of G' and G'' would be carried out in the linear viscoelastic region.

As was also the case for determining the duration of thermal stability, a major problem in determining the strain range over which the modulus values remained within the permitted variation of 3% was in determining the initial modulus value. Again, it is suggested that for results exhibiting a high degree of scatter it may be preferable to fit a suitable function to the data and determine values of the linear viscoelastic moduli by extrapolation of the data to small values of strain. The higher scatter was considered to be due to the fact that the instruments were likely to be operating at the lower limit of their range and possibly also due to settling of the sample.

The trend of decreasing strain limit with increasing angular frequency indicates that it is preferable, for these materials, to determine the strain limit using a high value of frequency. However, the frequency should not be so high as to cause additional problems related to specimen distortion or fracture.

For the polyethylene material the problem of determining the limit of strain for testing under linear viscoelastic conditions was further complicated by the increase in moduli values with time as observed in the time sweeps, figures 1 and 2. The increase in moduli values due to the degradation opposed the decrease in moduli values due to the onset of non-linear viscoelastic behaviour with the consequence that the thus measured strain limit would be greater than actual. Therefore in carrying out testing one should be aware of the possible interactions between effects of degradation and non-linear viscoelastic response of the material on strain sweep measurements.

5.3 DYNAMIC PROPERTIES MEASUREMENT

The repeatability limits r of the measurements of G' and G'' are small indicating good repeatability of measurements: 95% confidence levels were in the range 3.7 - 9.4%. However the reproducibility limits R are considerably higher being in the range 21 - 32% (on average a factor of x4 higher) indicating significant differences in results between laboratories arising from variations in the testing procedures and equipment used.

The potential causes of these differences are due to the uncertainty limits in calibration of the instrument (see section 2.1 and 2.2), degradation, non-linear viscoelastic behaviour of the sample and differences in the testing procedure. The uncertainty limits of testing, due to the accepted tolerances of the method as specified in the section 2.1, are estimated to be of the order of 5%. However, the uncertainty in the torque measurement may be significantly higher if the instrument is used in the lower part of its torque range as the current specification for the tolerance on torque measurement is 2% of full scale deflection. For a reading of 10% of full scale deflection this tolerance equates to a 20% error. In addition to these potential source of error there are additional uncertainties due to non-parallelism and non-axial alignment of the plates, edge effects, machine inertia, sample inertia and machine compliance. These additional factors have not necessarily been corrected for in the testing carried out by the various laboratories for this round robin.

5.4 GENERAL

A general point raised from this work is that it is necessary to optimise the test conditions so that testing is carried out using a sensible range of the measuring instrument in order to

minimise the errors associated with those measurements. This is a particular problem for rheological measurements where the measured properties can vary by four decades in magnitude, for example figure 13.

6 PROPOSED PRECISION STATEMENT FOR ADOPTION IN ISO 6721-10

The following precision data have been determined during a test program made in 1995, comprising 10 laboratories in total at 3 angular frequencies on polyethylene and polypropylene samples. The instruments used included both controlled strain and controlled stress type rheometers.

Polyethylene at 190 °C, G'					
Angular frequency, rad.s^{-1}	Mean level	Within the laboratory		Between the laboratories	
	m (Pa)	Sr (%)	r (%)	S_R (%)	R (%)
1	6130	3.0	8.4	9.4	26.4
10	25500	2.0	5.5	8.9	24.8
100	91300	1.6	4.4	7.9	22.2

Polyethylene at 190 °C, G''					
Angular frequency, rad.s^{-1}	Mean level	Within the laboratory		Between the laboratories	
	m (Pa)	Sr (%)	r (%)	S_R (%)	R (%)
1	8320	1.6	4.5	8.5	23.9
10	28900	1.3	3.7	8.4	23.4
100	79600	1.2	4.3	7.5	21.0

Polypropylene at 210 °C, G'					
Angular frequency, rad.s^{-1}	Mean level	Within the laboratory		Between the laboratories	
	m (Pa)	Sr (%)	r (%)	S_R (%)	R (%)
1	1590	3.4	9.4	11.3	31.7
10	12000	2.5	6.9	10.5	29.3
100	47800	2.5	7.1	9.3	26.1

Polypropylene at 210 °C, G''					
Angular frequency, rad.s^{-1}	Mean level	Within the laboratory		Between the laboratories	
	m (Pa)	Sr (%)	r (%)	S_R (%)	R (%)
1	3880	2.4	6.6	10.3	28.8
10	15400	2.4	6.8	9.5	26.7
100	36000	2.7	7.7	9.1	25.6

The difference between two individual results obtained on an identical material using this test method with "repeatability conditions" will not exceed the repeatability limit r on average more than 5 times out of 100 when the method is applied normally and correctly.

Individual results obtained on an identical material submitted to a test by two laboratories will not exceed the reproducibility limit R on average more than 5 times out of 100 when the method is applied normally and correctly in reproducibility conditions.

7 CONCLUSIONS

On the basis of the work reported here the following conclusions are made (all repeatability and reproducibility values quoted are for 95% confidence levels):

- Reproducibility values for G' were typically 25% for HDPE and 29% for PP.
- Reproducibility values for G'' were typically 23% for HDPE and 27% for PP.
- Repeatability values for G' were typically 6% for HDPE and 8% for PP.
- Repeatability values for G'' were typically 4% for HDPE and 7% for PP.
- For HDPE and PP the highest values for reproducibility were 26% and 32% respectively, and for repeatability they were 8 and 9% respectively.
- Reproducibility limits were a factor of approximately $\times 4$ higher than repeatability limits, implying considerable variation in equipment performance and/or utilisation.
- A precision statement for the standard ISO 6721-10 detailing repeatability and reproducibility limits for measurement of the storage modulus G' and loss moduli G'' using oscillatory rheometers has been provided, section 6.
- In testing in accordance with the specification of the standard ISO-CD 6721-10 the uncertainties in the measurement of G' and G'' were estimated to be approximately 5% for the polyethylene and polypropylene materials tested herein.
- Difficulties in determining the initial modulus values in time and strain sweep measurements can result in significant variations in the determined values for the duration of thermal stability and the limiting strain for linear viscoelastic behaviour.
- The limiting strain value for linear viscoelastic behaviour decreased with increasing angular frequency indicating that, for these materials, it is preferable to determine the limiting strain value using a high angular frequency. This is provided that the use of the high frequency does not distort the specimen shape thereby invalidating measurements.
- It is not sufficient to determine the duration of thermal stability and the limiting strain for linear viscoelastic behaviour by using only one of the parameters G' or G'' . Both G' and G'' should be used.
- Opposing effects of degradation and non-linear viscoelastic behaviour can result in the determined limiting strain value for linear viscoelastic behaviour being too high.

In summary, the repeatability and reproducibility levels have significant implications for testing using this method, whether comparing data obtained on the same instrument for quality control applications, comparing data obtained on the same material but using different instruments, or using the data for predictive modelling. The levels of repeatability and reproducibility must be taken into account in assessing the value of test results.

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Table 4: Analysis of results of measurements of G' for the polyethylene (material A/HFU000) at 190 °C and at the selected angular frequencies of 1, 10 and 100 rad.s^{-1} (values presented in brackets are percentages of the mean, m).

G' for HDPE at 190 °C and 1 rad.s^{-1}								
Lab. ref. no.	Lab mean G' (Pa)	Standard deviation G' (Pa)	no. of tests	m (Pa)	S_r (Pa)	S_R (Pa)	r (Pa)	R (Pa)
8	4880	123	3	6130	180 (3.0%)	569 (9.4%)	505 (8.4%)	1594 (26.4%)
11	6880	91.9	2					
16i	6140	145	3					
16j	6090	54.1	3					
19	6530	76.7	2					
20	6060	171	7					
27	6040	308	4					

G' for HDPE at 190 °C and 10 rad.s^{-1}								
Lab. ref. no.	Lab mean G' (Pa)	Standard deviation G' (Pa)	no. of tests	m (Pa)	S_r (Pa)	S_R (Pa)	r (Pa)	R (Pa)
8	20900	383	4	25500	499 (2.0%)	2260 (8.9%)	1400 (5.5%)	6320 (24.8%)
11	28500	212	2					
16i	26000	395	3					
16j	26400	405	3					
19	27300	134	2					
20	26100	540	7					
27	24500	704	4					

G' for HDPE at 190 °C and 100 rad.s^{-1}								
Lab. ref. no.	Lab mean G' (Pa)	Standard deviation G' (Pa)	no. of tests	m (Pa)	S_r (Pa)	S_R (Pa)	r (Pa)	R (Pa)
8	77400	1040	4	91300	1430 (1.6%)	7250 (7.9%)	4000 (4.4%)	20300 (22.2%)
11	100000	70.7	2					
16i	90300	1680	3					
16j	95500	1730	3					
19	97700	278	2					
20	94200	1490	7					
27	86600	1580	4					

One standard deviation value of a fit of a 4th order polynomial to $\log(G', \text{Pa})$ versus $\log(\text{angular frequency, rad.s}^{-1})$ expressed as a percentage = 9.6%. Number of data points = 572. Angular frequency range = 0.03 - 398 rad.s^{-1} .

Table 5: Analysis of results of measurements of G'' for the polyethylene (material A/HFU000) at 190 °C and at the selected angular frequencies of 1, 10 and 100 rad.s^{-1} (values presented in brackets are percentages of the mean, m).

