



**Effect of pressure-volume-temperature behaviour of
polymer melts on extrudate swell measurements**

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ABSTRACT

The compressibility of polymer melts is not normally taken into account in modelling the flow phase of processing. The fluid is assumed to be incompressible. Consequently this assumption leads to additional uncertainties in the results of modelling of processing. The potential contribution of the effect of melt compressibility on the swelling behaviour of polymer extrudates was examined. Results of pressure-volume-temperature measurements were analyzed. The compressibility of three polymers: LDPE, PS and a mineral filled PP, were similar and in the range 4 - 9 % on application of a pressure of 100 MPa. The compressibility increased with increasing temperature. The results indicated that the effect of compressibility on extrudate swell behaviour was small.

The effect of pressure on shear viscosity has also been examined, again with the purpose of helping to assess the uncertainties in modelling extrusion processing. The results indicate that very substantial increases in the shear viscosity can occur when the polymer is subjected to high processing pressures. The effect of the pressure dependence of viscosity on predictions of processing needs to be assessed.

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Approved on behalf of Managing Director, NPL
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1 INTRODUCTION

This work was undertaken as part of the Department of Trade and Industry Engineering, Automotive and Metals Division's (EAM) programme on processability, Project 5 on the determination of the elasticity of polymer melts. This project is one of a wider range of projects on the processability of materials funded by EAM.

The compressibility of polymer melts is not normally taken into account in modelling the flow phase of processing (1). The fluid is assumed to be incompressible. Consequently this assumption leads to additional uncertainties in the results of modelling of processing. This work was undertaken to investigate the potential contribution of the effect of melt compressibility on the swelling behaviour of polymer extrudates. Results of pressure-volume-temperature measurements were analyzed to assess the magnitude of the effect of compressibility on extrudate swell behaviour. In addition, in modelling polymer processing the rheological properties of the polymer are assumed to be independent of pressure, despite their being substantial evidence to indicate that the effect of pressure can be very significant (2-6). The effect of pressure on shear viscosity has also been examined with the aim of providing information so that the uncertainties in modelling extrusion processing due to pressure dependent material's properties may be assessed.

2 EXPERIMENTAL DETAILS

Three materials were tested in this work: a low density polyethylene (LDPE - NPL reference HAC001), a polystyrene (PS - NPL reference HAU001) and a mineral-filled polypropylene (PP + min - NPL reference HAR002). Measurements were performed over a range of temperatures and pressures. Where necessary, data were calculated by interpolation to determine specific volume data at intermediary temperatures to provide more suitable comparison with the pressure dependence of viscosity data. These measurements were carried out by RAPRA Technology Ltd (6). Die swell measurements on various polymers have been reported by Rides and Allen (8).

3 RESULTS

The raw experimental data for the effect of pressure¹ and temperature on the specific volume and viscosity of the three materials are presented in figures 1, 2 and 4 for LDPE, figures 7, 8 and 10 for PS, and figures 13, 14 and 16 for a mineral filled PP (6, 7). Both unfilled grades exhibited a linear relationship between the specific volume and temperature, Figures 1 and 7 for LDPE and PS respectively. However, for mineral-filled PP the plot of results was not so linear. Nevertheless a linear interpolation was used to obtain specific volume values at temperatures corresponding to those at which pressure dependence of viscosity measurements were made, figures 4, 10 and 16.

Plots of specific volume as a function of pressure have also been used to determine the specific volume at atmospheric pressure (ie a measured pressure of zero), figures 2, 8 and 14. A quadratic equation was used to fit the data and to extrapolate values to a measured pressure of zero. The values at a measured pressure of zero have then been used to scale the specific volumes. The resulting data were plotted as percentage changes in specific volume due to the application of pressure, figures 3, 9 and 15. The changes in specific volume were qualitatively similar for all three materials. On increasing the pressure from 0 MPa to 100 MPa the specific volume decreased by approximately 6 - 9% for LDPE, 4 - 7% for PS and 5 - 9% for a mineral filled PP, figures 3, 9 and 15 respectively. The above values for LDPE yielded bulk modulus values in the range $1.1 - 1.7 \times 10^9$ Pa which were approximately 30%

¹All stated pressures are relative to atmospheric pressure, and are not absolute pressures.

higher than values obtained by Cogswell (9) for a LDPE under similar conditions. A possible reason for the lower values of bulk modulus reported by Cogswell (9) could be due to entrapment of air in the sample. The mineral filled PP grade was approximately 15% by volume of talc filler. If it is assumed that the talc was incompressible then this would have had a 15% affect on the compressibility of the material thus reducing the effect of pressure on specific volume by approximately 1% from 6 - 10% to the measured 5 - 9%. This effect is small and accounts for the similar values obtained for the filled and unfilled grades. For both the unfilled LDPE and PS grades the percentage change in specific volume was greater at higher temperatures. However, for the mineral-filled PP grade the maximum variation was obtained at 170 °C and not at the maximum temperature. This was considered to be a consequence of the scatter in results, figure 14, and its effect on extrapolation to obtain the specific volume at a pressure of zero. Nevertheless, the range of the percentage increase in specific volume was similar to that for the other two materials.

The raw data for the shear viscosity as a function of pressure are presented in figures 4, 10 and 16. These data were analyzed and re-plotted as percentage changes in viscosity from the zero pressure value, figures 5 and 6 for LDPE, figure 11 and 12 for PS and figure 17 for mineral-filled PP. The changes in viscosity on application of pressure are significantly higher than the changes in specific volume. In increasing pressure from 0 MPa to 50 MPa the percentage increases in shear viscosity were of the order of 20% for LDPE, 75 - 180% for PS and 25 - 60% for mineral filled PP. The increase in viscosity with pressure was found not to be shear rate dependent, figures 5 and 11, but was temperature dependent, figures 6 and 12, for both LDPE and PS. The increase in viscosity with pressure was greater at lower temperatures. For the mineral-filled PP the scatter in data was such that it was not possible to clearly determine any dependencies of the data on the test parameters, although similar trends were apparent, figure 17.

4 DISCUSSION

Results of extrudate swell measurements on various polymers are presented by Rides and Allen (8). The pressures used in the extrudate swell testing were typically up to 30 MPa. On the basis of the results presented herein, a pressure of 30 MPa would equate to a change in specific volume of approximately 1.5 - 3%. Capillary extrusion rheometers are normally displacement controlled devices, that is their speed and not the extrusion pressure is controlled. As the polymer passes through the die the pressure to which it is subjected decreases. This will result in an increase in the specific volume of the material and consequently an increase in the volume flow rate of material in progressing along the length of the die towards the exit. This factor is not normally taken into account in modelling extrusion flow. However, extrudate swell results (8, 10) indicate that the absolute error in the percentage extrudate swell with flow rate due to an error in the volume flow rate of say 3% due to the compressibility of the material is at most $1.5\%^2$ and typically less than $1\%^2$. One standard deviation values for the percentage extrudate swell were typically in the range 0.5 - $2\%^2$ (8). Therefore it can be seen that the effect of melt compressibility on extrudate swell, due to the change in specific volume of the melt, was negligible and was typically less than the value of one standard deviation of the measured percentage extrudate swell values.

However, the increase in viscosity due to the applied pressure was significant. For extrusion pressures of 30 MPa this would equate to an increase in viscosity of 12% for the LDPE, 50 - 100% for PS and 15 - 50% for the mineral-filled PP. Examination of the equations used to determine shear viscosity from capillary rheometry data indicates that the error in viscosity is approximately proportional to the error in the flow rate value (see Appendix A). The effect

² The quoted errors for percentage extrudate swell are absolute values, for example for an extrudate swell value of 30% an error of $\pm 2\%$ is equivalent to extrudate swell values in the range 28% - 32%.

of this increase in viscosity on extrudate swell values may be significant. It is necessary to assess the effect of the pressure dependence of viscosity using numerical modelling techniques. However, there would still be considerable uncertainty over the validity of the experimental data used to determine the values of the parameters of the constitutive model. The measurements reported here have shown that shear viscosity is dependent on pressure. Measurements to assess the effect of pressure on other rheological properties, for example extensional viscosity, would also be required to obtain a reliable description of the material behaviour. As a first approximation it could be assumed that all rheological properties would be affected by a similar factor as shear viscosity. On a final note, the pressure dependence of viscosity is of relevance to flow simulation of injection moulding as well as extrusion and its effects have so far been largely ignored.

5 CONCLUSIONS

On the basis of the work reported here the following conclusions are made:

- The compressibility of the three polymers tested was similar and in the range 4 - 9 % on application of a pressure of 100 MPa, the value increasing with increasing temperature.
- The effect of compressibility on the extrudate swell behaviour of polymers due to the error in the volume flow rate passing through the die was shown to be negligible and was typically less than the value of one standard deviation of the measured percentage extrudate swell values.
- The effect of compressibility of polymers on their shear viscosity is large. Shear viscosities may increase by several hundred percent on application of 100 MPa of pressure.
- The effect of the pressure dependence of shear viscosity, and presumably of other rheological properties, on extrusion modelling is likely to be very significant. The magnitude of this effect needs to be assessed through the use of flow simulation techniques.

6 ACKNOWLEDGEMENTS

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The authors would like to acknowledge RAPRA Technology Ltd for experimental results provided as part of the project PMP4 Determination of the viscosity of polymers as a function of cure, temperature and pressure.

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Appendix A Effect of an error in the flow rate on the determination of shear viscosity using capillary extrusion rheometers.

