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Polymer Melts at
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from Compression
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March 2002

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ABSTRACT

A novel method has been investigated to assess the thermal properties of polymer melts by compression heating at elevated pressure. The energy input and the resulting temperature rise are measured which are then be used to determine a specific heat capacity under pressure. A sample of polymer is heated to the test temperature within a cylindrical pressure vessel. The pressure is controlled through a piston fitted with PTFE seals. The temperature increases with increase in pressure.

Measurements of a high-density polyethylene (HDPE) at 208 °C, showed an increase in temperature of 3 °C as the pressure was increased from 20 MPa to 80 MPa. The sample was found to cool back to a temperature approximately equal to the initial temperature after a delay of about 100 seconds. During subsequent release of the pressure a further cooling occurred before the whole system returned to equilibrium again. The duration of the pressure ramp and of the cooling were of the same order. The experimental results were analysed by two different mathematical approaches. The form of the time temperature behaviour was predicted reasonably well. Specific heat values derived from these analyses were, however, not sufficiently close to the expected values to allow the method to be recommended in its current form. A more rapid application of pressure is thought to be needed.

A system was developed that can track changes in temperature due to compression heating down to $\pm 0.01^{\circ}\text{C}$.

An elevated pressure DSC was also commissioned to provide thermal data up to about 7 MPa. These were compared with the above measurements.

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ISSN 1473-2734

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Prepared as a deliverable of milestone 5 of the project
MPM1.5: Heat transfer in polymer processing,
a project of the Department of Trade and Industry EID programme
on measurements related to the processability of materials

Approved on behalf of Managing Director, NPL
by Dr C Lea, Director, NPL Materials Centre

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1. Introduction

Heat transfer is recognised as an important aspect of polymer processing because of the potential to enhance productivity by improving heat transfer and also because of the potential to degrade product quality through poor heat transfer. Accurate measurement of heat transfer parameters is important to enable optimised process conditions to be determined, particularly through the use of appropriate modelling. The three main thermal properties under investigation in this project are thermal conductivity, specific heat and latent heat. A review paper [1] has shown that there are important variations between independent measurements, as high as 50% for thermal conductivity, for example. Indeed, it has been established [2] that thermal conductivity can vary considerably with temperature and with pressure. For polymer processing, data are needed at the temperatures and pressures used in commercial situations. In injection moulding, for example, temperatures can be from 80°C to about 300°C and pressures from atmospheric pressure up to about 200 MPa. There is thus a need to investigate methods of obtaining thermal properties of polymers under these conditions. Two approaches to this need are reported in this document.

Firstly, a novel method has been investigated to assess the thermal properties of polymer melts by compression heating at elevated pressure. In this method a sample of polymer is heated to the test temperature within a cylindrical pressure vessel. The pressure is controlled through a piston fitted with polytetrafluoroethylene (PTFE) seals. As pressure increases and volume decreases, a rise in temperature results. The energy input and the temperature rise are measured and these are used to determine a specific heat capacity under the test conditions. In order to account for heat losses during the compression cycle, a mathematical model of the process is necessary. Experiments were carried out in the pressure range 20 MPa to 160 MPa at constant wall temperature and the results presented in Section 4 and the model's ability to fit the experimental data is considered in Sections 3 and 4. Two methods of analysis of the experimental results are presented.

In a second approach an elevated pressure Differential Scanning Calorimeter (DSC) has been assessed as a method of obtaining thermal property data, including specific heat. There have been a number of reports in the literature of failed attempts to operate DSC at above atmospheric pressure [3, 4] and one recent report from Japan indicating that the approach may be promising [5]. Results are presented and discussed Section 6.

This report presents the work of milestone 5 (deliverable 1) of Project MPM1.5 on Heat Transfer in Polymer Processing.