G'' for HDPE at 190 °C and 1 rad.s^{-1}								
Lab. ref. no.	Lab mean G'' (Pa)	Standard deviation G'' (Pa)	no. of tests	m (Pa)	S_r (Pa)	S_R (Pa)	r (Pa)	R (Pa)
8	6900	119	3	8320	134 (1.6%)	711 (8.5%)	375 (4.5%)	1990 (23.9%)
11	9260	35.4	2					
16i	8440	97.3	3					
16j	8580	134	3					
19	8850	27.1	2					
20	8590	128	7					
27	7910	202	4					

G'' for HDPE at 190 °C and 10 rad.s^{-1}								
Lab. ref. no.	Lab mean G'' (Pa)	Standard deviation G'' (Pa)	no. of tests	m (Pa)	S_r (Pa)	S_R (Pa)	r (Pa)	R (Pa)
8	24200	408	3	28900	383 (1.3%)	2420 (8.4%)	1070 (3.7%)	6770 (23.4%)
11	31300	0	2					
16i	29500	258	3					
16j	29900	547	3					
19	30700	71.4	2					
20	30100	378	7					
27	26700	434	4					

G'' for HDPE at 210 °C and 100 rad.s^{-1}								
Lab. ref. no.	Lab mean G'' (Pa)	Standard deviation G'' (Pa)	no. of tests	m (Pa)	S_r (Pa)	S_R (Pa)	r (Pa)	R (Pa)
8	69100	917	3	79600	1210 (1.2%)	5970 (7.5%)	3390 (4.3%)	16700 (21%)
11	86000	212	2					
16i	81000	1570	3					
16j	81700	1620	3					
19	85000	264	2					
20	82500	1290	7					
27	73800	992	4					

One standard deviation value of a fit of a 4th order polynomial to $\log(G'', \text{Pa})$ versus $\log(\text{angular frequency, rad.s}^{-1})$ expressed as a percentage = 7.6%. Number of data points = 572. Angular frequency range = 0.03 - 398 rad.s^{-1} .

Table 6: Analysis of results of measurements of G' for the polypropylene (material C/HFV000) at 210 °C and at the selected angular frequencies of 1, 10 and 100 rad.s^{-1} (values presented in brackets are percentages of the mean, m).

G' for PP at 210 °C and 1 rad.s^{-1}								
Lab. ref. no.	Lab mean G' (Pa)	Standard deviation G' (Pa)	no. of tests	m (Pa)	S_r (Pa)	S_R (Pa)	r (Pa)	R (Pa)
3	1480	28.3	2	1590	53.4 (3.4%)	179 (11.3%)	150 (9.4%)	502 (31.7%)
6	1320	4.79	2					
16i	1500	33.1	3					
16j	1710	34.3	3					
19	1840	75.0	2					
20	1730	81.3	5					
27	1440	29.1	4					

G' for PP at 210 °C and 10 rad.s^{-1}								
Lab. ref. no.	Lab mean G' (Pa)	Standard deviation G' (Pa)	no. of tests	m (Pa)	S_r (Pa)	S_R (Pa)	r (Pa)	R (Pa)
3	11200	141	2	12000	295 (2.5%)	1260 (10.5%)	825 (6.9%)	3520 (29.3%)
6	10100	52.5	2					
16i	11500	161	3					
16j	12700	213	3					
19	13500	525	2					
20	13300	414	5					
27	11000	174	4					

G' for PP at 210 °C and 100 rad.s^{-1}								
Lab. ref. no.	Lab mean G' (Pa)	Standard deviation G' (Pa)	no. of tests	m (Pa)	S_r (Pa)	S_R (Pa)	r (Pa)	R (Pa)
3	44900	212	2	47800	1220 (2.5%)	4460 (9.3%)	3400 (7.1%)	12500 (26.1%)
6	40900	136	2					
16i	46700	210	3					
16j	49800	584	3					
19	52700	1970	2					
20	52300	1940	5					
27	44100	570	4					

One standard deviation value of a fit of a 4th order polynomial to $\log(G', \text{Pa})$ versus $\log(\text{angular frequency, } \text{rad.s}^{-1})$ expressed as a percentage = 12.2%. Number of data points = 431. Angular frequency range = 0.01 - 398 rad.s^{-1} .

Table 7: Analysis of results of measurements of G'' for the polypropylene (material C/HFV000) at 210 °C and at the selected angular frequencies of 1, 10 and 100 rad.s^{-1} (values presented in brackets are percentages of the mean, m).

G'' for PP at 210 °C and 1 rad.s^{-1}								
Lab. ref. no.	Lab mean G'' (Pa)	Standard deviation G'' (Pa)	no. of tests	m (Pa)	S_r (Pa)	S_R (Pa)	r (Pa)	R (Pa)
3	3620	42.4	2	3880	91.6 (2.4%)	399 (10.3%)	256 (6.6%)	1120 (28.8%)
6	3270	11.7	2					
16i	3740	45.9	3					
16j	4080	60.2	3					
19	4350	163	2					
20	4260	131	5					
27	3540	55.0	4					

G'' for PP at 210 °C and 10 rad.s^{-1}								
Lab. ref. no.	Lab mean G'' (Pa)	Standard deviation G'' (Pa)	no. of tests	m (Pa)	S_r (Pa)	S_R (Pa)	r (Pa)	R (Pa)
3	14400	141	2	15400	372 (2.4%)	1470 (9.5%)	1040 (6.8%)	4110 (26.7%)
6	13100	56.4	2					
16i	15100	103	3					
16j	16000	175	3					
19	16900	623	2					
20	16900	581	5					
27	14100	180	4					

G'' for PP at 210 °C and 100 rad.s^{-1}								
Lab. ref. no.	Lab mean G'' (Pa)	Standard deviation G'' (Pa)	no. of tests	m (Pa)	S_r (Pa)	S_R (Pa)	r (Pa)	R (Pa)
3	33800	70.7	2	36000	988 (2.7%)	3300 (9.1%)	2770 (7.7%)	9220 (25.6%)
6	30100	117	2					
16i	36500	146	3					
16j	37000	320	3					
19	39100	1370	2					
20	39200	1670	5					
27	33400	364	4					

One standard deviation value of a fit of a 4th order polynomial to $\log(G'', \text{Pa})$ versus $\log(\text{angular frequency, rad.s}^{-1})$ expressed as a percentage = 9.0%. Number of data points = 431. Angular frequency range = 0.01 - 398 rad.s^{-1} .

APPENDIX 1 Uncertainties in the measurement of the storage modulus G' and loss modulus G'' .

The storage and loss moduli are given by the expressions

$$G' = \frac{32 d T_o \cos \delta}{\theta_o \pi D^4}$$

and

$$G'' = \frac{32 d T_o \sin \delta}{\theta_o \pi D^4}$$

respectively, where d is the plate gap, T_o the torque amplitude, δ the loss angle, θ_o the angular displacement amplitude and D the plate diameter.

The corresponding fractional uncertainties are then given by the expressions

$$\underline{G'} = (\underline{d}^2 + \underline{T_o}^2 + (\underline{\cos \delta})^2 + \underline{\theta}^2 + 4 \times \underline{D}^2)^{0.5}$$

and

$$\underline{G''} = (\underline{d}^2 + \underline{T_o}^2 + (\underline{\sin \delta})^2 + \underline{\theta}^2 + 4 \times \underline{D}^2)^{0.5}$$

where the underline indicates the fractional uncertainty of each of the terms. The fractional uncertainty is determined as the ratio of the uncertainty in the value of the term due, for example, to its calibration and/or resolution divided by the value of the term. For example, for measurement of angular displacement which has an accuracy of $\pm 20 \times 10^{-6}$ rad and, say, an amplitude of 20×10^{-4} rad the fractional uncertainty of the measurement is 0.01.

To include contributions due to the uncertainty in the measurement of angular frequency ($\pm 2\%$ assuming a 1:1 dependence of G' and G'' on angular frequency) and the effects due to degradation ($\pm 2\%$) and non-linear viscoelasticity ($\pm 3\%$) then the above expressions for the uncertainties in the measurement of G' and G'' can be re-written as

$$\underline{G'} = (\underline{d}^2 + \underline{T_o}^2 + (\underline{\cos \delta})^2 + \underline{\theta}^2 + 4 \times \underline{D}^2 + \underline{F}^2 + \underline{DE}^2 + \underline{SL}^2)^{0.5}$$

and

$$\underline{G''} = (\underline{d}^2 + \underline{T_o}^2 + (\underline{\sin \delta})^2 + \underline{\theta}^2 + 4 \times \underline{D}^2 + \underline{F}^2 + \underline{DE}^2 + \underline{SL}^2)^{0.5}$$

where $\underline{F}$ is the fractional uncertainty due to the error in angular frequency, $\underline{DE}$ is the fractional uncertainty due to degradation effects and $\underline{SL}$ is the fractional uncertainty due to non-linear viscoelasticity effects.

APPENDIX 2 Computation of mean, standard deviations, repeatability and reproducibility limits.

Repeatability and reproducibility can be defined (10) as:

REPEATABILITY: The closeness of agreement between successive results obtained with the same method on identical test material, under the same conditions (same operator, same apparatus, same laboratories and/or same times).

REPRODUCIBILITY: The closeness of agreement between individual results obtained with the same method on identical test material, but under different conditions (different operator, different apparatus, different laboratories and/or different times).

In accordance with ISO document TC61 SC5 GT 21 N18E (4) 'Determination of the precision of a test method - practical guide' the mean, standard deviations and repeatability and reproducibility limits are determined as follows, where:

n_i = number of tests carried out by laboratory i,
 $\bar{Y}_i$ = mean of the n_i tests,
 S_i = standard deviation of n_i tests,
 m = mean of all laboratories,
 S_r = standard deviation within a laboratory per level,
 S_R = standard deviation for the total deviation between the laboratories per level,
 r = repeatability limit ($= 2.8 S_r$),
 R = reproducibility limit ($= 2.8 S_R$),
 p = number of laboratories.