In accordance with ISO 11443 Plastics - Determination of the fluidity of plastics using capillary and slit die rheometers (11) the following can be determined. The shear viscosity η is defined as the ratio of shear stress σ to shear rate $\dot{\gamma}$.

$$\eta = \sigma / \dot{\gamma}$$

The calculation of shear stress does not include a flow rate term. The shear rate, however, is given by the expression

$$\dot{\gamma} = 4Q/(\pi R^3)$$

where Q is the volume flow rate and R the capillary die radius. Thus, it can be deduced that the shear viscosity is proportional to the reciprocal of the volume flow rate,

$$\eta \propto 1/Q.$$

As a first order approximation for small errors, the error in the shear viscosity will be the same as the error in the volume flow rate. For example a 5% error in the volume flow rate will result in a 5% error in the shear viscosity.

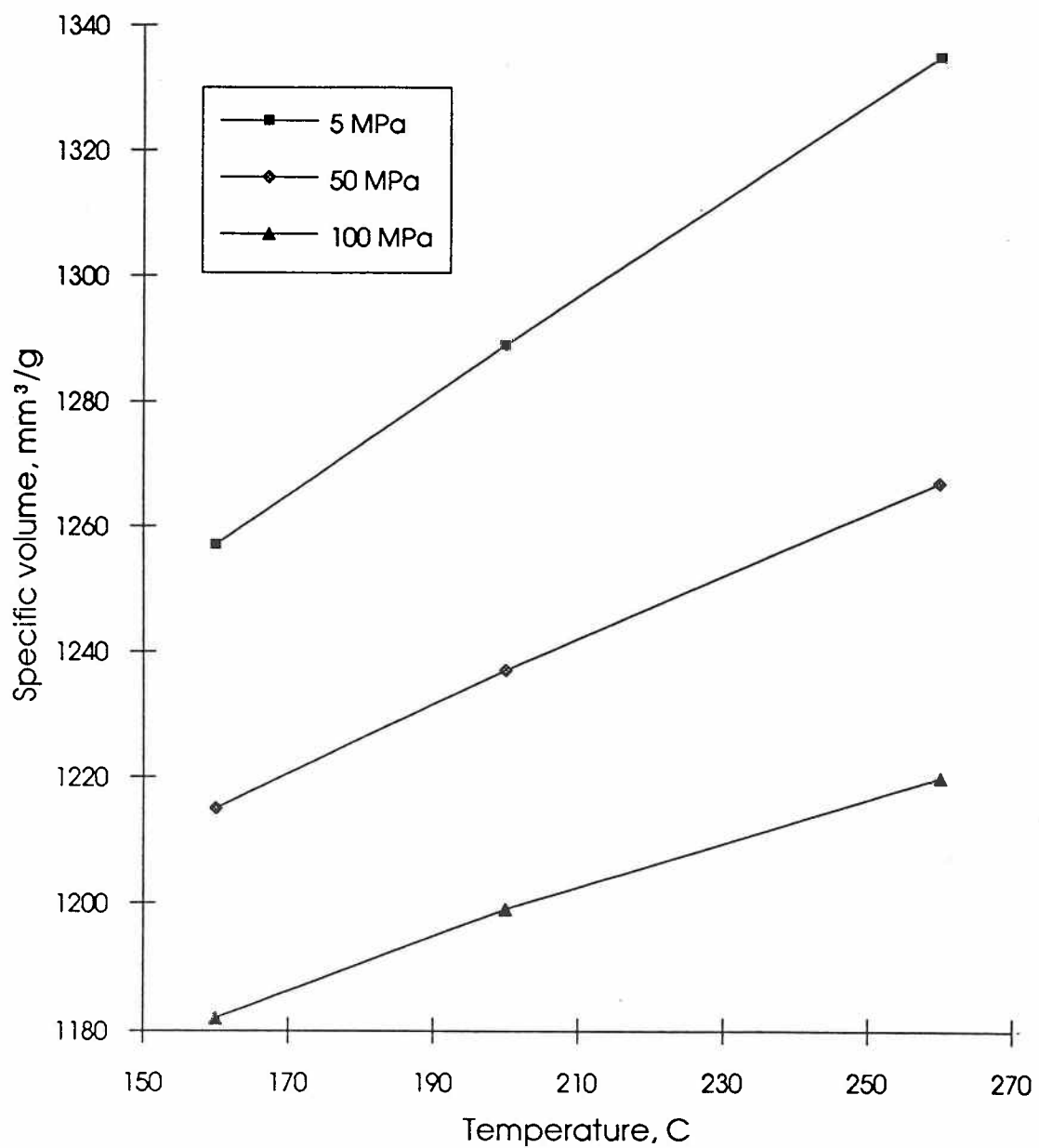


Fig. 1 The effect of temperature on the specific volume of LDPE (HAC001) for a range of pressures.

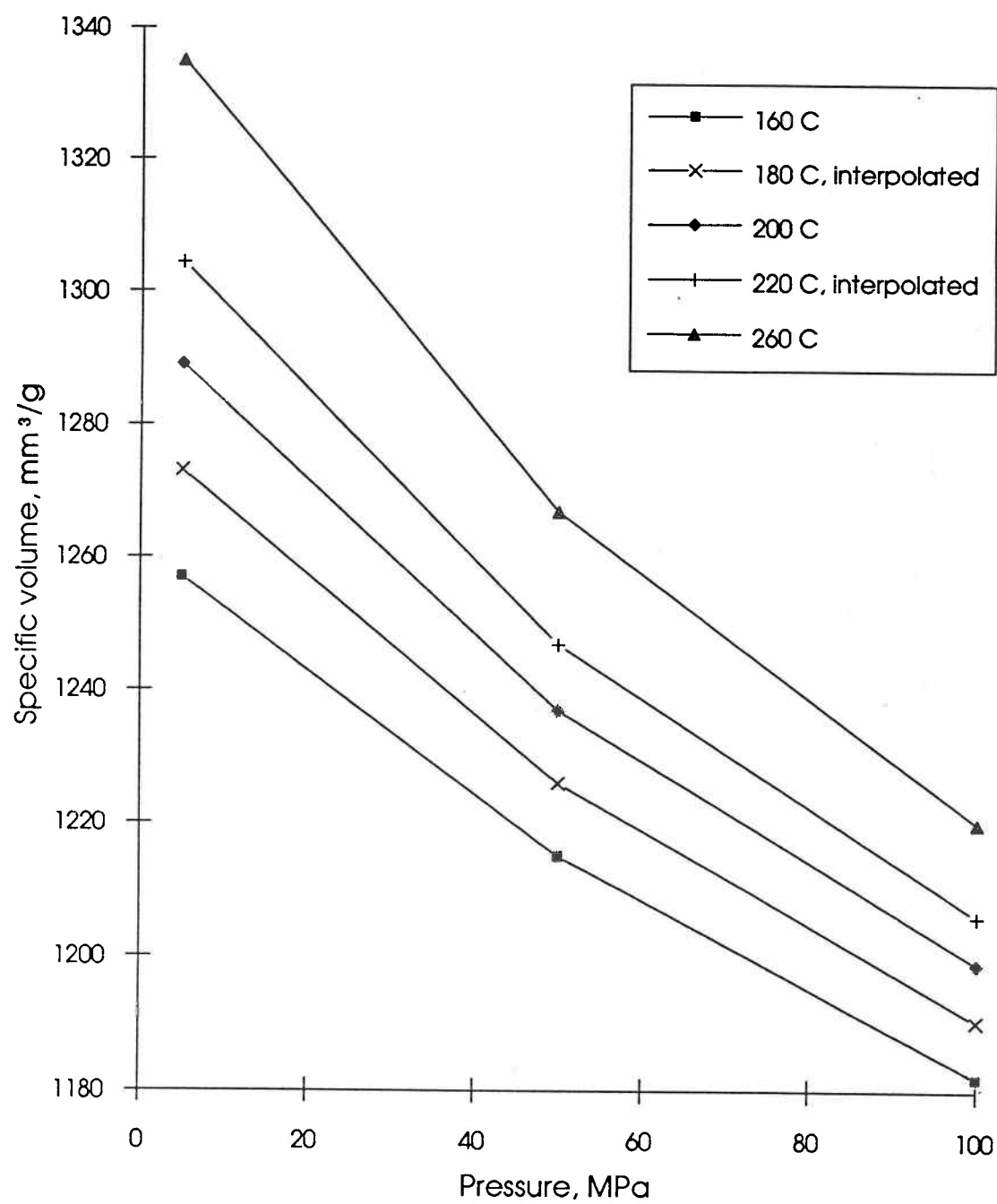


Fig. 2

The effect of pressure on the specific volume of LDPE (HAC001) for a range of temperatures.