2. Compression Heating Method

Equipment normally used for PVT measurements of polymer melts was adapted for this compression-heating study. The high-density polyethylene used in all experiments was NPL code HGH-800 (supplied by BP Chemicals). The measurement apparatus was supplied by SWO (now Haake) and a schematic view is presented in

Figure 1. The temperature is measured at the centre of the polymer sample. The original temperature measuring system has been upgraded to a system with higher accuracy ($\pm 0.01^{\circ}\text{C}$); a syringe needle type thermocouple Pico TC-08, fitted into the lower piston.

The basis of the method is that a temperature rise occurs when work is done on the polymer melt through compression. The rate of doing work per unit volume on the sample is given by the stress multiplied by the strain rate. Stress is calculated from the force on the piston and its cross-sectional area and the strain rate is determined from the piston speed and the original sample length. The temperature of the melt is measured with a thermocouple. If there were no heat losses the calculation of specific heat would be simple as the energy needed to raise the temperature of a known amount of material is measured directly. However, the timescale of the application of pressure was found to be similar to the cooling time, indicating that heat losses were significant (see Fig. 2). During any later decompressions resulting in cooling, heat can re-enter from the surroundings.

An approximate method to estimate the specific heat of a cylindrical sample using compression heating is presented in Appendix A.

An alternative mathematical analysis, given in Appendix B, was also developed which modelled both the temperature rise from the work done in compressive heating and the heat transfer from the polymer melt to its surroundings. For calculation purposes, this model assumes that the heat produced by the work done is uniform throughout the material.

The data required by these models are:

- Temperature measured at the centreline (as a function of time during pressure changes)
- Pressure
- Length of sample (as a function of time during pressure changes)
- Cross sectional area (of piston and sample)
- Time
- Mass of sample

A plot of temperature measured from the thermocouple against time is obtained as a constant pressure ramp is applied, held and then removed (see Fig. 2).

3. Models of Compression Heating

Two models have been used to investigate the most appropriate method of analysis of compression heating data. In the first method (see Appendix A) the specific heat is calculated directly from the maximum temperature rise in the sample, its mass and the work done on the sample (which in turn is calculated from its change in length and its cross-sectional area), with a correction to allow for loss of heat to the surroundings. The temperature field is assumed to be similar in heating and in cooling.

The derivation of the second model and its assumptions are presented in Appendix B. This approach provides the direct solution of the governing differential equation for the compression cycle.

Two applications of this model B are studied in this report. For the first application of the model a MATLAB program was written, Thetrun1, which used the least squares method to determine the best values of the two unknown parameters, thermal conductivity K and the thermal diffusivity k .

For the second application another MATLAB program was written, Thetrun1par, which allowed the fixing of a single unknown parameter (k or K) to be input to the model and the model determined the curve of best fit by adjusting the other unknown parameter. Again the least squares method was used to determine an estimate for the unknown parameter. Equal weighting of the experimental points was employed in both models.

The inputs to the programs were the experimental data for the centreline temperature, strain and pressure. For the single parameter model, values of thermal parameters were obtained at elevated temperature and pressure. It should be noted that the temperature and pressure are not constant during the experiment, so that in effect average values are obtained over the temperatures and pressures of the experiment. However, this is only strictly valid where the changes in temperature and pressure are small compared with their absolute values.

The density can be measured as a function of temperature and pressure from the PVT apparatus. If the density is known, then specific heat C is calculated using

$$C = \frac{K}{\rho k} \quad (1)$$

where ρ is the density. Values for thermal diffusivity and thermal conductivity, obtained from the two-parameter and one-parameter models, are presented in the next section.

4. Results and Discussion of Compression Heating Data

Preliminary work showed that a significant increase in temperature could be achieved by measuring the temperature of the sample using the PVT machine thermocouple system as measured from the top piston. However, it was decided that a more accurate temperature measurement could be obtained from a “stand alone” temperature logger with a sensor situated in the lower piston.