Given that

$$\begin{aligned} T_1 &= \sum n_i \bar{Y}_i \\ T_2 &= \sum n_i \bar{Y}_i^2 \\ T_3 &= \sum n_i \\ T_4 &= \sum n_i^2 \\ T_5 &= \sum (n_i - 1) S_i^2 \end{aligned}$$

then

$$S_r^2 = \frac{T_5}{(T_3 - p)}$$

$$S_L^2 = \left[\frac{T_2 T_3 - T_1^2}{T_3(p - 1)} - S_r^2 \right] \left[\frac{T_3(p - 1)}{T_3^2} - T_4 \right]$$

$$S_R^2 = S_L^2 + S_r^2$$

and

$$m = T_1 / T_3$$

$$r = 2.8 S_r$$

$$R = 2.8 S_R$$

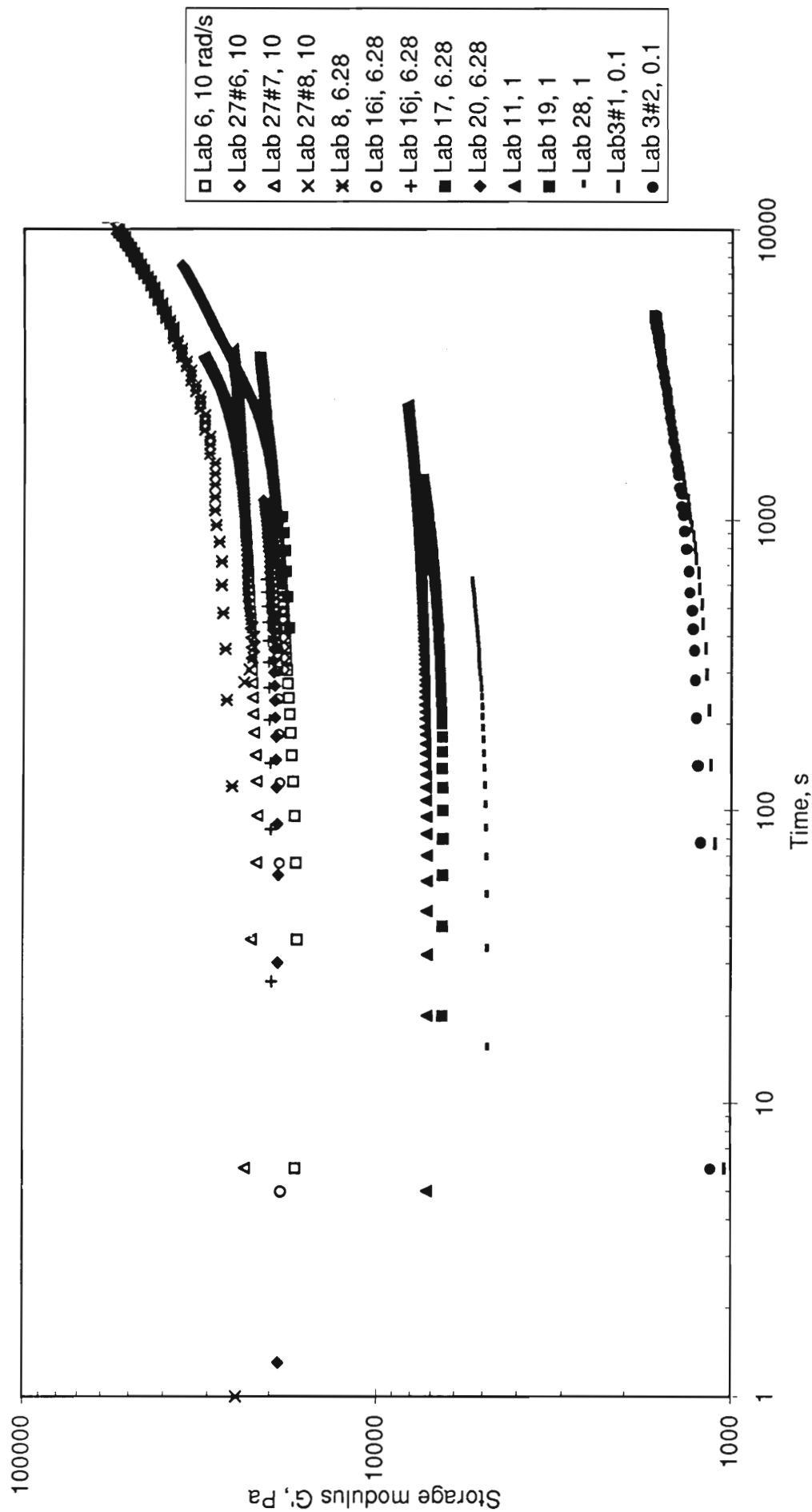


Figure 1 Time sweep: storage modulus G' measurements to determine the thermal stability of HDPE (HFU000) at 190 °C.
Legend gives the laboratory reference number and angular frequency (rad.s^{-1}) used in the measurements.

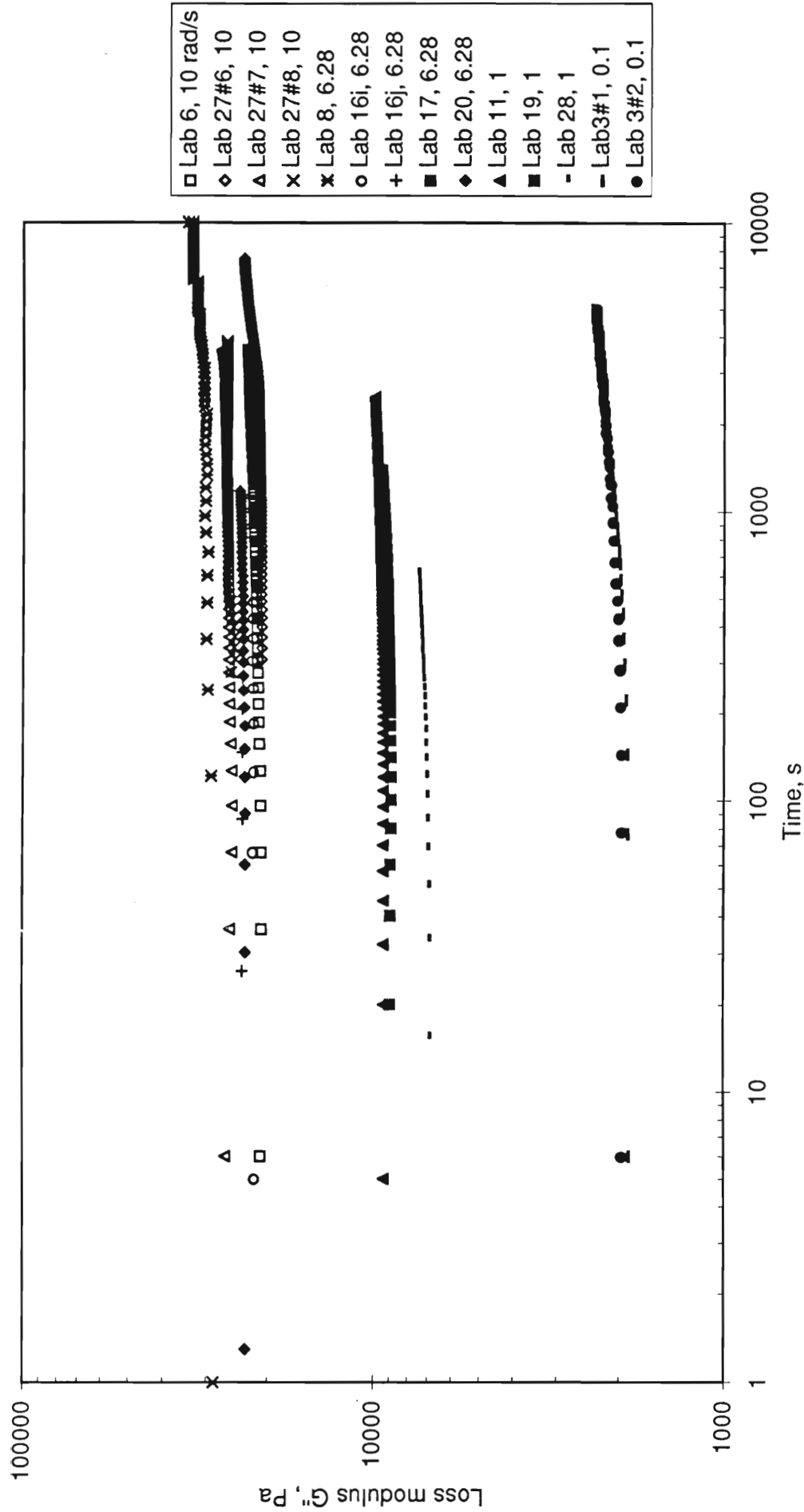


Figure 2 Time sweep: loss modulus G'' measurements to determine the thermal stability of HDPE (HFU000) at 190 °C. Legend gives the laboratory reference number and angular frequency (rad.s⁻¹) used in the measurements.