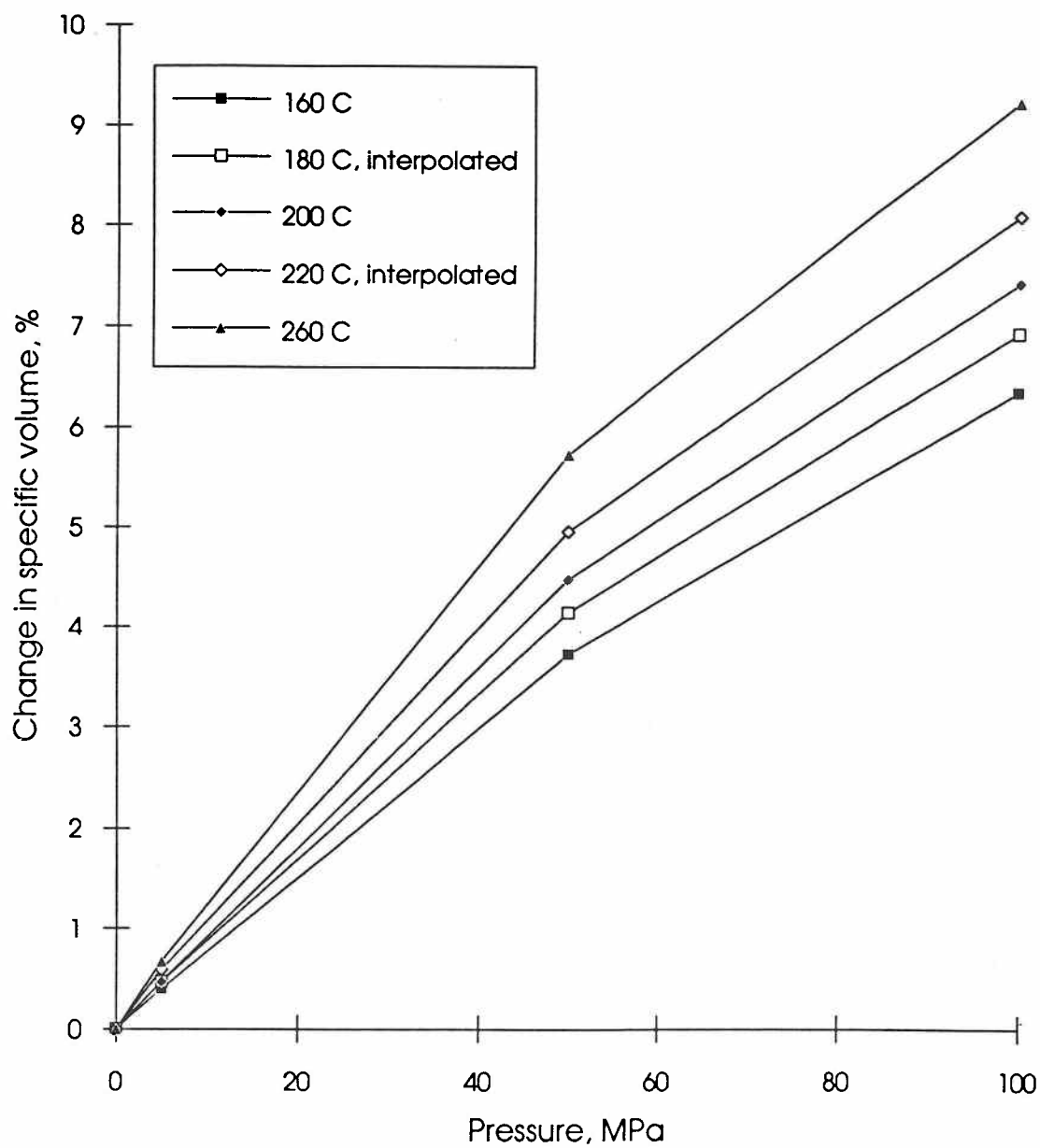


Fig. 3 The effect of pressure on the specific volume of LDPE (HAC001) for a range of temperatures, expressed as a percentage, indicating the effect of pressure on flow rate during extrusion testing and processing.

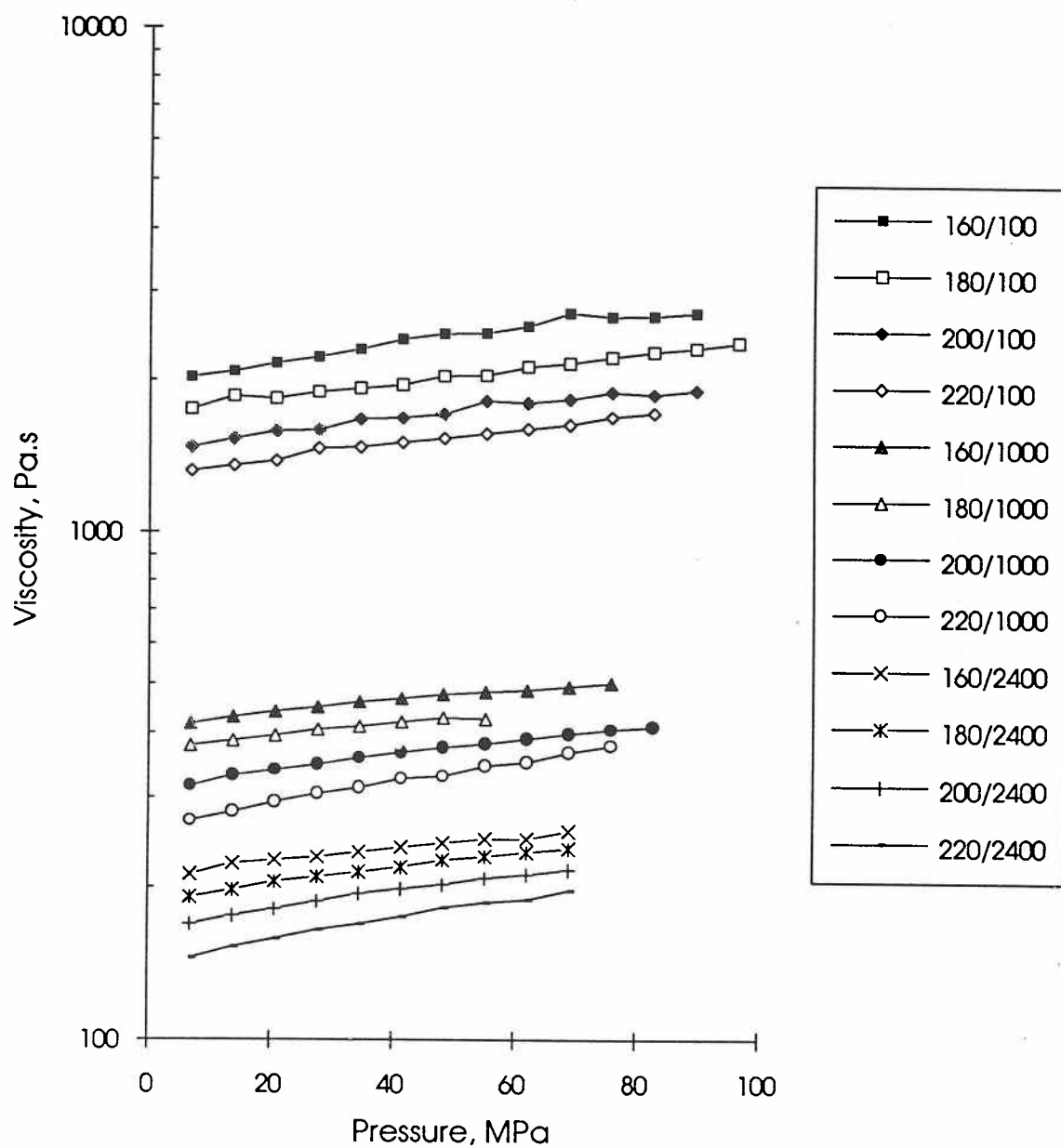


Fig. 4

The effect of pressure on the shear viscosity of LDPE (HAC001) for a range of temperatures and apparent shear rates. The legend gives the temperature ($^{\circ}C$) and the shear rate (s^{-1}).

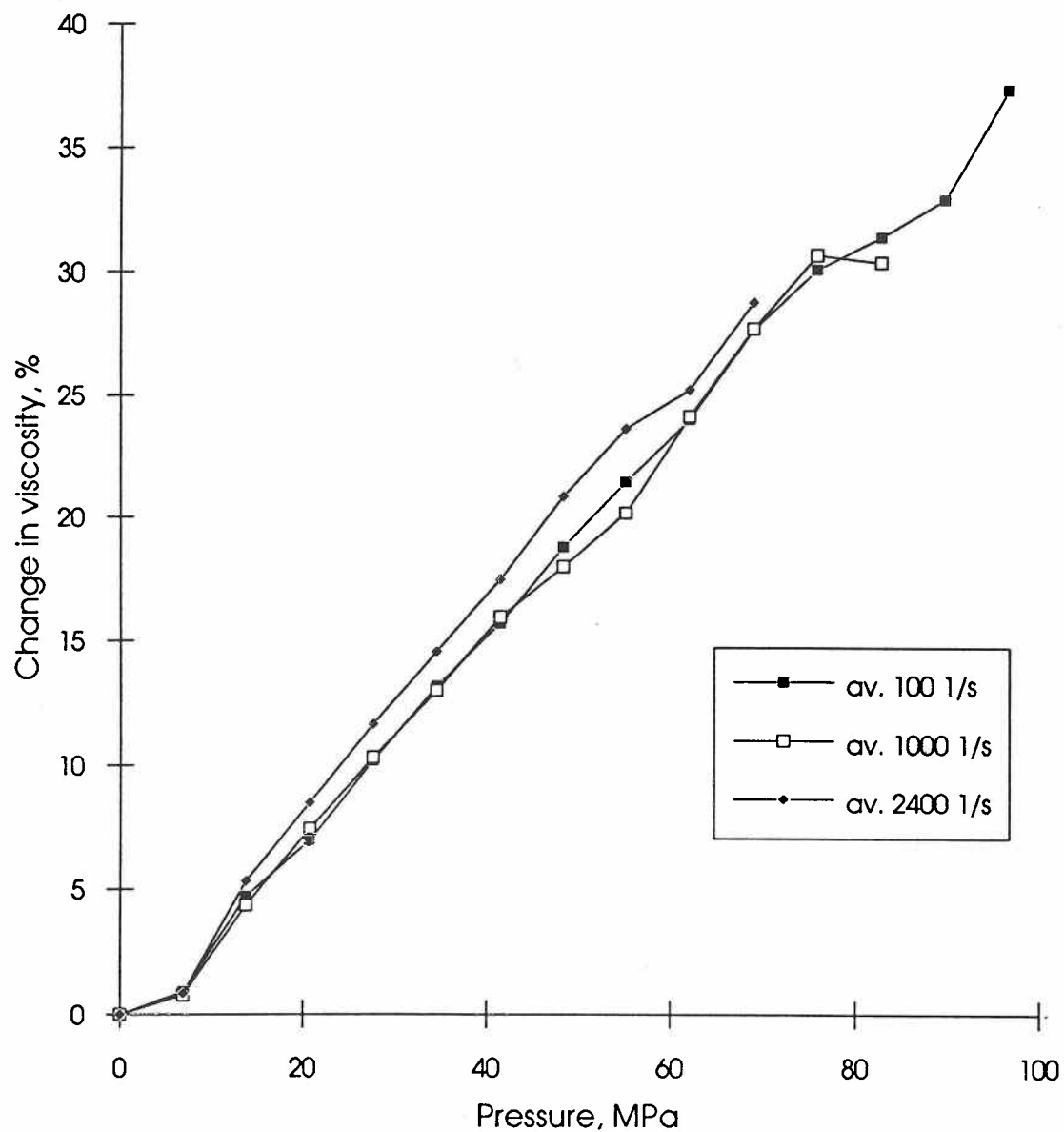


Fig. 5

The effect of pressure on the shear viscosity of LDPE (HAC001) expressed as a percentage change from the viscosity at zero pressure, indicating the relative independence of the behaviour to shear rate. Temperature averaged values for each shear rate are presented.

