



**THE PRESSURE DEPENDENCY OF THE SHEAR VISCOSITY OF POLYMER
MELTS : AN INTERNATIONAL ROUND ROBIN STUDY**

S Chakravorty, M Rides, C R G Allen and C S Brown

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ABSTRACT

Polymer melt viscosity has been reported to increase by as much as 500% when the pressure is raised from atmospheric to the level at which much processing takes place i.e. typically 125 MPa. Currently, industry is either unaware or does not appreciate the full extent of the effects caused by this particular process parameter. Process modelling work, that currently depends on data obtained primarily at atmospheric level, is also demanding more and more experimental pressure dependent melt viscosity data that can be used with increased confidence to simulate actual process events. Unfortunately, the availability of such data is limited in the literature and is of unknown reliability.

National Physical Laboratory (NPL) has recognized this measurement problem and consequently initiated an international intercomparison exercise (round robin) to produce pressure dependent melt viscosity data under a set workplan from various sources. This allowed the reproducibility, as well as reliability of the results generated by different techniques to be determined. Four organizations took part and their results are discussed in this report.

The apparent shear viscosity of polymer melts increased exponentially with pressure at a given shear rate in all cases. Intercepts of the plots showed systematic variation of viscosity with pressure at each shear rate. The slopes of the plots varied between 0.004 and 0.010 s at 200°C and between 0.005 and 0.011 s at 180°C. Experimental results showed an increase of viscosity in polystyrene to 200-300% with pressure at 70 MPa compared with atmospheric pressure. When extrapolated to 125 MPa, this represented a good agreement with the published work. The results from all sources were found to be reproducible to within $\pm 36\%$ (at 95% confidence level) at 200°C for shear rates of 500-1000 s⁻¹. At 180°C and at a common shear rate of 1000 s⁻¹, the reproducibility of the results was within $\pm 20\%$ (at 95% confidence level).

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Approved on behalf of Managing Director, NPL, by Dr M K Hossain,
Director, Centre for Materials Measurement and Technology

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1 INTRODUCTION

Wide ranges of pressure and temperature are encountered in polymer processing operations, such as injection moulding. However, while the temperature dependence of polymer melt viscosity has been extensively studied, the pressure dependence has not. There is relatively a small literature on the effect of pressure on viscosity for polymeric materials [1-9], although work on pressure effects in low molecular weight materials has a history dating back to the 1930's [8].

Pressure causes the melt viscosity to increase very substantially (Figs.1-3). For example, the viscosity increases by 500% in polystyrene at 200°C when the pressure is raised from atmospheric to 125MPa, a typical pressure during processing [7]. A large increase of T_g with increasing pressure has also been noticed [7]. The combination of high pressure and low temperature was also reported to promote crystallisation of materials, leading to processing difficulties not predicted by low pressure crystallisation kinetics [5,6].

The behaviour of polymer melts at high pressure is complex. At low shear rates there is a rough analogy between increasing the pressure and decreasing the temperature, both of which cause the viscosity to increase, very rapidly if one is near the glass transition and less so if one is far away from T_g . At high shear rates, it has been reported that the effect of pressure is strongly dependent on the elastic modulus [7].

These days, injection mould designers are finding the need to predict with greater accuracy the pressure required to force the melt through runners and moulds of often complex geometries. It has become necessary to ensure that pressure can be controlled in the cavities during cooling and that the polymer is not thermally or shear degraded during the injection process. Also, work on mathematical modelling [10,11] of the flow of polymer along the screw, in the flow channels in the moulding machine and in the die, demand good quality viscosity data over a range of pressures approaching 150 MPa, over a range of temperatures and shear rates from 3 to 1000 s⁻¹. It is surprising therefore to find only a handful of publications in the open literature on this subject in the last 10 years [12-17], presumably due to the fact that the measurement of viscosity at high pressure is quite a difficult task.

The National Physical Laboratory (NPL) in the United Kingdom realised this serious measurement difficulty and the considerable impact of this parameter on polymer processing. NPL identified an immediate need for a systematic study to determine the effect of pressure on polymer melt viscosity in order to meet both industrial and academic needs. Particular attention was given to producing, under controlled conditions, experimental data that are industrially relevant and will allow the reproducibility of the results obtained from various sources to be identified. The considerable industrial significance of this work led NPL to initiate an International Round Robin in November 1994, the results of which are discussed in this report. Twentyfive potential participants across the world were invited and four, including NPL, responded favourably and agreed to meet the relevant requirements of the round robin. The participants were:

Moldflow Pty Ltd., Australia

Rapra Technology Ltd., U.K.

University of Cambridge, U.K.

National Physical Laboratory, U.K.

2 RESULTS AND DISCUSSION

Each of the four participating establishments was allocated a special code (Labs A to D) in random order for their results and will, henceforth be referred to only by that code. Previous work [7] reported a large pressure dependence on viscosity in polystyrene. Based on this fact, a suitable polystyrene material (manufactured by Huntsman Chemical Company Ltd., U.K. and supplied by NPL with the material codes HAU 002 - HAU 005) was selected for use in this round robin. The work programme is given in Appendix 1. All shear viscosity values presented in this work were not corrected for entrance pressure drop and Rabinowitsch, the method that gives the true melt velocity profile [6]. The equipment used to measure the apparent shear viscosity values ranged from modification to a capillary rheometer (RACER), ACER capillary extrusion rheometer with 'Thrust' adaptor, multi-pass rheometer to a modified injection moulding machine (Boy). The main requirements of the round robin that were common to all participants were:

One material, Polystyrene (PS)

Two temperatures (200°C and 180°C)

Five shear rates at 200°C

One shear rate at 180°C

Four pressures at each shear rate.

The results from Labs A-D, showing plots of apparent shear viscosity of the PS melt as a function of average pressure at given shear rates at 200°C and 180°C, are presented in Figs 4 to 11. For clarity and ease of comparison, most figures are presented in the same scale. Lab C used back pressure instead of average pressure; however, this does not alter the slope of the plots significantly. In all cases, the test results at each shear rate generated viscosity vs pressure plots with positive slopes that were fitted using an exponential function. The variation in slopes of the plots from Labs A-D is summarised in Table 1. Results that were provided, in addition to above requirements, are also included in this report.

At 200°C, the results of Labs A, B and D were found to be consistent with average slopes of ~ 0.005 to ~ 0.004 s (Table 1). The results of Lab C produced plots of relatively higher slopes ($\sim 0.01 \pm 0.008$ s) than the rest of the results. However, the data obtained between 500-1000 s^{-1} shear rates were found to be comparable (slope ~ 0.005 s) with the results of the other three Laboratories. The shear viscosity values increased by 200-300% when the pressure was raised to ~ 70 MPa. When extrapolated to 125 MPa (typical processing pressure), the plots indicated a 400-500% increase in viscosity values at 200°C, which agreed well with the published literature on a similar material [7]. All results are compiled into one diagram (Fig. 12) to examine the reproducibility of the data at given shear rates. It is difficult to establish any trend from the figure at first sight. However, when the high shear rate data of Lab C are removed from Fig. 12, the reproducibility of the remaining data at corresponding shear rates becomes much clearer (Fig. 13). The pressure dependency of the melt viscosity data for all Labs at 500 and 1000 s^{-1} shear rates was found to be reproducible to within ± 36 % (at 95% confidence level).

All data at 180°C generated plots with higher positive slopes compared to the 200°C data, except Lab C, and indicated, as in the previous case, more accurate curve fitting using an exponential function (Figs. 8-11). However, a few inconsistent results of Lab C at higher temperature (Fig. 12) and at high shear rates distorted the trend and data analysis of this Lab at 180°C and made

interpretation of their results difficult. Slopes of the plots varied between 0.005 to 0.011 s, while any conclusion on the average slope remained unclear. The details are given in Table 1. In general, the results of Labs A and D tended to show lower slopes (with mean ~ 0.005 s) than Labs B and C (slope ~ 0.010 s). The results of the viscosity vs pressure data from Labs A, B and C were compared at a common shear rate of 1000 s^{-1} in Fig. 14 (In case of Lab D, the data were only available at 1250 s^{-1} shear rate, but the plot is still shown alongside others to make a rough comparison. An estimated 50% reduction in the apparent shear viscosity value can be noticed.). It is concluded that all data at this shear rate are reproducible to within $\pm 20\%$ (at 95% confidence level) at 180°C .