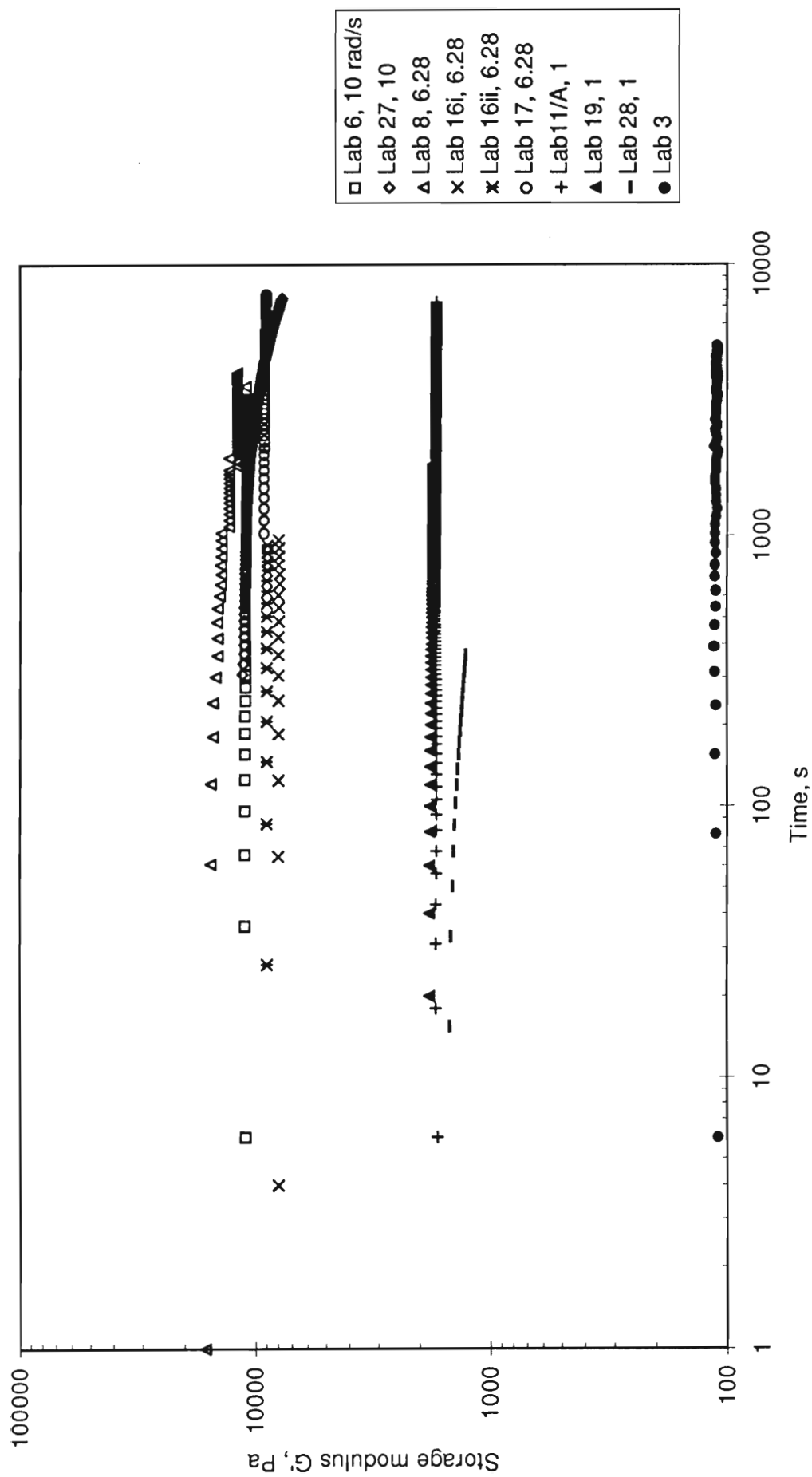


Figure 3 Time sweep: storage modulus G' measurements to determine the thermal stability of PP (HFV000) at 210 °C. Legend gives the laboratory reference number and angular frequency (rad.s⁻¹) used in the measurements.

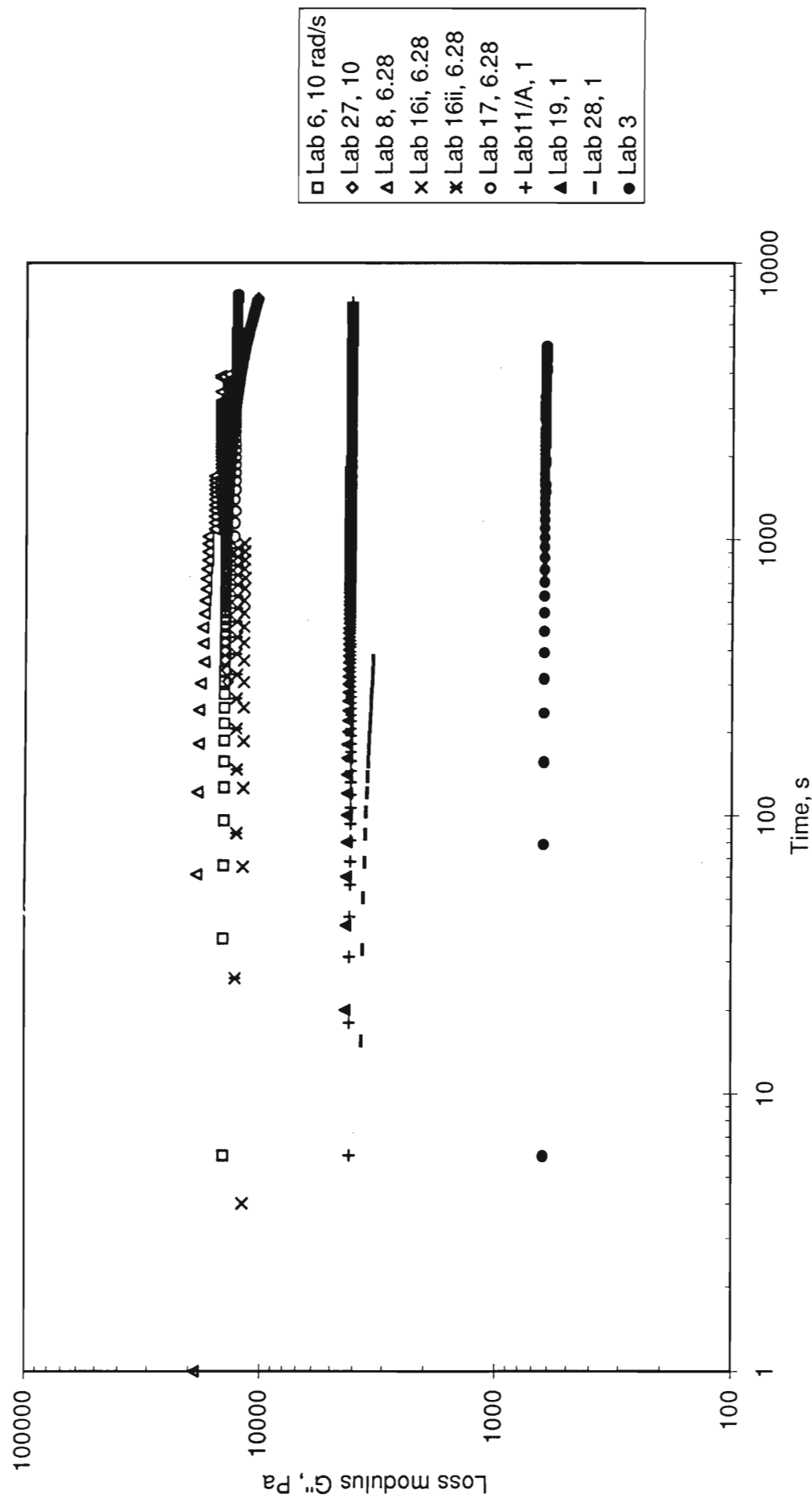


Figure 4 Time sweep: loss modulus G'' measurements to determine the thermal stability of PP (HFV000) at 210 °C. Legend gives the laboratory reference number and angular frequency (rad.s^{-1}) used in the measurements.