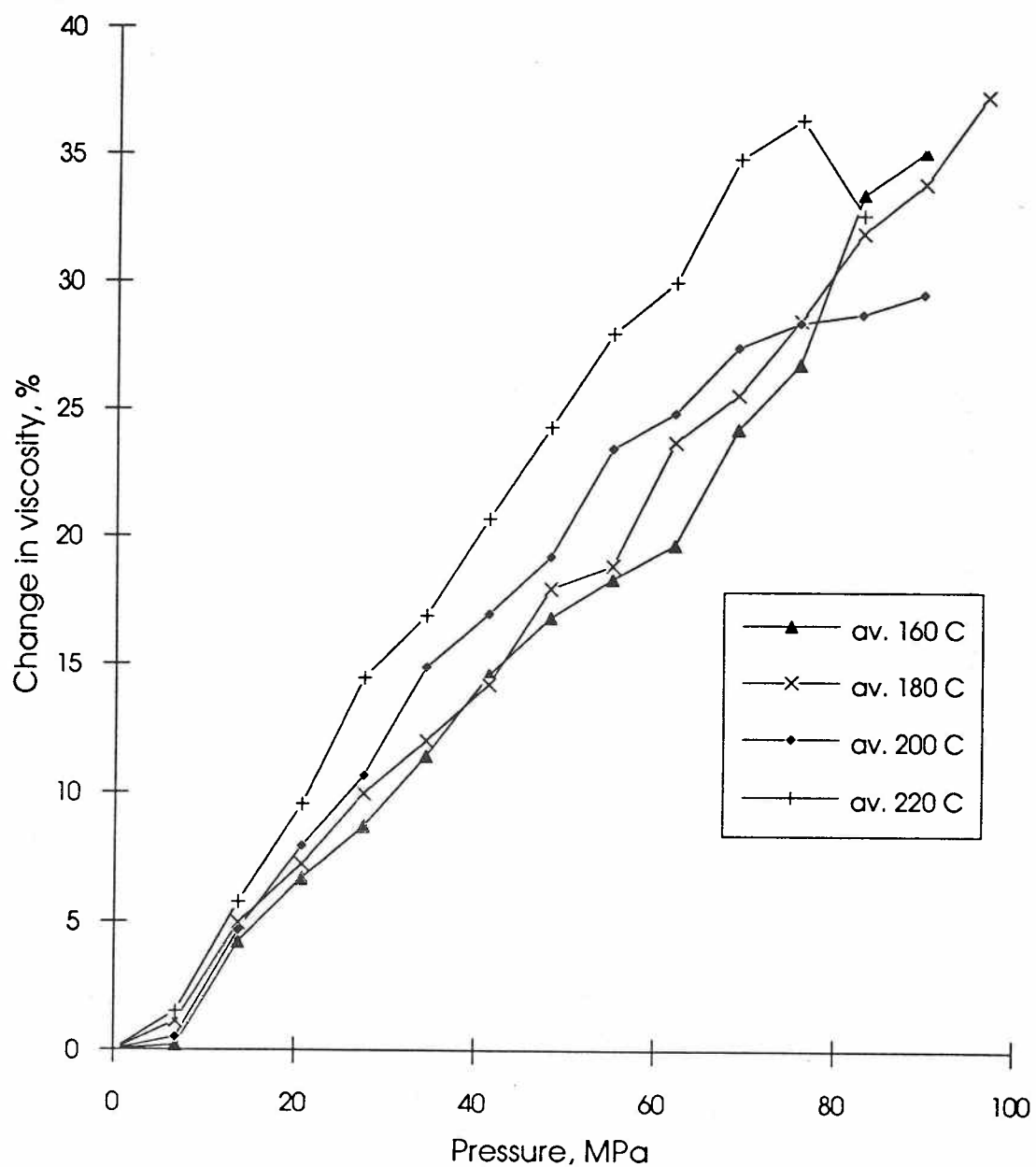


Fig. 6

The effect of pressure on the viscosity of LDPE (HAC001) expressed as a percentage change from the viscosity at zero pressure, indicating the temperature dependence of the behaviour. Shear rate averaged values for each temperature are presented.

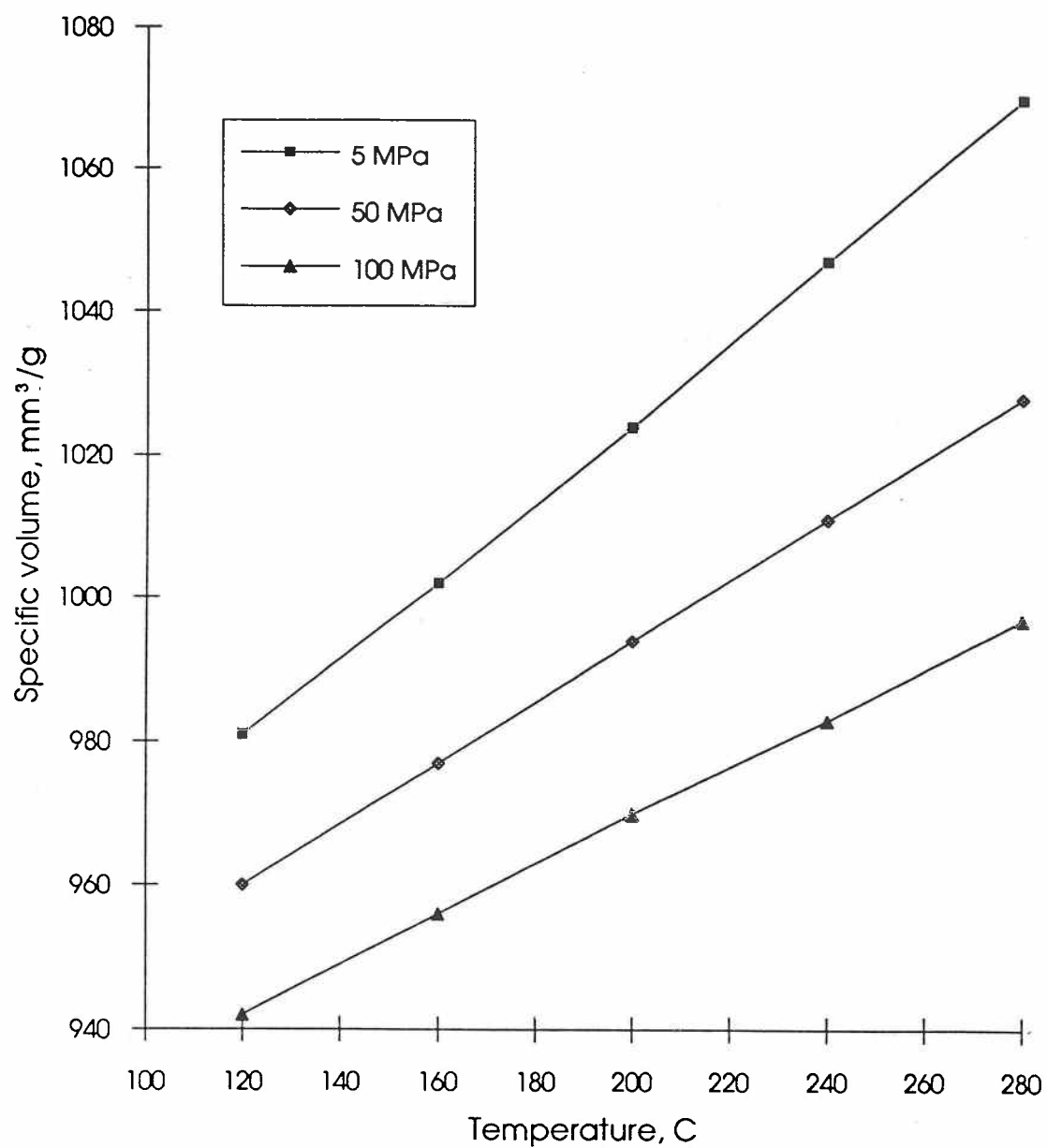


Fig. 7 The effect of temperature on the specific volume of PS (HAU001) for a range of pressures.