3 CONCLUSIONS

- 1) In all cases, the apparent shear viscosity increased exponentially with pressure at each shear rate.
- 2) Intercepts of the shear viscosity plots varied systematically with pressure in every case i.e. higher the shear rate, lower the intercept.
- 3) Slopes of the pressure dependence of shear viscosity plots varied between 0.004 and 0.010 s at 200°C and between 0.005 and 0.011 s at 180°C . The plots obtained from the data set of a given Laboratory generated very similar slopes (variation ± 0.001 to 0.002) in nearly all cases. Lab C was the only exception (variation ± 0.005 to 0.008).
- 4) The apparent shear viscosity of polystyrene melt increased by 200-300% at 70 MPa compared with its value at atmospheric pressure. When extrapolated to 125 MPa, this represented a good agreement (i.e. ~ 400 -500% increase in shear viscosity) with the published literature.
- 5) The results from all sources were found to be reproducible to within $\pm 36\%$ (at 95% confidence level) at 200°C for shear rates of 500 - 1000 s^{-1} .
- 6) The reproducibility of the results at 180°C and at a common shear rate of 1000 s^{-1} was estimated to be within $\pm 20\%$ (at 95% confidence level).

4 ACKNOWLEDGEMENTS

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TABLE 1
Results of Pressure Dependency of the Shear Viscosity of Polymer Melts Round Robin
Material : Polystyrene

Establishment	200 °C			180 °C		
	Apparent Shear Rate, s ⁻¹	Slope, s	Mean Slope, s	Apparent Shear Rate, s ⁻¹	Slope, s	Mean Slope, s
LAB A	100	0.0064	~0.005 ± 0.001			0.006
	500	0.0055				
	1000	0.0051		1000	0.0059	
	2000	0.0041				
	4000	0.0048				
LAB B	200	0.0046	~ 0.005 ± 0.001			0.011
	500	0.0043				
	1000	0.0054		1000	0.0112	
	2000	0.0064				
	4000	0.0056				
LAB C	100	0.0098	~ 0.010 ± 0.008	100	0.0048	~ 0.010 ± 0.005
	550	0.0053		550	0.0095	
	1000	0.0058		1000	0.0102	
	2400	0.0104		2400	0.0103	
	5500	0.0181		5500	0.0129	
LAB D	60	0.0042	~ 0.004 ± 0.001			~ 0.005 ± 0.002
	700	0.0037		400	0.0065	
	1150	0.0028		1250	0.0030	
	2300	0.0036		2200	0.0040	
	4500	0.0038				

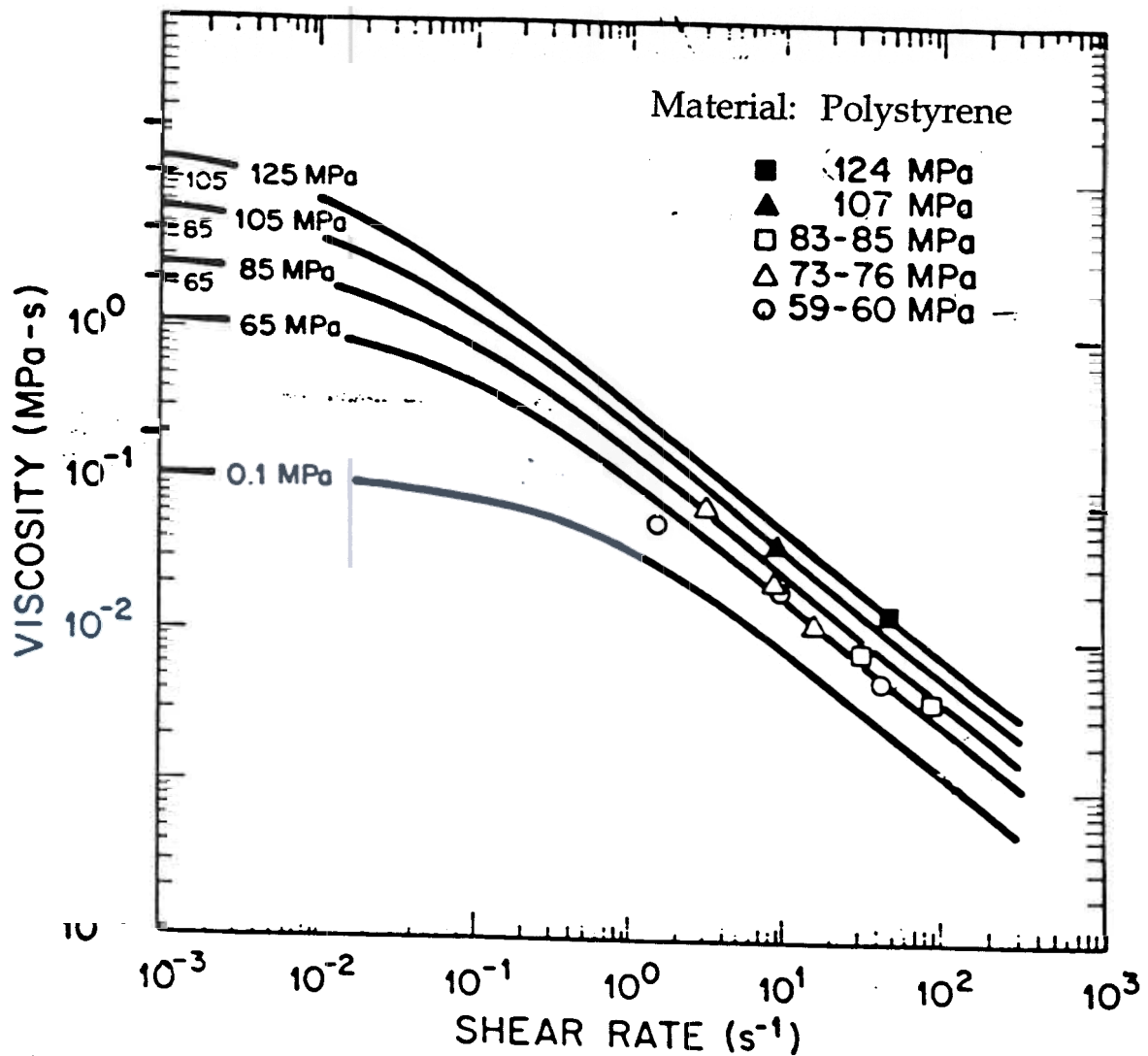


Fig. 1 Summary plot of high pressure viscosity data, showing zero shear data of Cogswell and McGowan and high shear rate data of the present work. The zero shear data, measured at low but unknown shear rates, are marked with short horizontal bars, corresponding to the pressures shown (in MPa); (—) model predictions based on eqs. (9)–(12), with $P_r^* = 3.25P^*$. [after ref. 7]

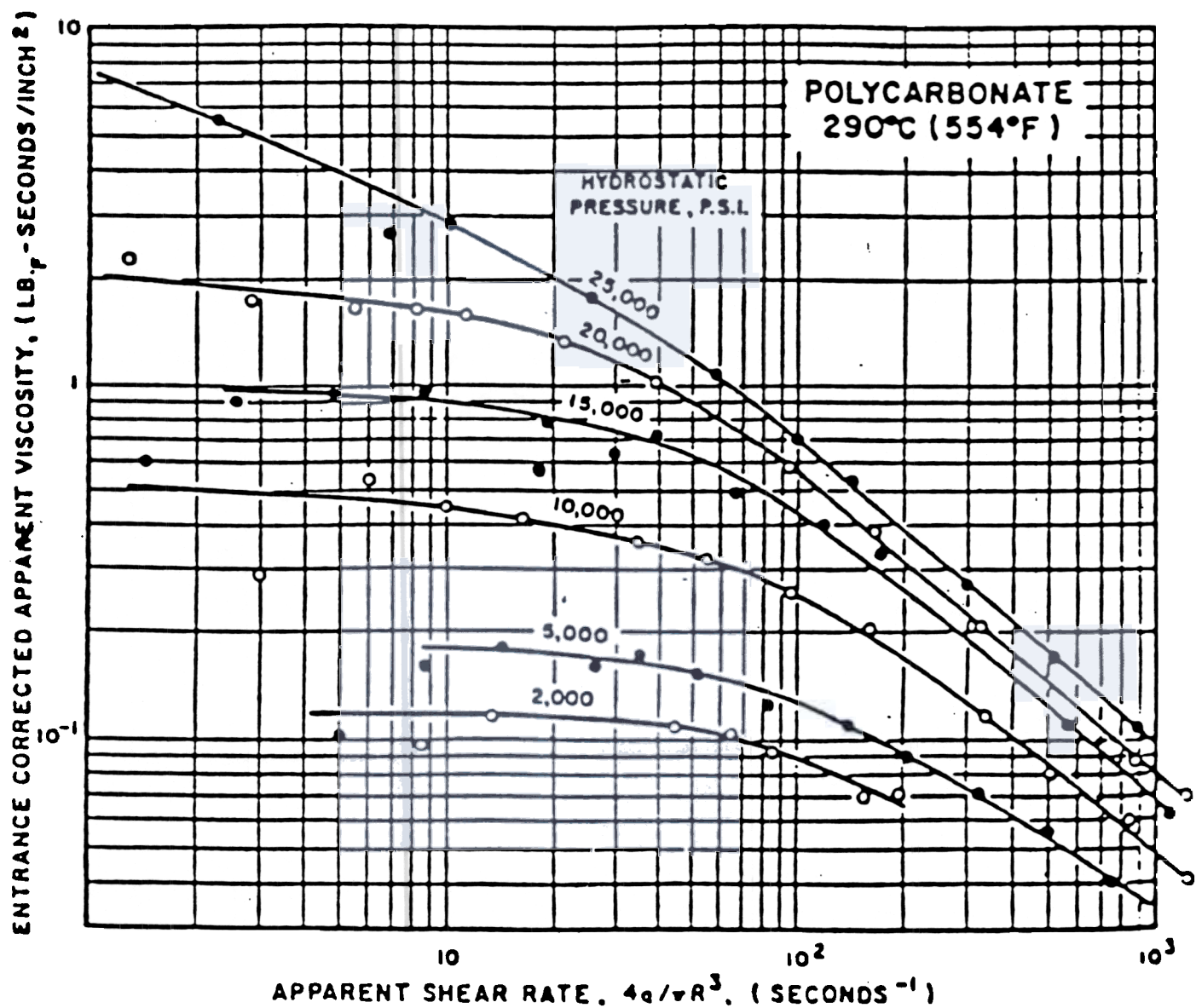


Fig. 2 Viscosity vs. shear rate curves of polycarbonate at various hydrostatic pressures. Temperature:

[after ref. 13]

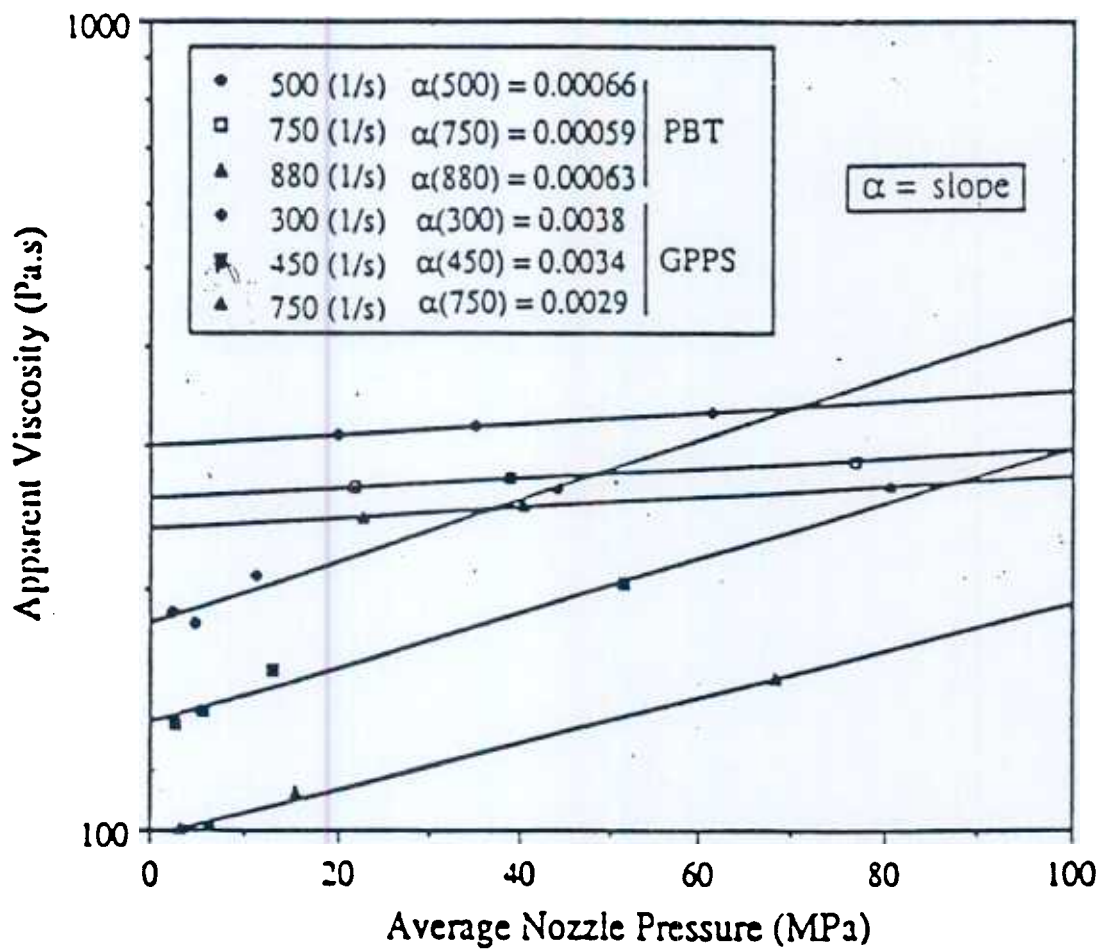


Fig. 3 Apparent viscosity vs. average melt pressure at several shear rates for PBT at 250°C and GPPS at 232°C

[after ref. 15]

LAB A 200 °C

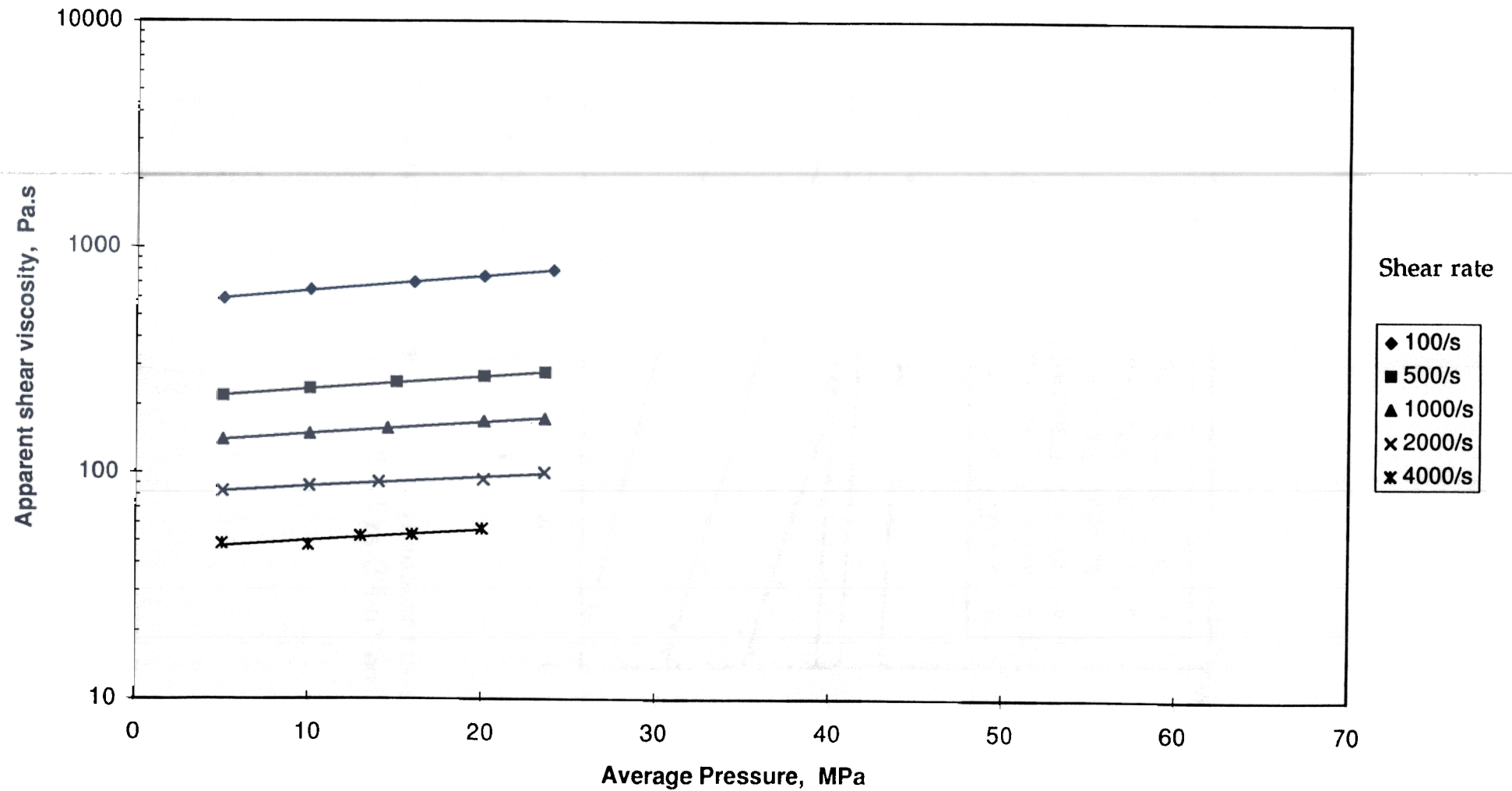


Fig. 4 Pressure dependency of shear viscosity round robin results from Lab A at 200 °C