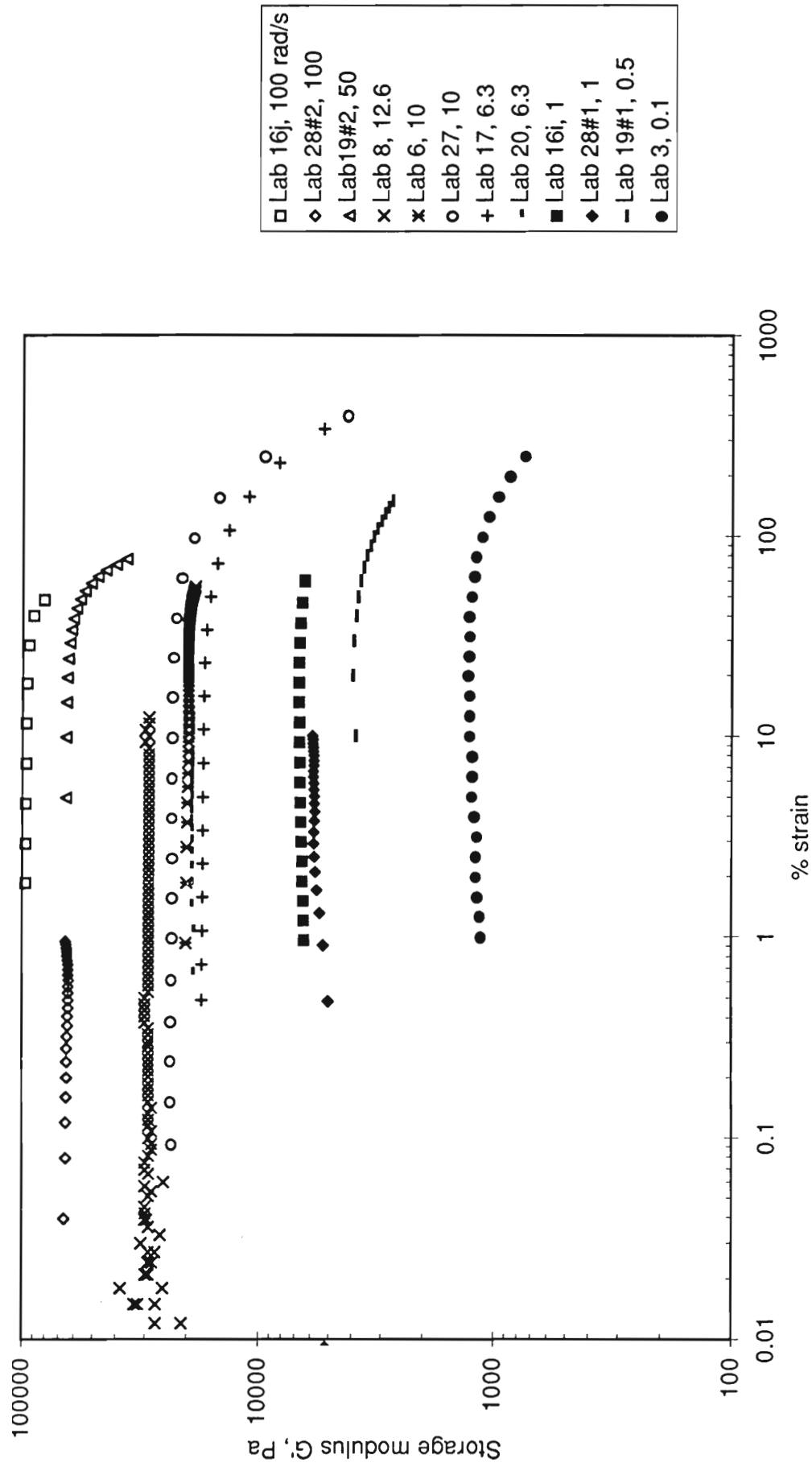


Figure 5 Strain sweep: storage modulus G' measurements to determine the limiting strain for linear viscoelastic measurements of HDPE (HFU000) at 190 °C. Legend gives the laboratory reference number and angular frequency (rad.s^{-1}) used in the measurements.

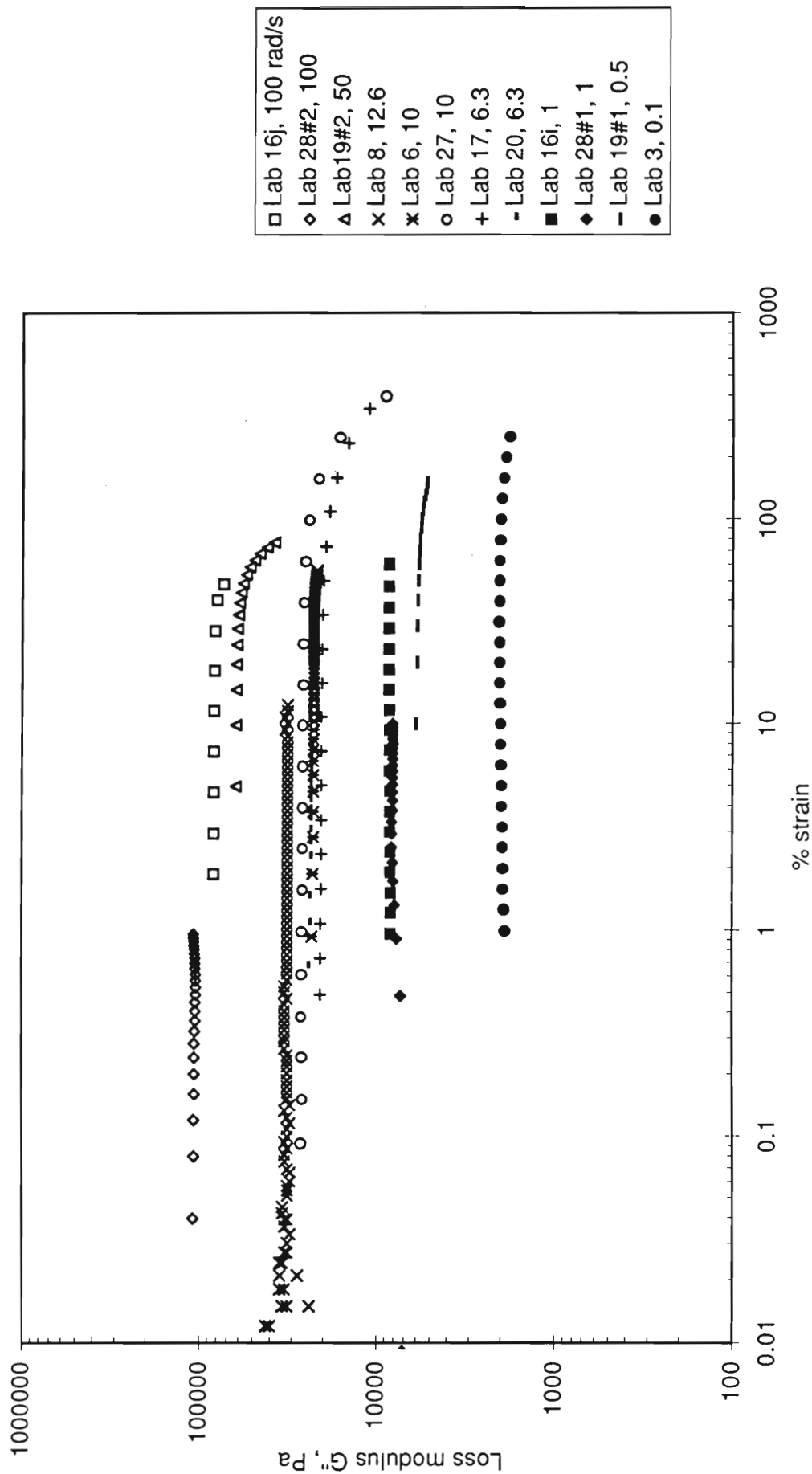


Figure 6 Strain sweep: loss modulus G'' measurements to determine the limiting strain for linear viscoelastic measurements of HDPE (HFU000) at 190 °C. Legend gives the laboratory reference number and angular frequency (rad.s^{-1}) used in the measurements.

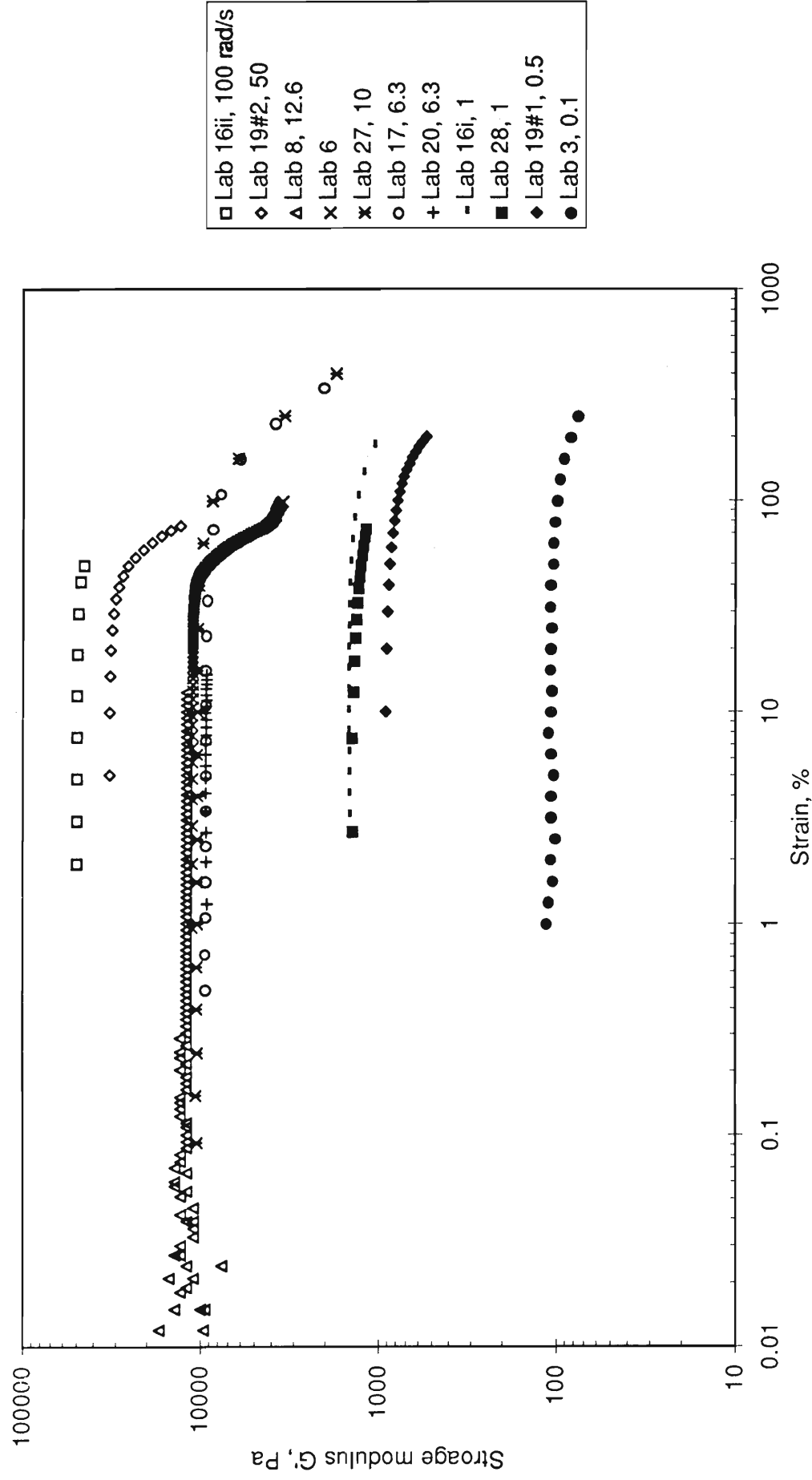


Figure 7 Strain sweep: storage modulus G' measurements to determine the limiting strain for linear viscoelastic measurements of PP (HFV000) at 210 °C. Legend gives the laboratory reference number and angular frequency (rad.s⁻¹) used in the measurements.