Tests were performed in the 20-160 MPa range with various pressure profiles. In order to obtain reliable displacement measurements a minimum pressure of 20 MPa was adopted. A smaller pressure increase (10 MPa) was chosen so that the pressure increase was small compared with the absolute pressure, thus bringing the experimental conditions closer to the conditions assumed in the model. However, a smaller pressure increase produces a smaller temperature rise, hence the need to

improve the accuracy of the temperature measurement, which has been implemented (see Section 2).

Results are reported for a study where the pressure on a consolidated polyethylene sample at 20 MPa was raised to 80 MPa lowered to 20 MPa then raised again to 80 MPa while allowing the sample temperature to equilibrate at each new pressure. Figure 2 shows the results for this experiment. An experiment was also carried out in the same manner where the pressure was increased from 20 MPa to 160 MPa as shown in Fig. 4. A further experiment incorporated a small pressure increment from 20 MPa to 30 MPa prior to rising to 80 MPa (Fig. 6 and Fig. 8) in an effort to reproduce just a 10 MPa change was also conducted. The experimental data are given in Figs. 2, 4, 6 and 8.

The analysis of the results following the approach outlined in Appendix A is given in Table 1.

Table 1: Compression Heating Results Analysis (Appendix A method)

	Pressure Jump (MPa)			
	20 to 160	20 to 80	20 to 80	20 to 30
Initial length (m)	0.0202	0.07348	0.07329	0.01909
Final length (m)	0.0184	0.07221	0.07220	0.01898
Initial Pressure (MPa)	20.0	20.0	19.9	20.0
Final Pressure (MPa)	160.0	80.3	80.3	30.7
Work done (J)	6.03	1.79	1.54	0.03
Initial temperature (°C)	207.92	208.08	208.11	208.19
Peak temperature (°C)	211.09	210.64	210.74	208.58
Specific Heat (Jkg⁻¹°C⁻¹)	3878	1430	1199	152

Notes:- Area of cylinder $4.69 \times 10^{-5} \text{m}^2$. Mass of polymer 0.653g.

In this approach only the peak temperature is used to calculate specific heat. A correction due to loss of heat to the surroundings is applied which assumes the temperature field is similar before and after the peak temperature. The pressure jump from 20 to 80 MPa was repeated. The temperature rise in the first case was 2.56 °C and in the second case 2.63 °C (a 3% difference). The change in length for the first case was 1.27 mm and for the second case 1.09 mm (a 14% difference). It may be that the PTFE seals used were compacted less the second time compared with the first time. There was less than 1% difference in the pressures. The combined result for the specific heat is a 16% difference. For these pressure jumps from 20 MPa to 80MPa the absolute values of specific heat were found to be lower than expected (a value of at least 2000 Jkg⁻¹K⁻¹ was expected – see Section 5). In fact, in this case, a model with no heat loss would give a value between 1800 and 2100 Jkg⁻¹K⁻¹, quite close to the expected value. However, the results from the much larger pressure jump from 20 to 160 MPa gave a much higher value for specific heat (3878 Jkg⁻¹K⁻¹). This may be due to an underestimate of the temperature rise or an insufficient allowance for heat loss or a pressure dependent specific heat. An error in the length measurement is not thought likely to be the cause of this higher than expected specific heat value. The

small temperature rise and length change from the case of the pressure jump from 20 to just 30 MPa make these results unreliable.

The same set of data was also analysed using the model presented in Appendix B. For convenience, plots were provided of the dimensionless centreline temperature $[(T - T_0)/T_0]$, where T_0 is the initial temperature, against normalised values of elapsed time $[(t - t_0)/(t_f - t_0)]$, where t_0 is the initial time and t_f is the final time, for the two-parameter model and the experimental data are shown in Figs. 3, 5, 7 and 9. The plots in Figs. 3, 5, 7 and 9 correspond to the experimental data given in Figs. 2, 4, 6 and 8 respectively. For all the two-parameter simulations, Table 2 shows the values for the parameters k and K obtained from the curve fitting. Corresponding values for specific heat are also shown in Table 2, which were calculated using equation (1). A constant mass of 0.6534 g was used to calculate an approximate value for density, which was estimated from the average volume of the sample.