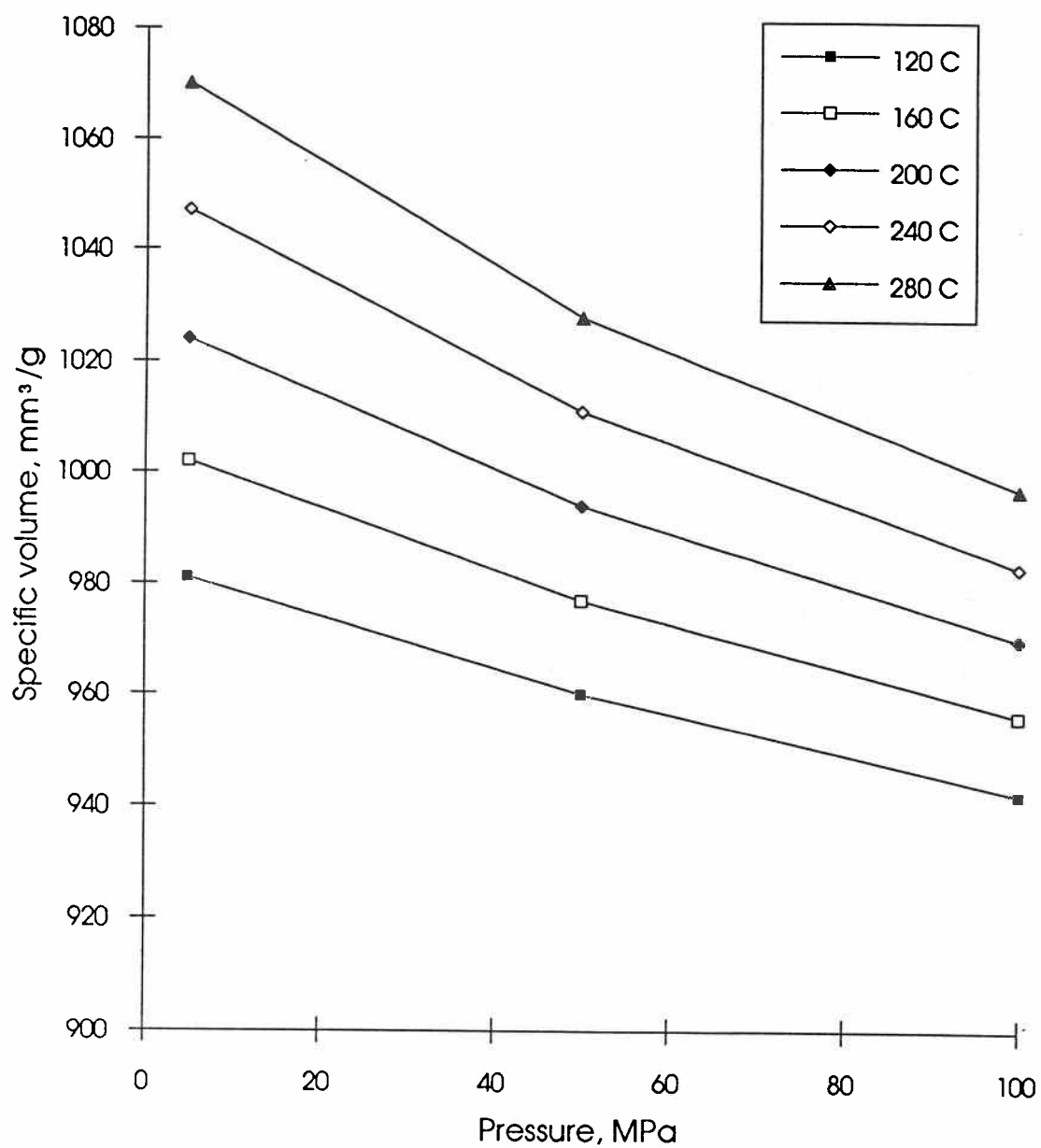


Fig. 8 The effect of pressure on the specific volume of PS (HAU001) for a range of temperatures.

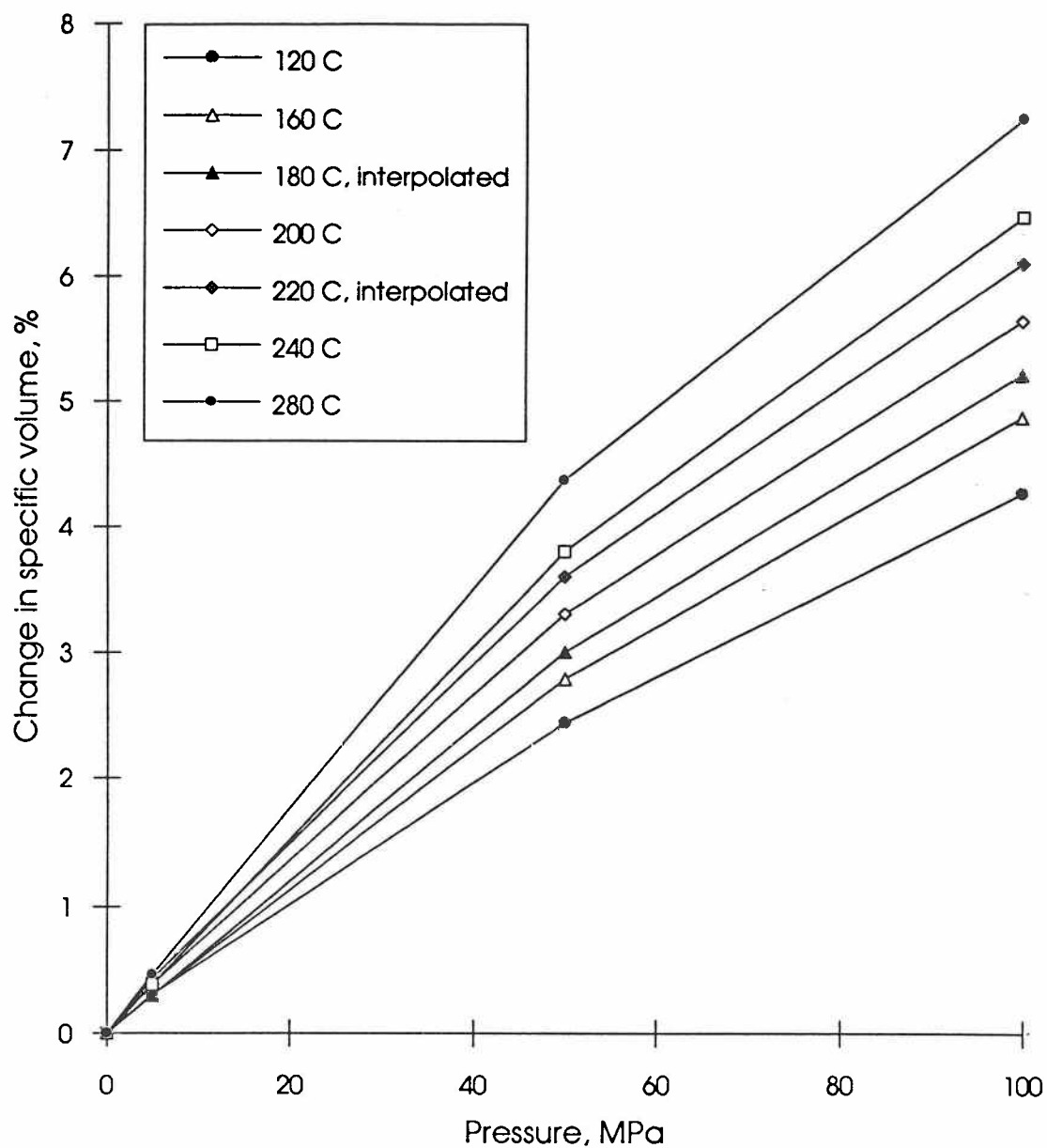


Fig. 9

The effect of pressure on the specific volume of PS (HAU001) for a range of temperatures, expressed as a percentage, indicating the effect of pressure on flow rate during extrusion testing and processing.

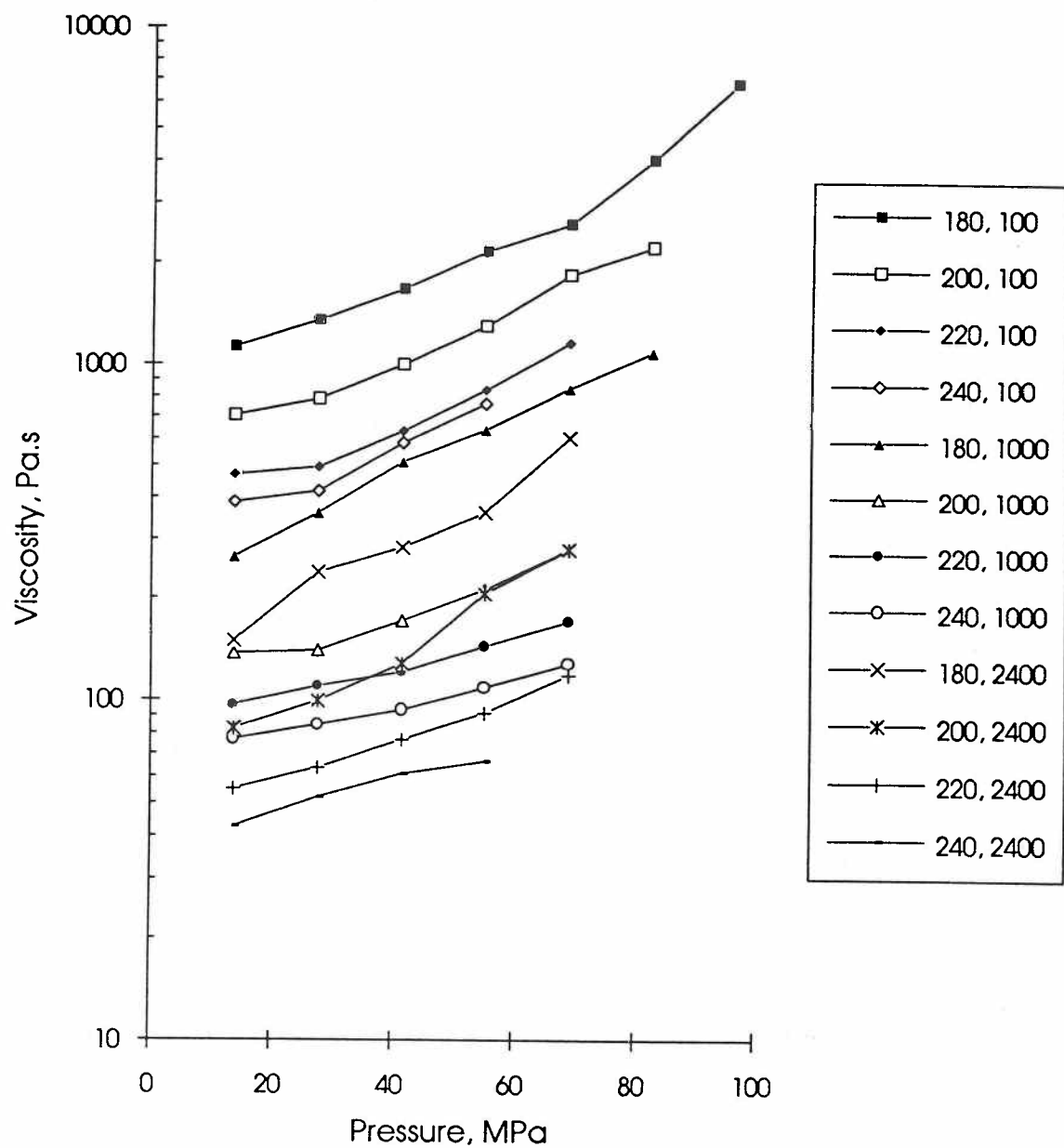


Fig. 10

The effect of pressure on the shear viscosity of PS (HAU001) for a range of temperatures and apparent shear rates. The legend gives the temperature ($^{\circ}\text{C}$) and the shear rate (s^{-1}).