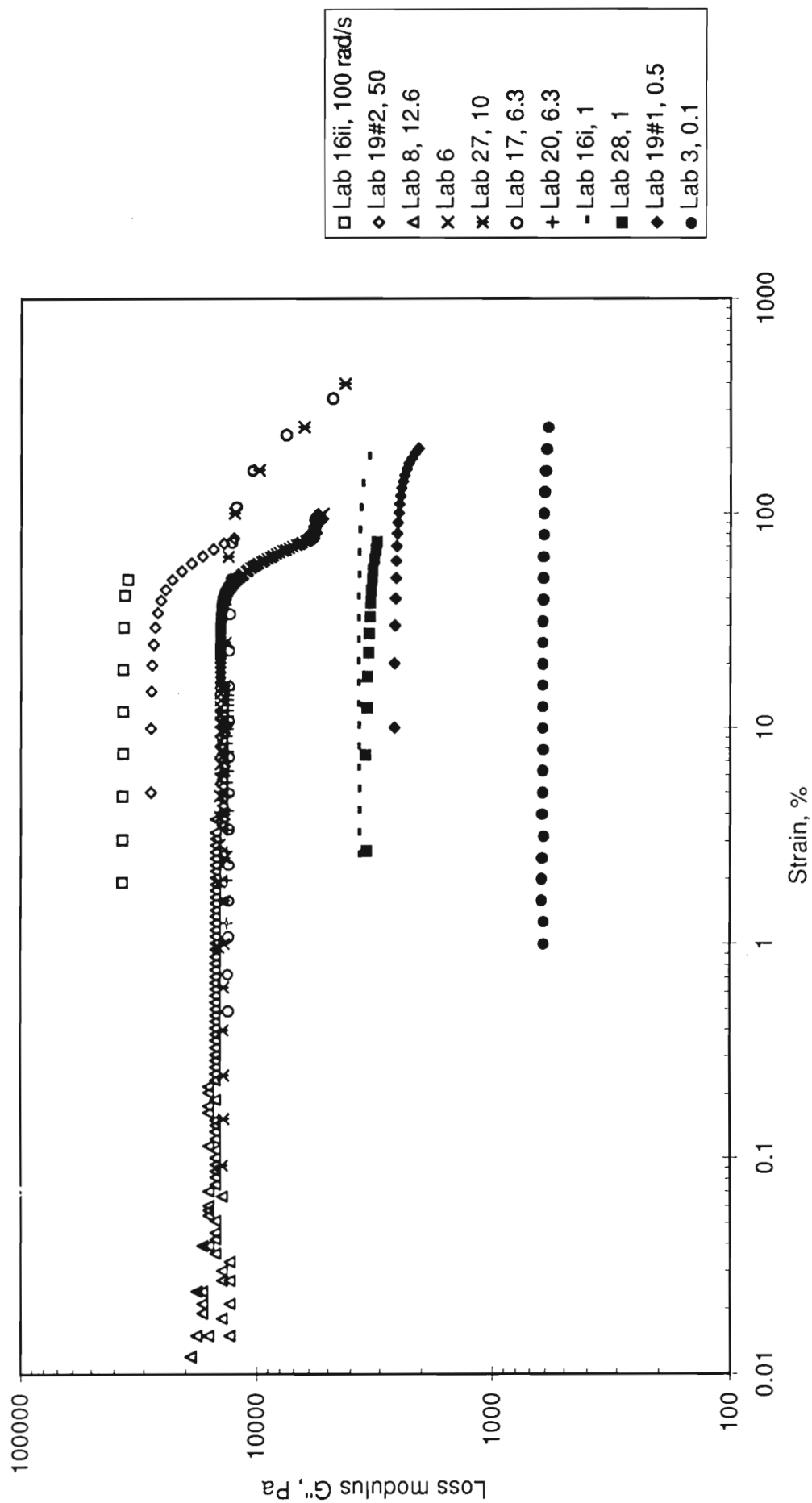


Figure 8 Strain sweep: loss modulus G'' measurements to determine the limiting strain for linear viscoelastic measurements of PP (HFV000) at 210 °C. Legend gives the laboratory reference number and angular frequency (rad.s^{-1}) used in the measurements.

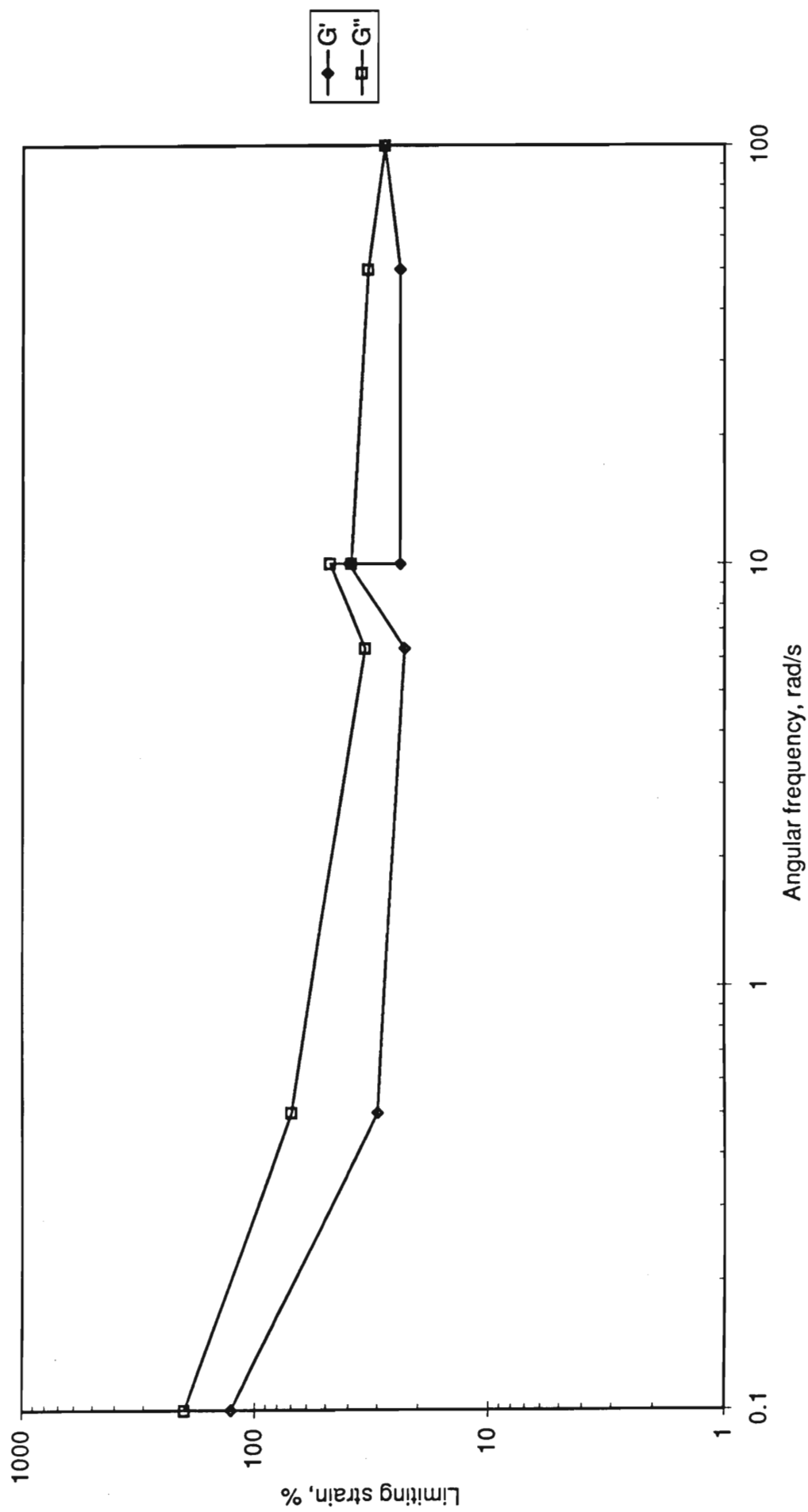


Figure 9 The effect of angular frequency on the determination of the limiting strain for linear viscoelasticity measurements of HDPE (HFU000) at 190 °C.