The values obtained for K and k provide a good fit for the model to the experimental time – temperatures data in most cases. Thermal conductivity is expected to increase with pressure and the results in Table 2 follow this trend. The data for the 20 to 30 MPa pressure jump given in Fig. 8 show a marked increase in noise, due to the thermocouple resolution error producing a significant contribution to the measured signal. The fit of the model in Fig. 9 is reasonable, considering the experimental scatter in this small pressure range.

For the single parameter model, an appropriate fixed value of k was taken from the literature [6]. The curve fit of the single parameter model to the data cycled between 20 MPa to 80 MPa is shown in Fig. 10 and this corresponds to the experimental data shown in Fig. 2. The accuracy of the curve fit is similar to that shown by the two-parameter model in Fig. 3. The value of K obtained is shown in Table 2 using a thermal diffusivity $k = 1.4 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$.

Table 2: Thermal Parameters for High Density Polyethylene obtained from two-parameter and one-parameter fits of the model presented in Appendix B.

Pressure Change (MPa)	k ($\text{m}^2 \text{ s}^{-1}$)	K ($\text{W}^{-1} \text{ K}^{-1} \text{ m}^{-1}$)	ρ (kg m^{-3})	C ($\text{J kg}^{-1} \text{ K}^{-1}$)
20-30	1.25×10^{-7}	0.055	714	617
20-160	1.87×10^{-7}	0.152	736	1103
20-30-80	1.95×10^{-7}	0.115	736	803
20-80-20-80	1.94×10^{-7}	0.102	724	727
20-80-20-80 (1 par. model)	1.40×10^{-7} (set)	0.094	724	927

The absolute values of the thermal properties may be compared to other measurements in the literature [6, 7]. The thermal diffusivity estimates at elevated pressure in Table 2 are slightly higher than those reported in the literature [6] at

atmospheric pressure, which are typically in the range from $1.0 \times 10^{-7} \text{ m}^2\text{s}^{-1}$ to $1.4 \times 10^{-7} \text{ m}^2\text{s}^{-1}$. The thermal conductivity values in Table 2 are consistently lower than the values measured directly in the literature [7], which were reported as $0.25 \text{ W}^{-1}\text{K}^{-1}\text{m}^{-1}$. However, the values obtained through this technique are of the same magnitude as values obtained through other methods. The derived specific heat values are all significantly lower than expected. The main factor contributing to this would seem to be the lower than expected thermal conductivity values.

When fixing a value of K (thermal conductivity), the MATLAB program produced a poor value of k (thermal diffusivity) although the time – temperature data was fitted. This was not unexpected because of the exponential term in the equation used to model the centreline temperature (see Appendix B, eqn. (2.12)). The parameter k appears in the exponential term, which strongly constrains the curve fitting routine when seeking an appropriate value to fit the experimental data. It is unfortunate that this is the case because reliable thermal conductivity values are more widely available at elevated temperatures and pressures.

5. Elevated Pressure DSC Method

The tests were carried out on a DSC cell enclosed within a steel cylindrical housing capable of operation up to 7 MPa pressures under nitrogen. The cell fits in as a plug-in module onto the TA Instruments TA2920 DSC unit shown in Fig. 11. The cell module has two gas flow control valves, a three-way valve, pressure gauge and release valve (Fig. 12). The cell construction is similar to the standard DSC and uses chromel-constantan thermocouples to monitor the temperatures (see Fig. 13). The sample and reference crucibles are placed on raised platforms within the constantan cell disc. Calibrations are performed in a similar way to the standard DSC.