LAB B 200 °C

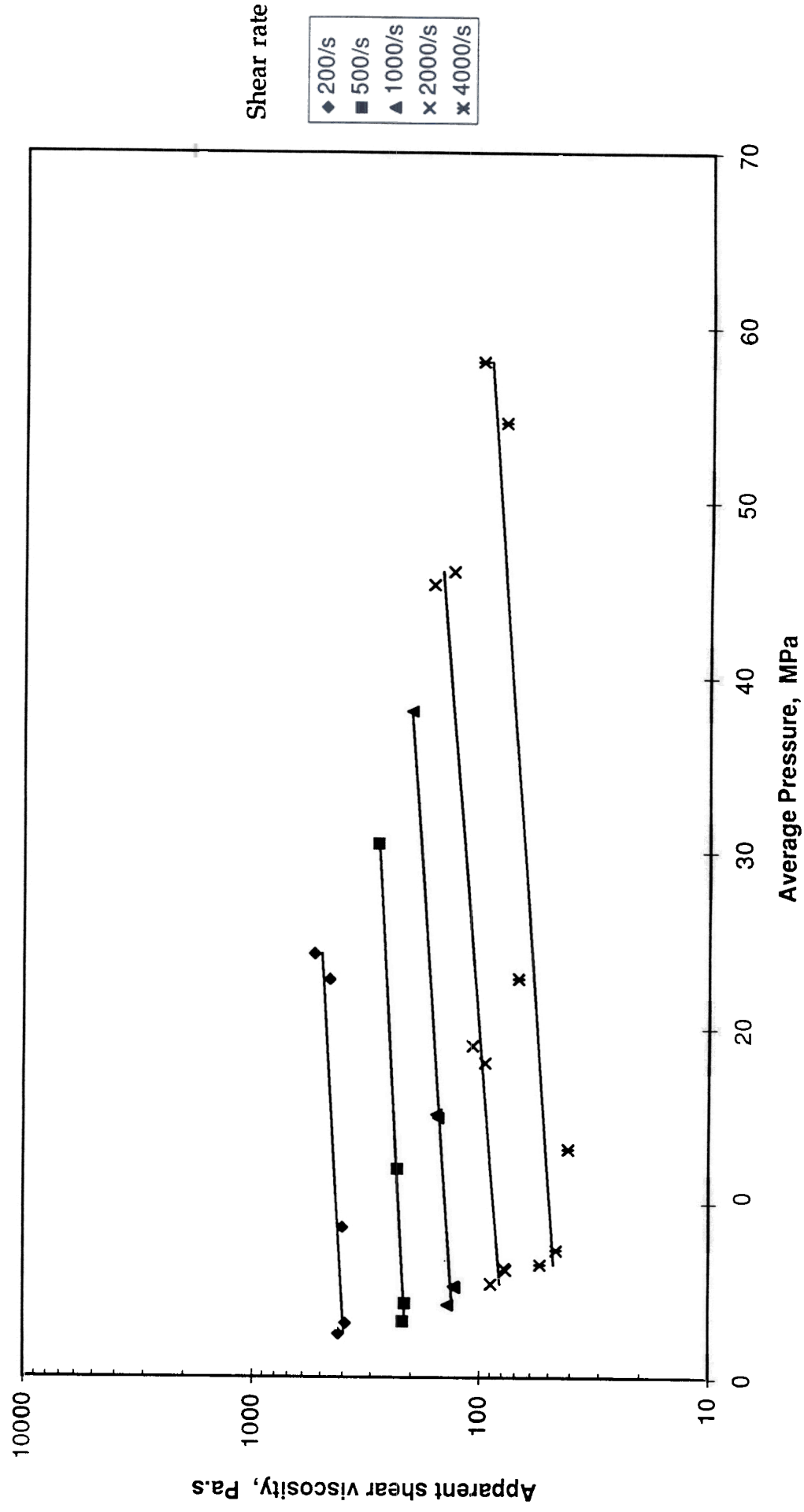


Fig. 5 Pressure dependency of shear viscosity round robin results from Lab B at 200 °C