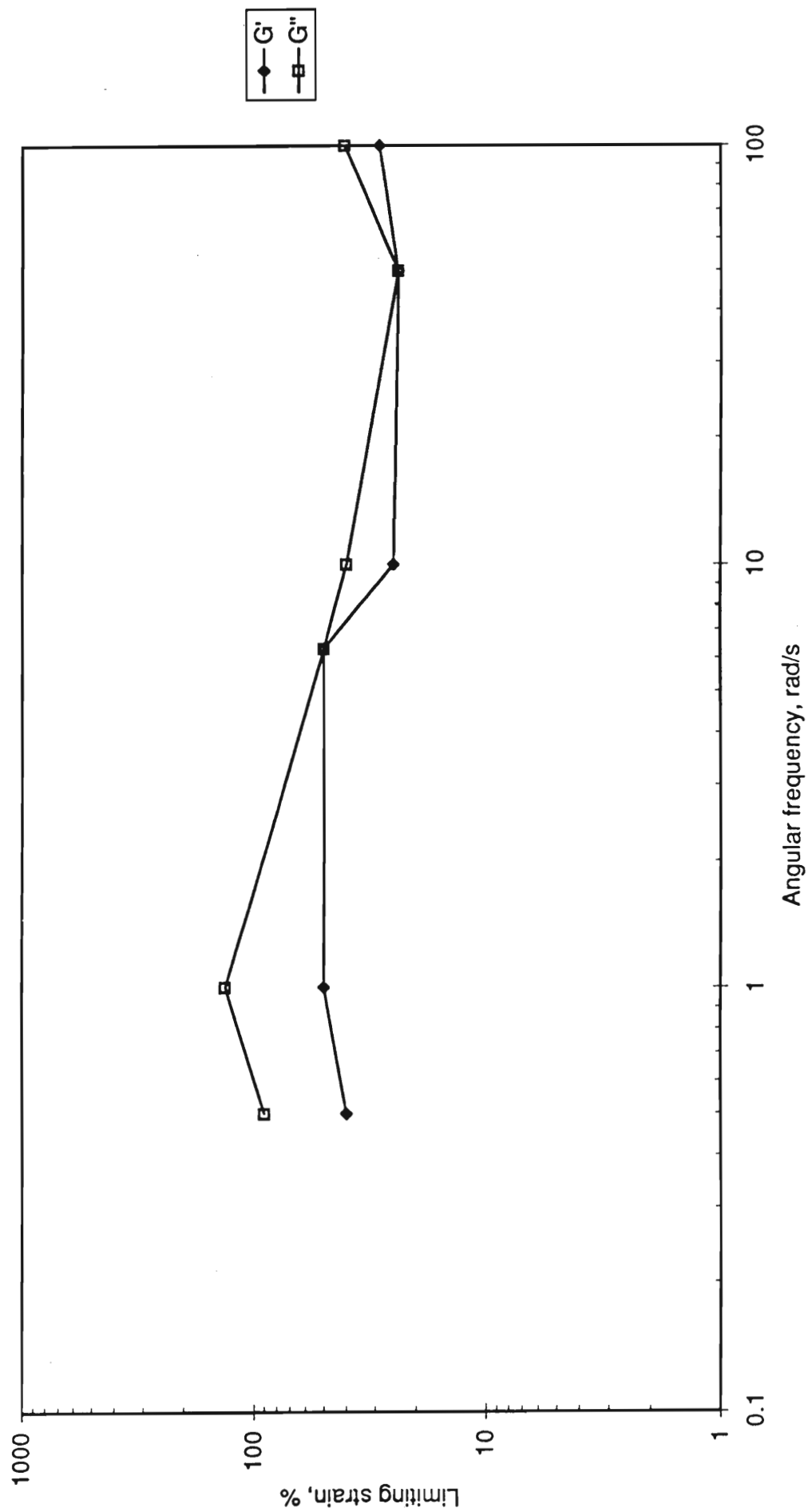


Figure 10 The effect of angular frequency on the determination of the limiting strain for linear viscoelasticity measurements of PP (HFV000) at 210 °C.

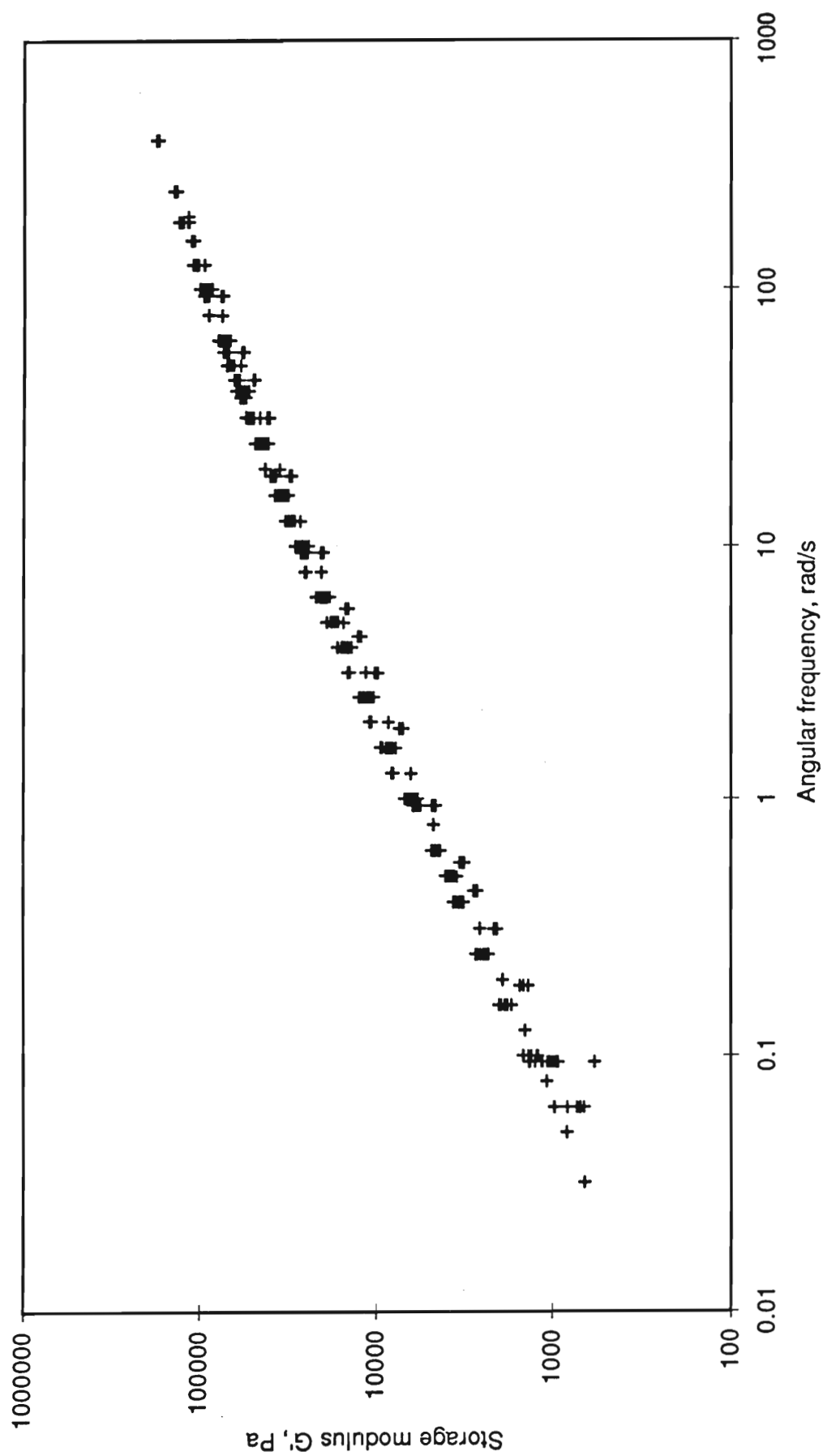


Figure 11 Storage modulus G' data obtained from frequency sweep measurements by eight laboratories for HDPE (HFU000) at 190 °C indicating the scatter in measured values.