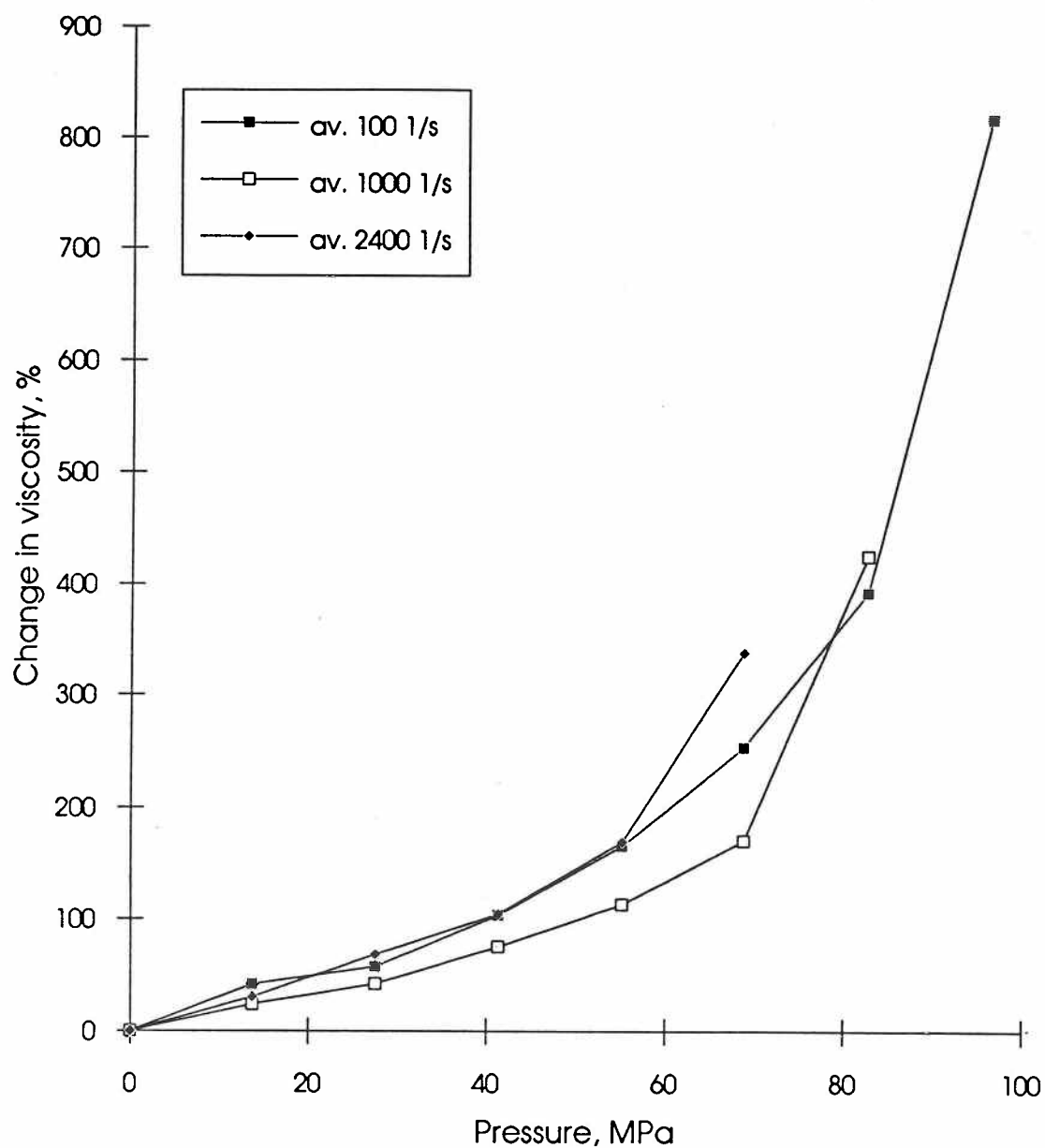


Fig. 11

The effect of pressure on the viscosity of PS (HAU001) expressed as a percentage change from the viscosity at zero pressure, indicating the relative independence of the behaviour to shear rate. Temperature averaged values for each shear rate are presented.

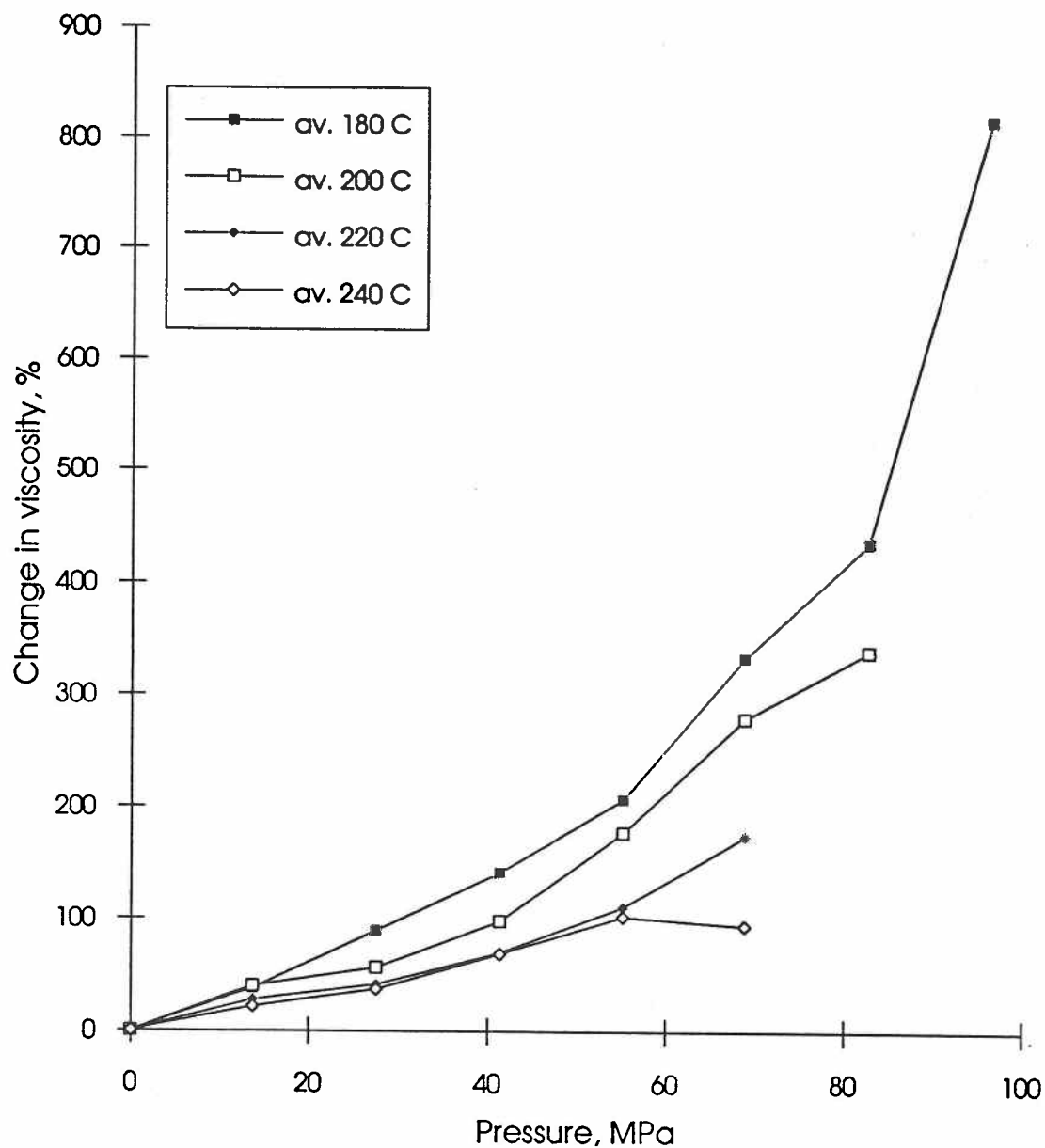


Fig. 12

The effect of pressure on the viscosity of PS (HAU001) expressed as a percentage change from the viscosity at zero pressure, indicating the temperature dependence of the behaviour. Shear rate averaged values for each temperature are presented.