LAB C 200 °C

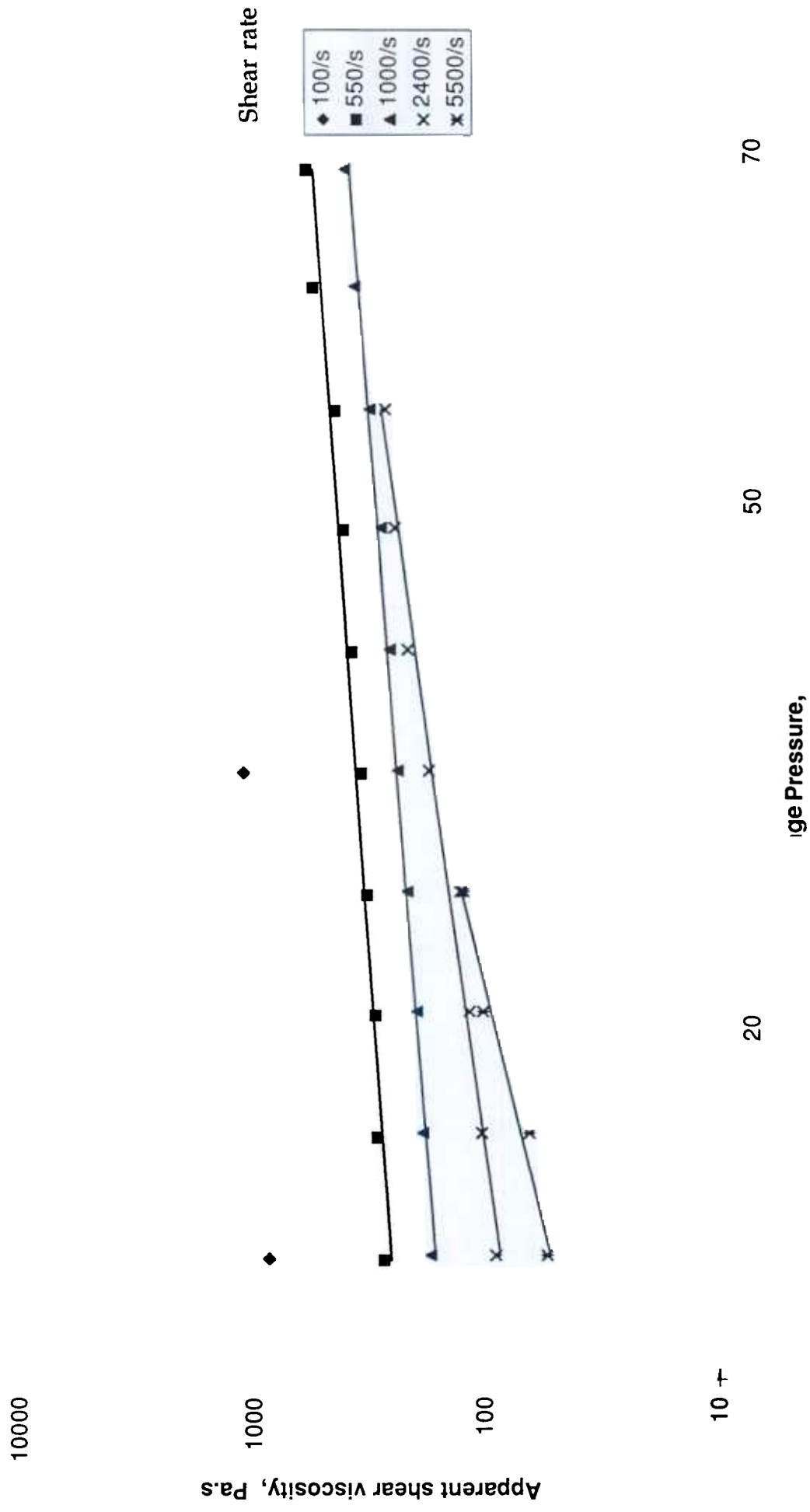


Fig. 6 P -ity round robin results from Lab C at 200 °C

LAB D 200 C

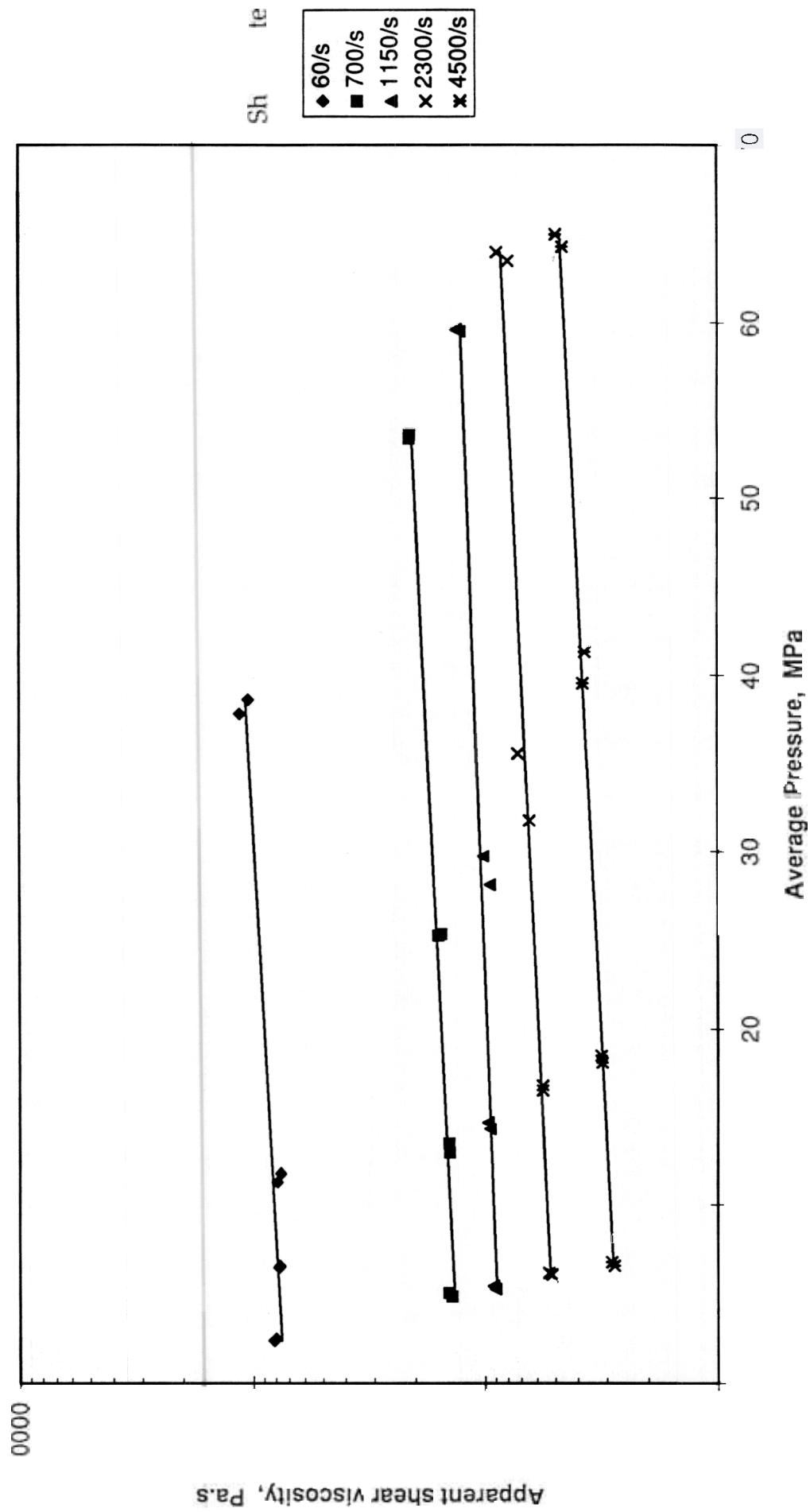


Fig. Pressure dependency of shea viscosity round robin results f La D 200 °C

LAB A 180 °C

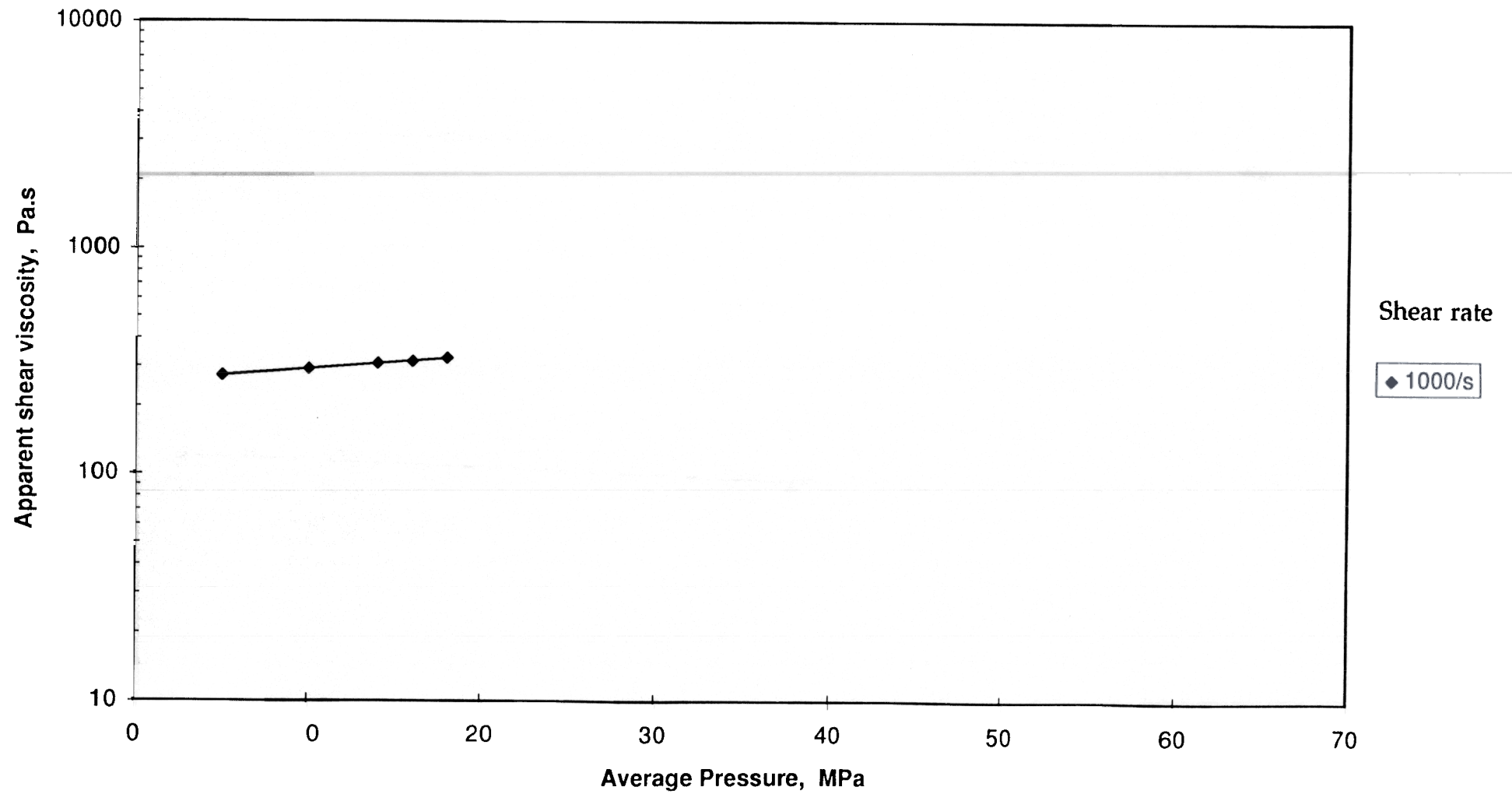


Fig. 8 Pressure dependency of shear viscosity round robin results from Lab A at 180 °C