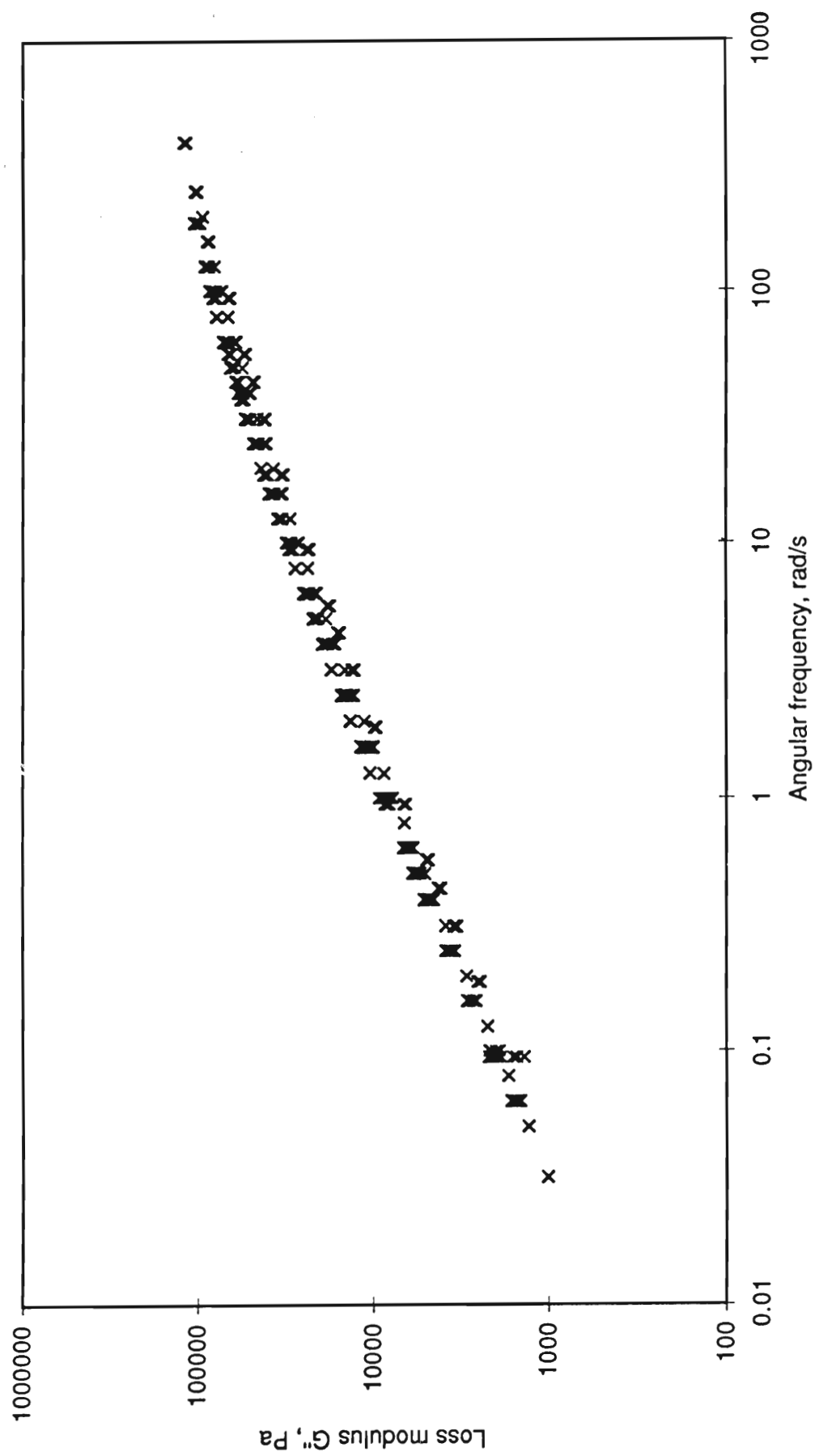


Figure 12 Loss modulus G'' data obtained from frequency sweep measurements by eight laboratories for HDPE (HFU000) at 190 °C indicating the scatter in measured values.

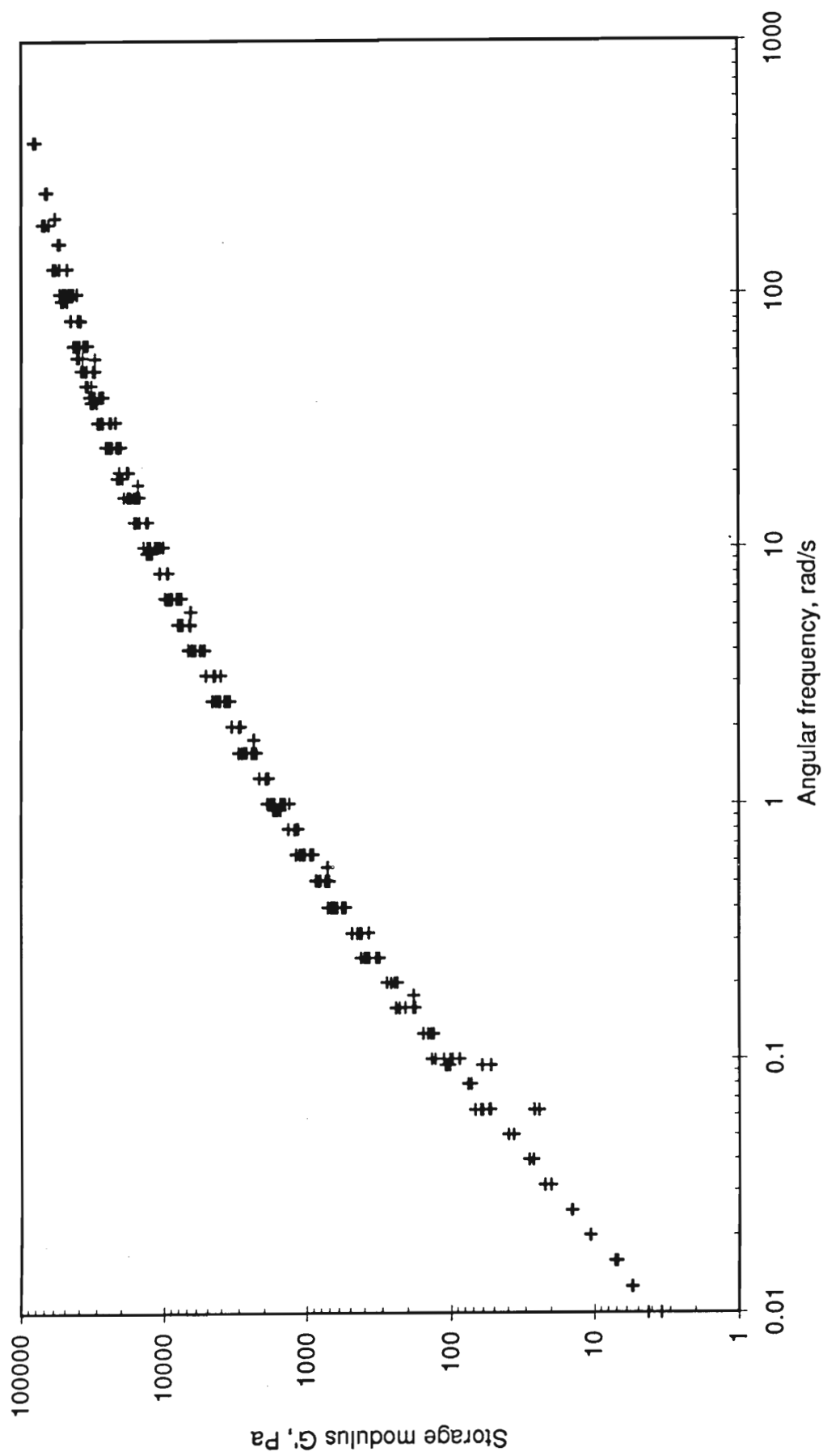


Figure 13 Storage modulus G' data obtained from frequency sweep measurements by eight laboratories for PP (HFV000) at 210 °C indicating the scatter in measured values.

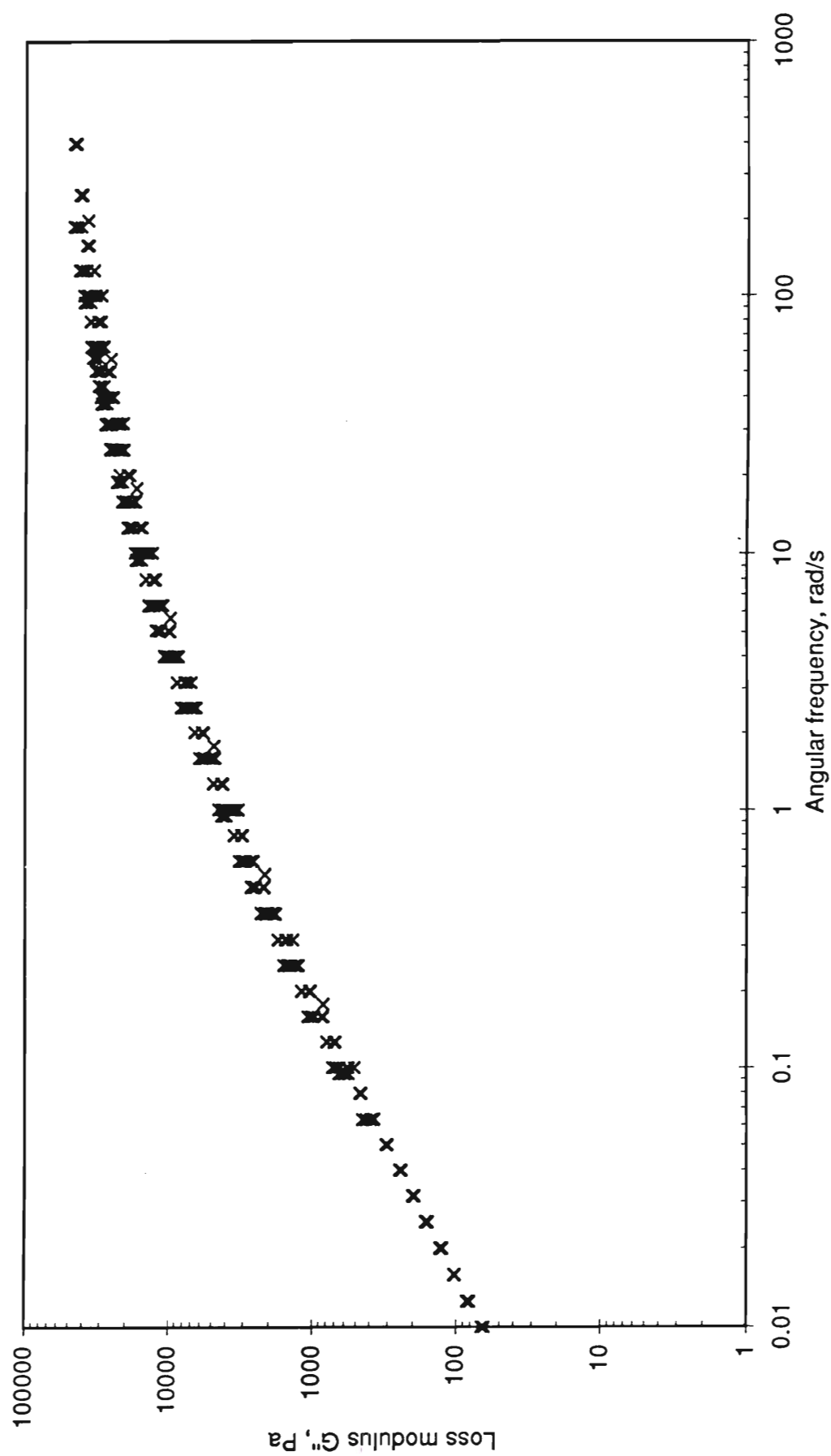


Figure 14 Loss modulus G'' data obtained from frequency sweep measurements by eight laboratories for PP (HFV000) at 210 °C indicating the scatter in measured values.