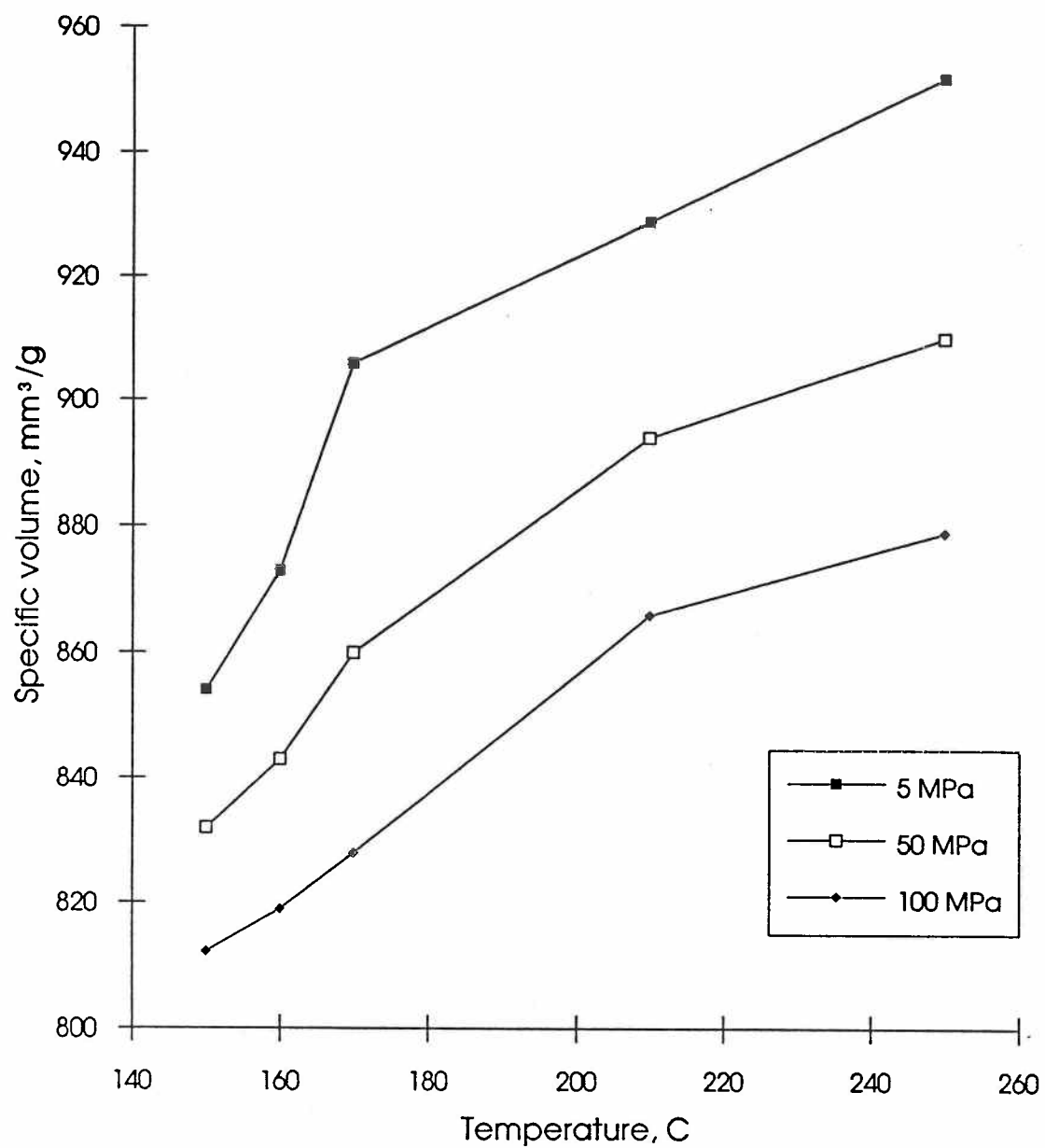


Fig. 13 The effect of temperature on the specific volume of PP + mineral filler (HAR001) for a range of pressures.

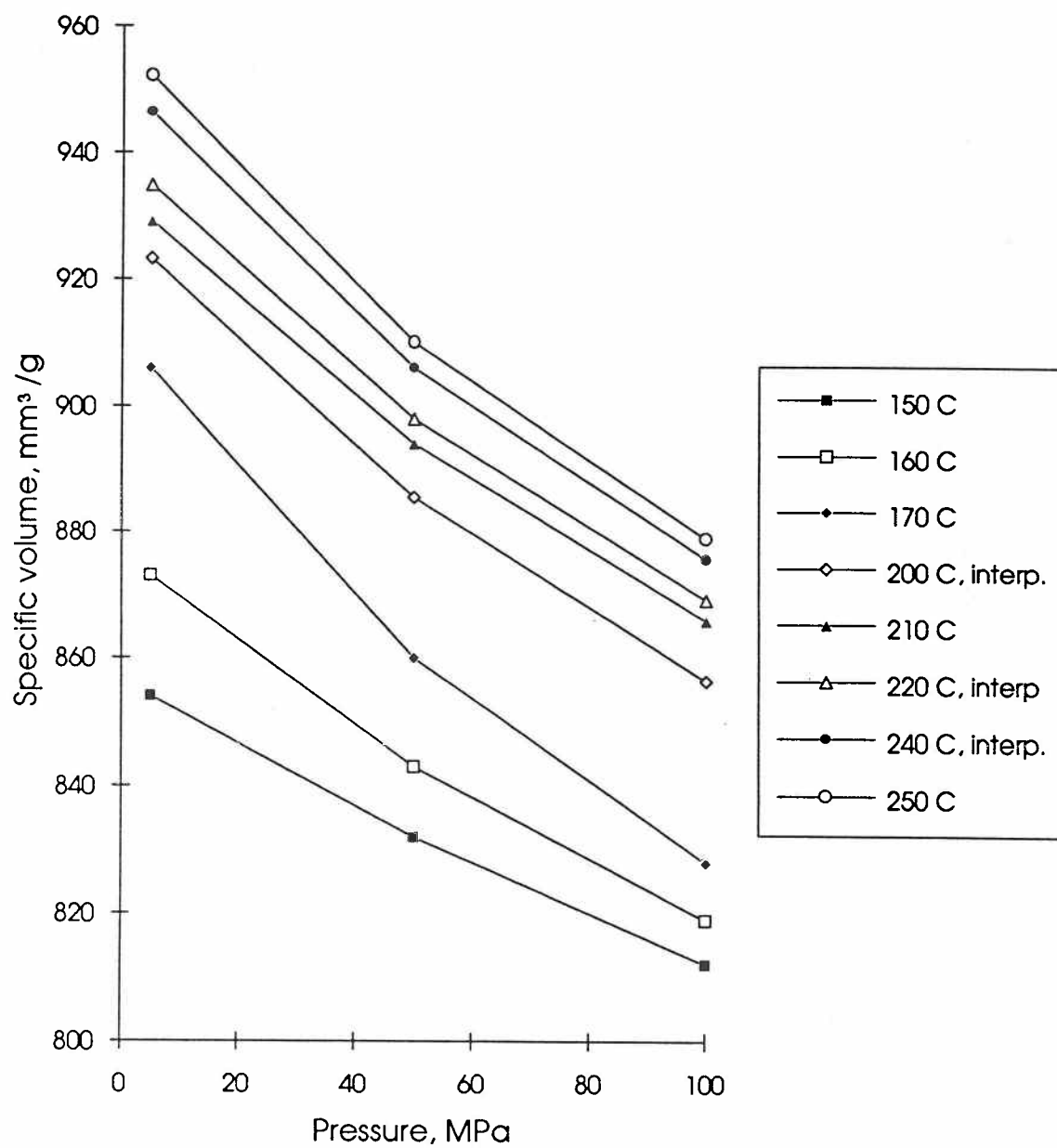


Fig. 14 The effect of pressure on the specific volume of PP + mineral filler (HAR001) for a range of temperatures.