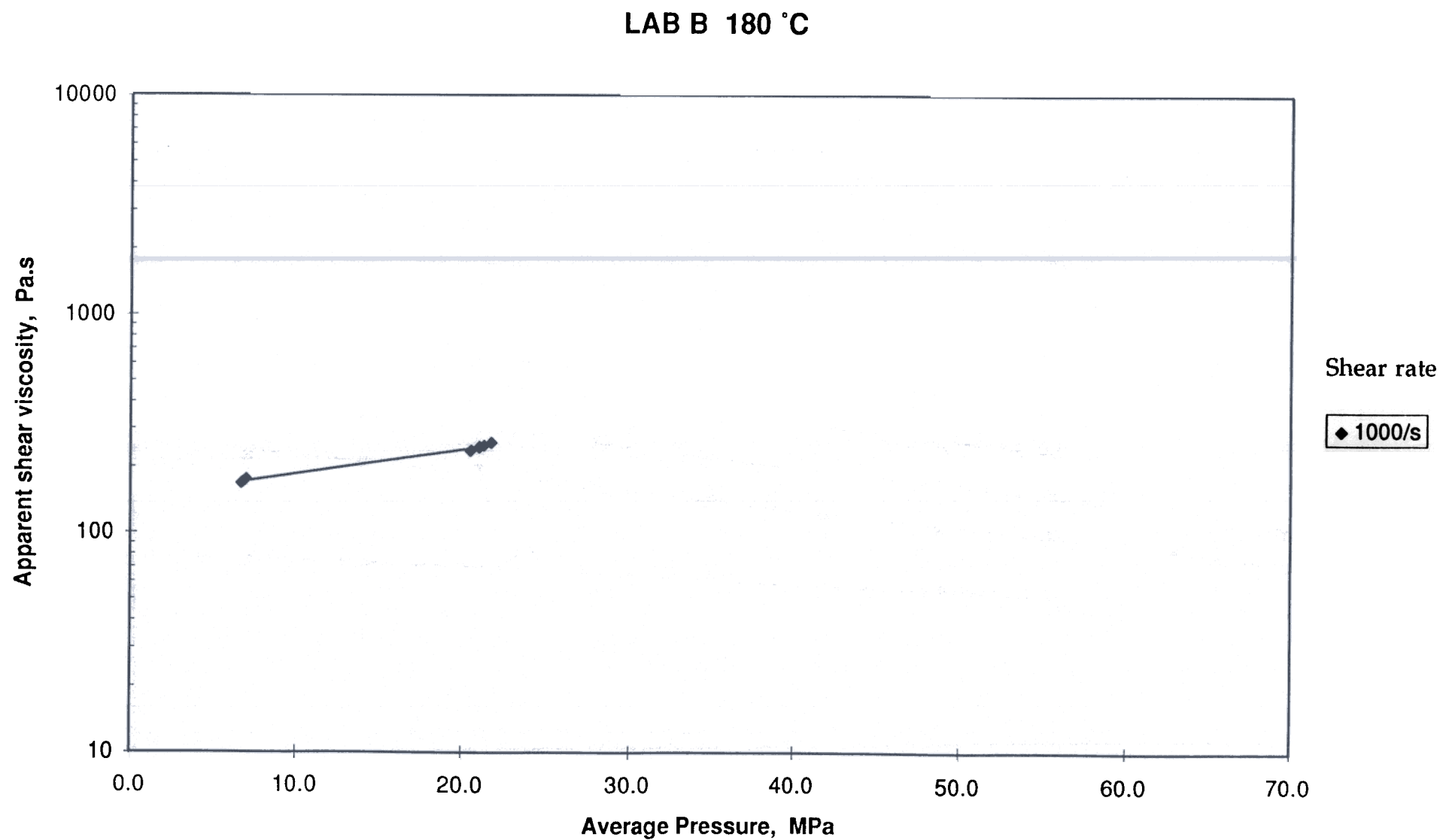


Fig. 9 Pressure dependency of shear viscosity round robin results from Lab B at 180 °C

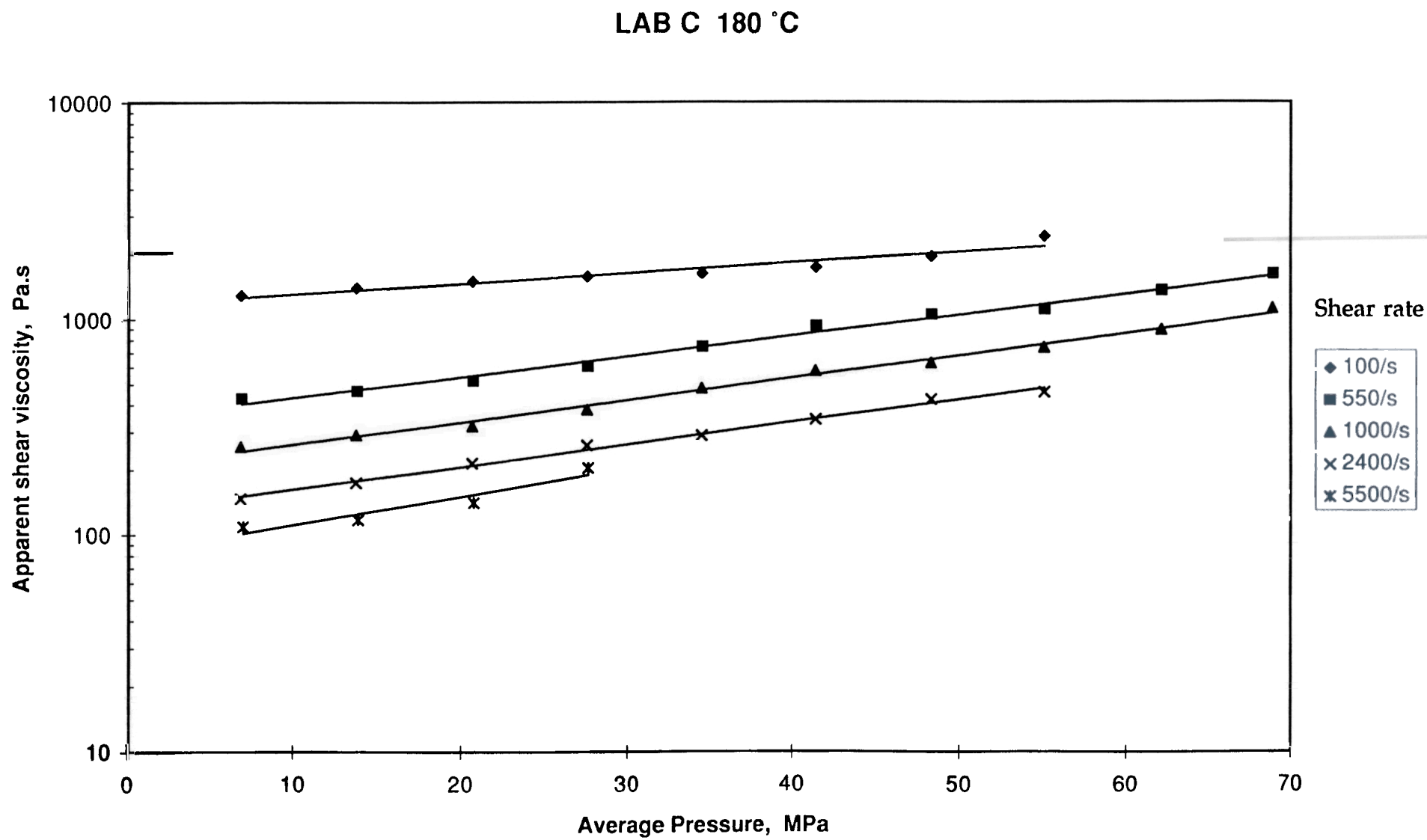


Fig. 10 Pressure dependency of shear viscosity round robin results from Lab C at 180 °C

LAB D 180 °C

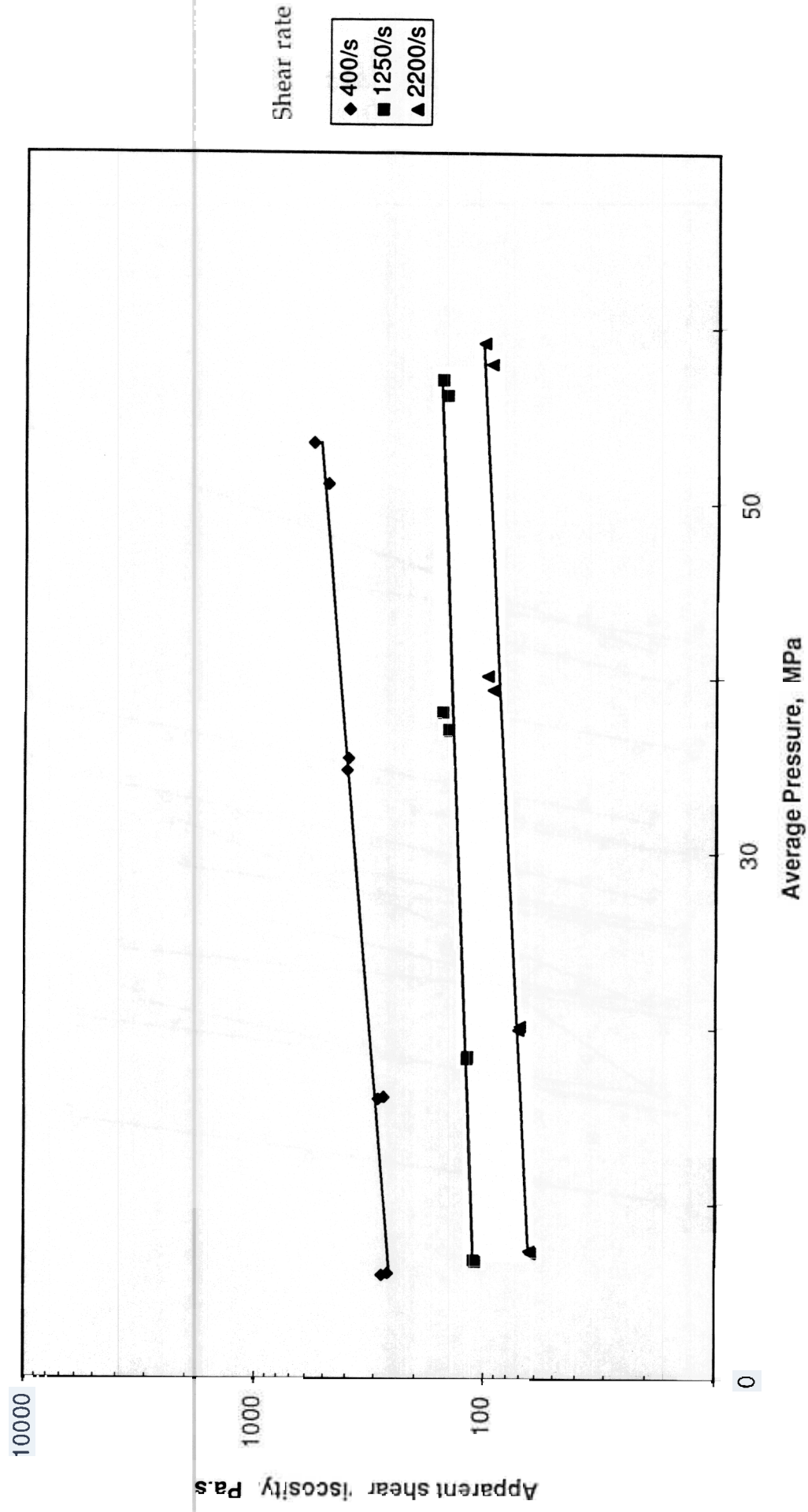


Fig. 11 Pressure dependency of shear viscosity round robin results from Lab D 180 °C