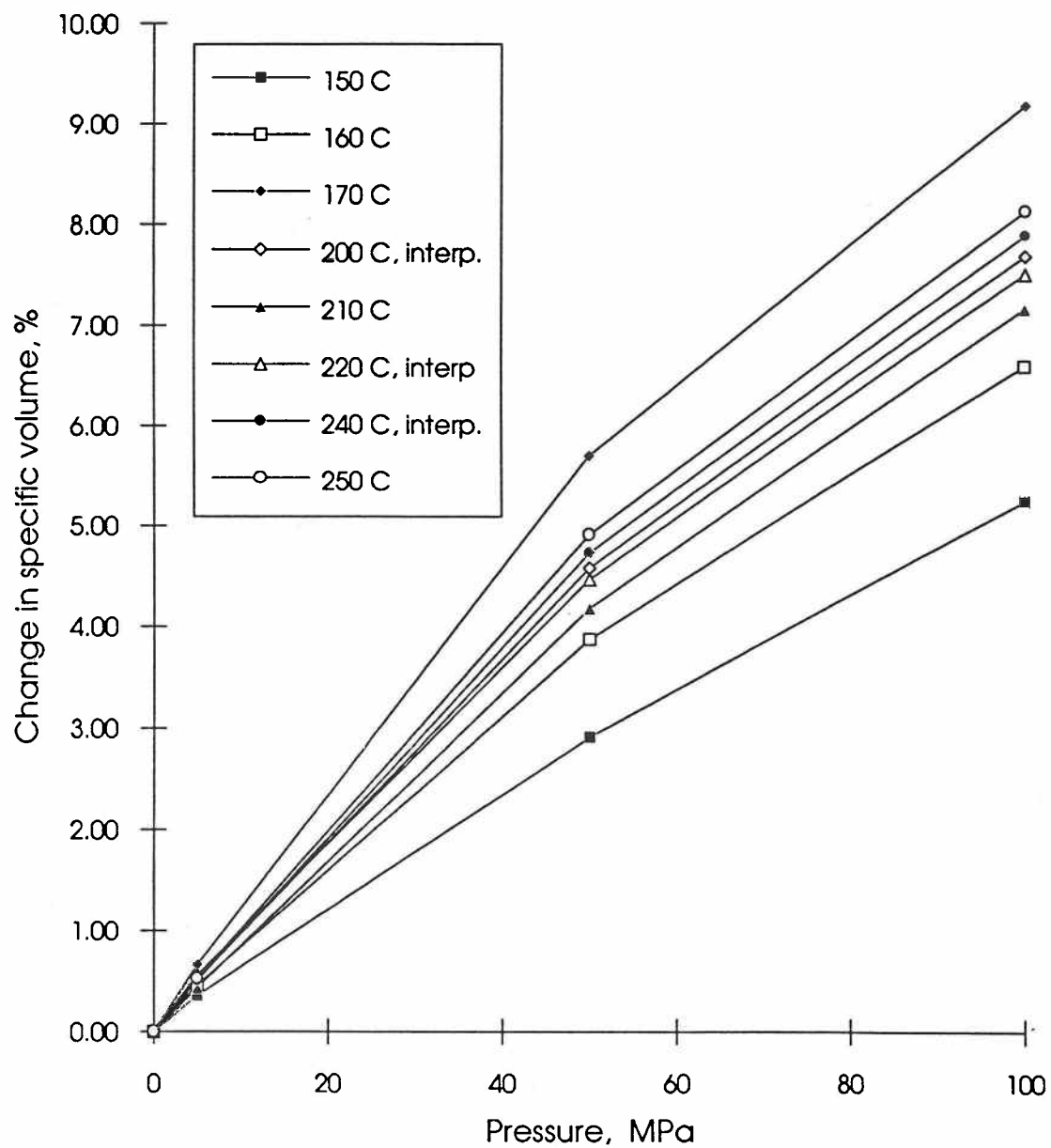


Fig. 15

The effect of pressure on the specific volume of PP + mineral filler (HAR001) for a range of temperatures, expressed as a percentage, indicating the effect of pressure on flow rate during extrusion testing and processing.

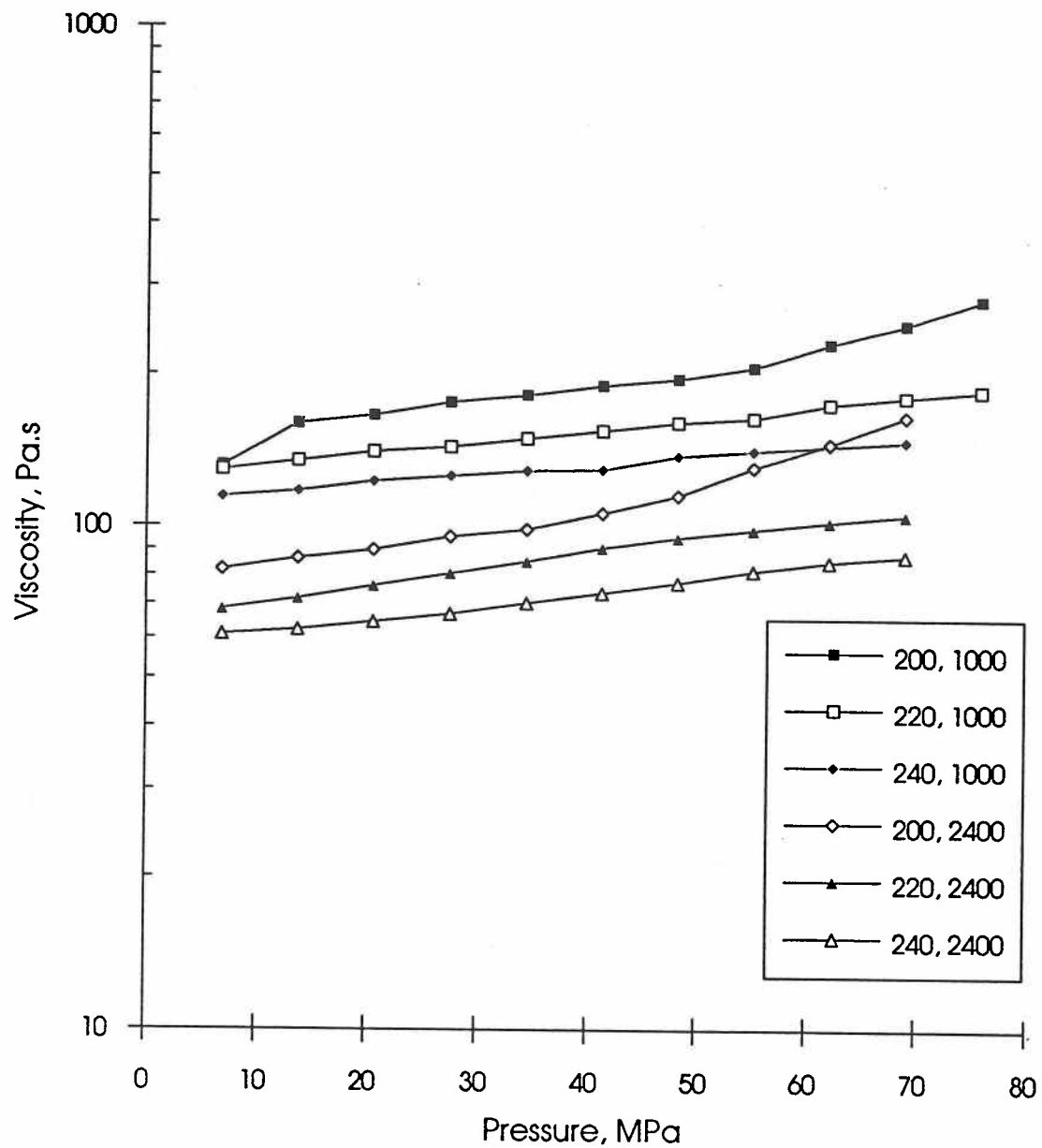


Fig. 16

The effect of pressure on the shear viscosity of PP + mineral filler (HAR001) for a range of temperatures and apparent shear rates. The legend gives the temperature ($^{\circ}\text{C}$) and the shear rate (s^{-1}).

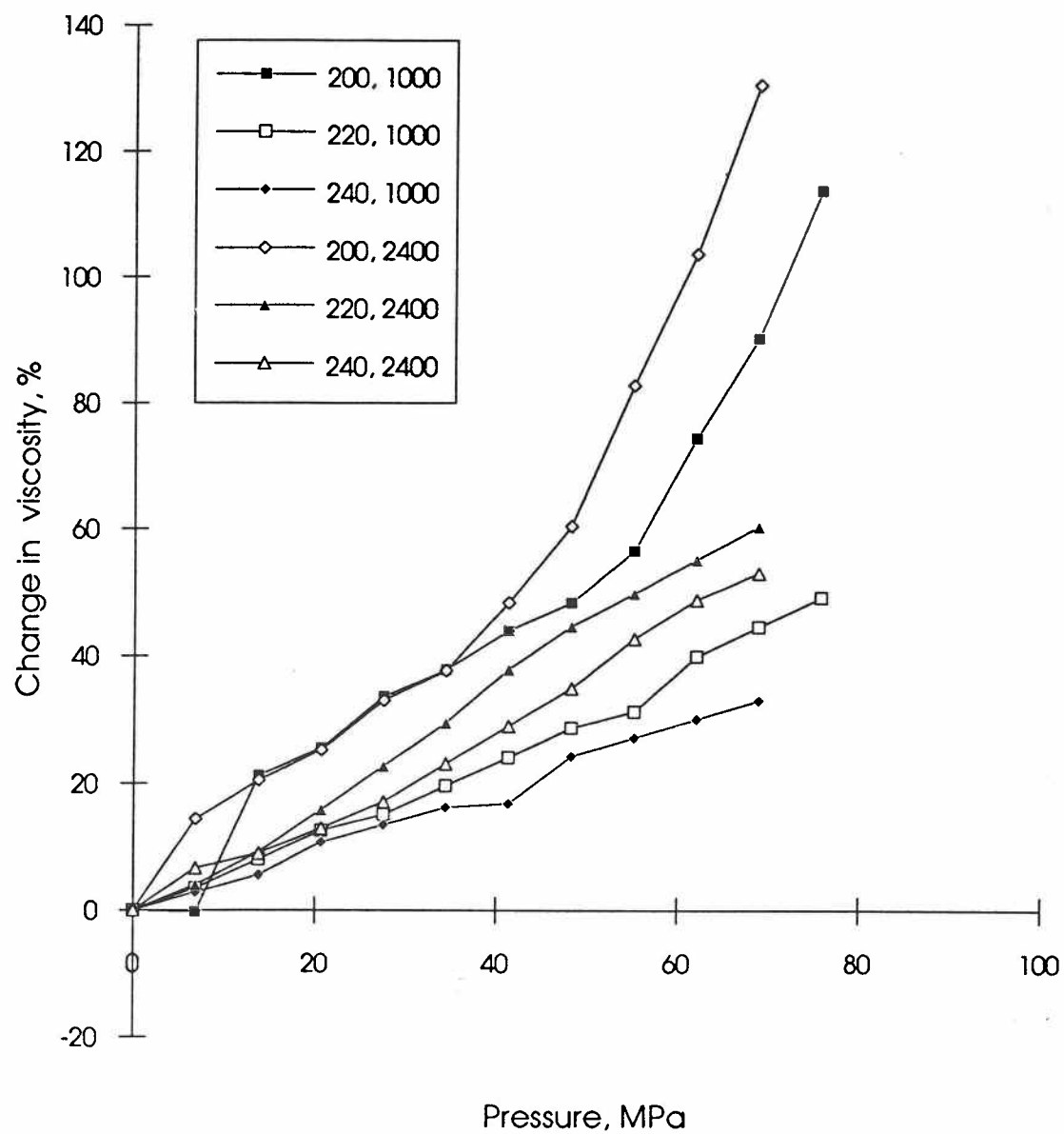


Fig. 17

The effect of pressure on the viscosity of PP + mineral filler (HAR001) expressed as a percentage change from the viscosity at zero pressure for a range of shear rates and temperatures. The legend gives the temperature ($^{\circ}\text{C}$) and the shear rate (s^{-1}).