Comparison of Data from Labs A-D at 200°C

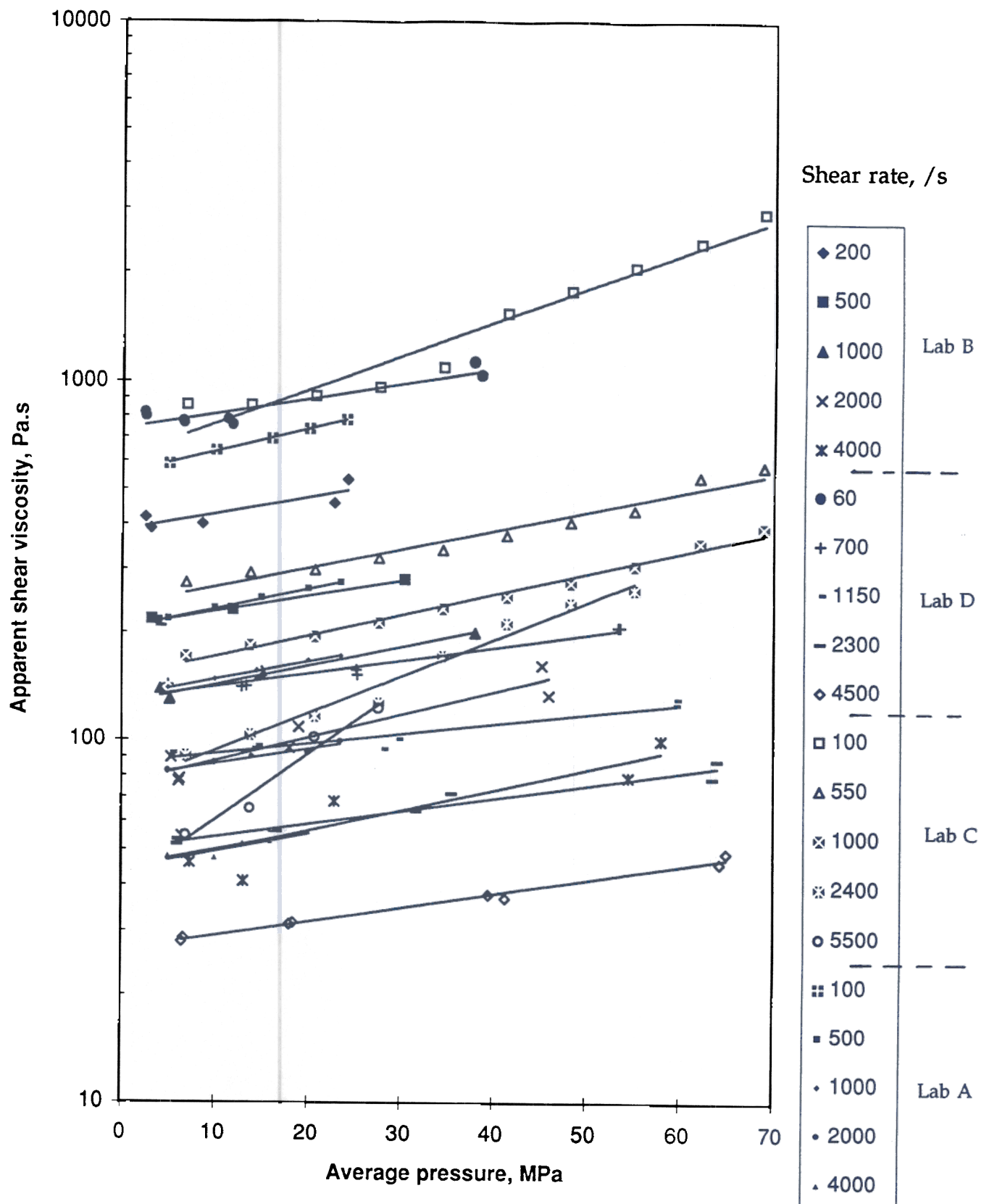


Fig. 12

Comparison of Edited Data from Labs A-D
at 200°C

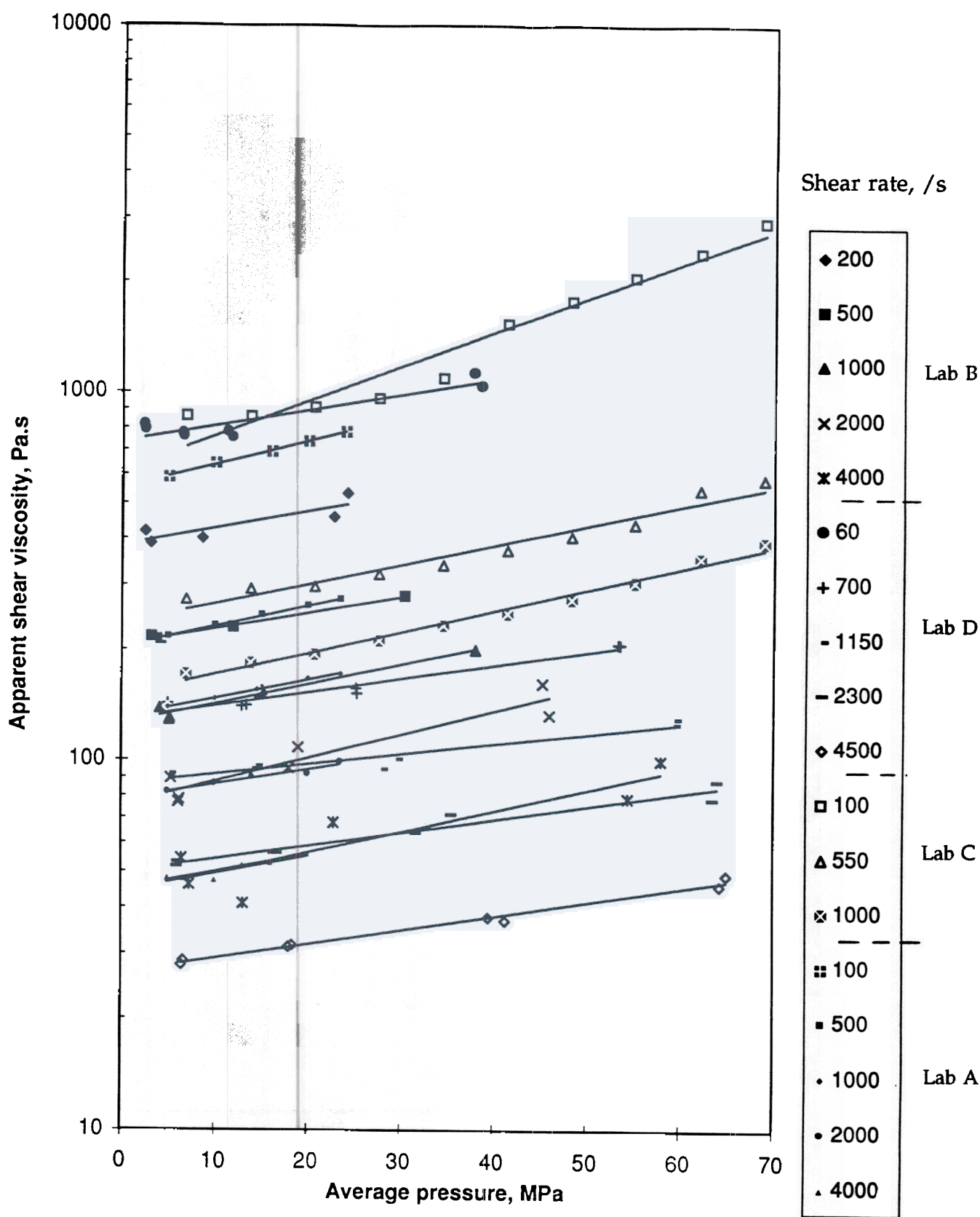


Fig. 13

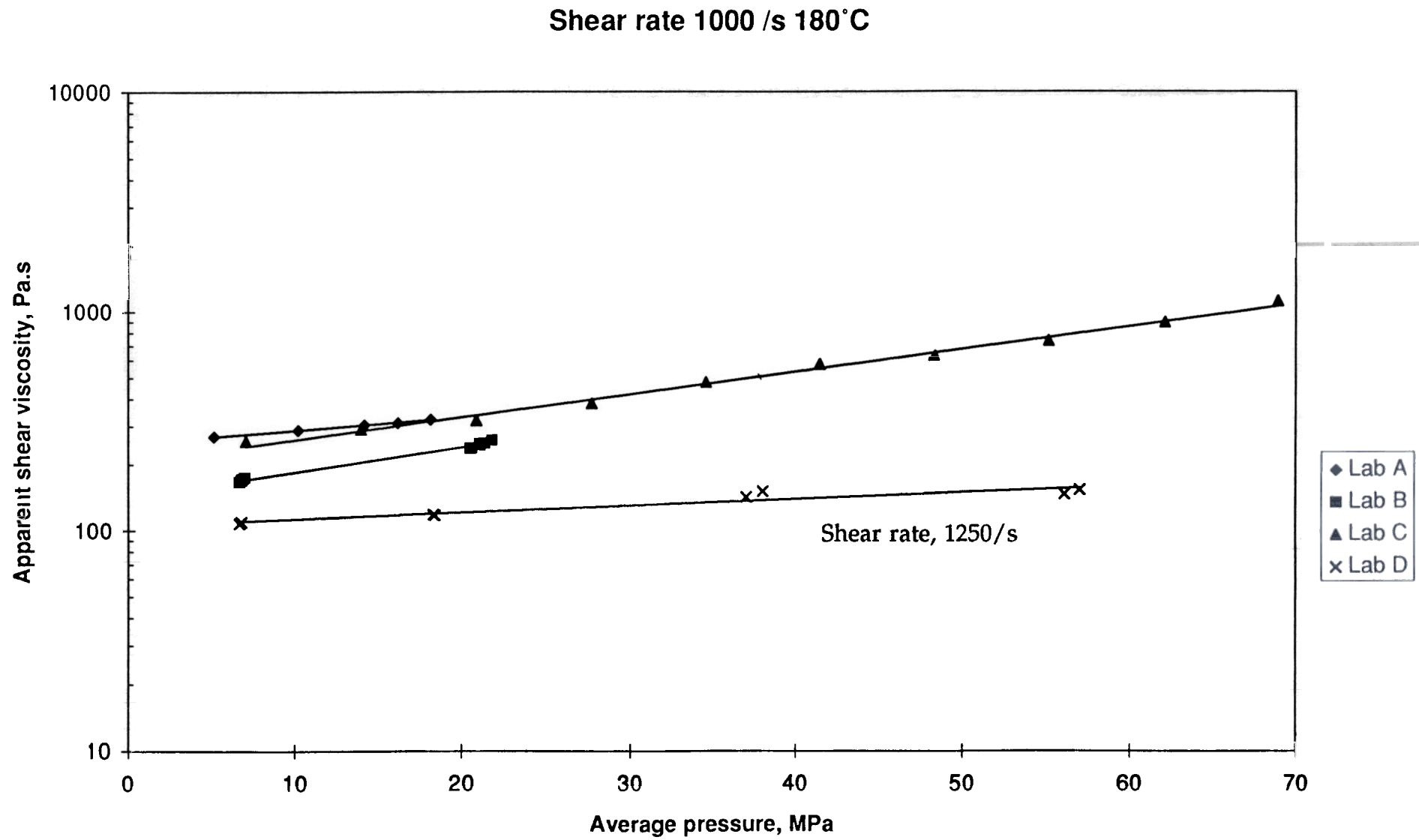


Fig. 14 Comparison of results from Labs A-D at 1000 s⁻¹ shear rate at 180°C

INTERNATIONAL ROUND ROBIN ON THE PRESSURE DEPENDENCE OF THE SHEAR VISCOSITY OF POLYMER MELTS

EXPERIMENTAL PLAN

The round robin will be based on the following parameters:

One material (Polystyrene)

Two temperatures (180° and 200 °C)

Five shear rates at 200 °C (1000/sec and four others to cover the common range of 35 - 4000/sec).

[Additional tests to cover the entire range of your equipment are optional, but would be beneficial to the work programme.]

One shear rate at 180 °C (1000/sec)

Four pressures at each shear rate (atmospheric pressure, 20 MPa and two others to cover the range of your equipment e.g. 50% and 90% of maximum).

[Additional tests to repeat the results at 20 MPa, 200 °C at 1000/sec, are optional, but would be beneficial to the work programme.]

BASIS FOR THE ROUND ROBIN

- 1) The minimum requirements for testing have been specified above. It is desirable that all participants carry out the minimum requirement.
- 2) Optional testing, if carried out by the participants, will be valuable to this study. The results will be used to establish trends beyond the common range.
- 3) The participants in the round robin have been assigned an establishment reference number. That number shall be known only by that establishment and the NPL. Results will be presented with reference to the establishment reference number only. All organisations that have taken part in the round robin will be listed by name only so that it will not be possible to work out the source of the other 4 sets of results.
- 4) A report on the round robin will be prepared and sent to all participants.
- 5) Information generated through this round robin will be disseminated by the NPL in the open literature, conferences etc.
- 6) All establishments must use the material sample (Polystyrene) provided by the NPL. Please return all unused material samples at the end of the experimental programme (to be kept by the NPL for possible future testing).
- 7) All establishments are to measure Shear Viscosity as functions of Pressure and Shear Rate.

TEST REPORT

- A) Examples of Test Report sheets are provided (A, B and C) and may be used for reporting results. Additional pages may be used, if necessary; but please indicate your establishment reference number and test reference number(s) on each page. Please provide information on all listed items and write N/A, against those which do not apply.
- B) Please keep a copy of all results sent to the NPL in case of further discussion in the future.
- C) Please return all forms, results and any additional papers to Dr. Sekhar Chakravorty at the address given below. In addition to providing the results on floppy disk (if possible), please also submit a hardcopy on paper of all test results.

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E-mail: SC@newton.npl.co.uk

TEST REPORT SHEET A
TO BE COMPLETED ONCE FOR EACH RHEOMETER USED

- A.1 Establishment reference number:
A.2 Name of organisation:
- A.3 Name of person carrying out testing:
A.4 Name of person to contact concerning discussion of results:
A.5 Address:

Telephone number:
Fax number:
E-mail code:
Rheometer details:
 manufacturer:
 model:
Description of the rheometer used:

- A.8 Barrel diameter (m):
A.9 Details of data logging equipment used:

Calibration details of rheometer, pressure transducer, thermometers and data logging facility:

State if any method has been used for determining entrance pressure drop values and for correcting shear viscosity data entrance pressure drop effects (optional requirement).

State any methods used for correcting the data for non-Newtonian velocity profile - Weissenberg-Rabinowitsch correction (optional requirement).

Details of any quality system or accreditation by which the rheometer and associated equipment is covered:

Any other information considered relevant.

TEST REPORT SHEET B
TO BE COMPLETED ONCE FOR EACH SET OF TESTS
(ie SINGLE BARREL CHARGE):

- B.15 Establishment reference number:
B.16 Your test reference number:
B.17 Date of test:
B.18 Material code:
B.19 Describe any pre-conditioning of the sample of environmental control used during testing:

- B.20 Test temperature - set value:
B.21 Test temperature - measured value:
B.22 Sample pre-heat time:
B.23 Dwell time:
B.24 Where applicable, dwell time corresponding to the appearance of an alternation in the substance:
B.25 Maximum permissible test duration:
B.26 Testing time:
B.27 Die geometry:
 length (m):
 internal diameter (m):
 entry angle:
 Pressure transducer details (quote serial number only if the details are presented in an earlier test report):
 pressure range:
 manufacturer:
 model:
 Flow rates (m^3s^{-1}) and pressures (MPa):

- B.30 Any visual observations, eg. fracture:

Please tick, if these are optional tests

optional test

☐

- B.32 Any other information considered relevant.

TEST REPORT SHEET C
FOR THE MATERIAL AT EACH TEMPERATURE:

Establishment reference number:

C.34 Test reference numbers used to determine the shear viscosity and entrance pressure drop values:

Shear viscosity (Nsm^{-2}) versus shear rate (s^{-1}) and pressure (MPa) [give corrected (if applicable) and uncorrected values]:

Shear Rate	Pressure	Shear Viscosity	
		Uncorrected	Corrected

Entrance pressure drop (MPa) versus flow rate (m^3s^{-1}) data.

Please tick, if this is an optional test

optional test ☐

Any other information considered relevant.