Samples of HDPE were heated in the DSC at normal and elevated pressure (2 MPa) at a rate of $10 \text{ }^\circ\text{C}/\text{min}$. The mass of the sample was 3.8 mg. Standard sealable aluminium pans were used. The sample was conditioned at 70°C in a vacuum oven overnight prior to testing. The specific heat in the melt, C_p , was calculated from the heat flow difference between the sample and the empty pan at the desired temperature (Fig. 14). A correction factor, Q , obtained from the heat flow difference between the empty pan and a standard material, sapphire, of known specific heat was applied (Fig. 15).

Hence for sapphire:

$$Q = \frac{C_p \text{ (standard value)}}{C_p \text{ (measured)}} \quad (2)$$

and for HDPE:

$$C_p = C_p \text{ (measured)} \cdot Q \quad (3)$$

6. Results of Elevated Pressure DSC Data

The specific heat of HDPE did not vary significantly with pressure (Table 2). As expected, there was an increase in specific heat with temperature [6].

Table 2: Average specific heat values for HDPE at normal and elevated pressure

Temperature (°C)	C_p at atmospheric pressure (J Kg ⁻¹ K ⁻¹)	C_p at pressure = 2 MPa (J Kg ⁻¹ K ⁻¹)
196.9	2024	2168
206.9	2130	2212
216.9	2211	2222

7. Discussion

The C_p values determined from the DSC are similar to generally accepted values for HDPE, e.g. 2200 J Kg⁻¹K⁻¹ in [8]. The difference between values measured at atmospheric pressure and at elevated pressure are not considered to be significant. Because of its limited upper pressure the technique does not cover the pressure range relevant to many industrial processes, which was the reason for investigating the compression heating method which was discussed in Section 4.

The specific heat value from compression heating is not measured at constant pressure (C_p) nor at constant volume (C_v), however, it is measured close to the conditions experienced in injection moulding, i.e. rapidly changing pressure and volume, so it could be argued that it is appropriate.

Specific heat values determined from the compression heating data using the analysis method in Appendix A gave variable results. For the large pressure jump (20 to 160 MPa) they were higher than expected, but for the smaller pressure jump (20 to 80 MPa) they were smaller than expected. It would appear that at high pressures the temperature rise is smaller than expected. It is not thought that any errors in length, mass or pressure could explain this effect. For the lower pressure jump (20 to 80 MPa), the model apparently overcorrects the heat loss, as the simple analysis with no heat loss gives values (1800 and 2100 Jkg⁻¹K⁻¹) close to that found by DSC (around 2200 Jkg⁻¹K⁻¹). It is also interesting to note that in the repeat run at the lower pressure jump a very similar temperature rise was recorded (3% difference), though a 14% difference in the length change was recorded. This could be due to a change in the compressibility of the PFTE seals.

Values determined from the compression heating data using the analysis method in Appendix B gave thermal diffusivity values typically slightly higher at elevated pressure than values obtained through traditional methods at atmospheric pressure. Values obtained for thermal conductivity at elevated pressure were about 50% less than those determined from traditional methods. Derived specific heat data were consequently lower (by at least 50%) than those determined from other methods such as DSC. Any error in the K , k (or ρ) values will translate into an error in C .

The assumptions of this model may not exactly replicate the experimental conditions, for example heat losses from the ends of the sample are ignored (though PTFE seals at the ends are considerably more insulating than the metal walls which should minimise this problem). The model also assumes for calculation purposes that K and k are not a function of pressure. There is a further assumption that the pressure and temperature rise is initially homogeneous.

Neither analysis provides a satisfactory method of obtaining specific heat data at elevated pressure despite the improvements that were made to the temperature measurement method and the attempts to model the heat loss during the application of pressure.

It is recommended that consideration is given to a much more rapid application of pressure than has been found to be possible with the current PVT equipment. This would mean that the effect of heat losses would be much less and thus the problem of the analysis of heat loss would be much reduced. A possible method of application of pressure over a short time interval could be an instrumented falling weight apparatus. A 1 Kg mass, for example, has kinetic energy of about 50 J after falling one metre. This is considerably more than the 6 J applied in the PVT apparatus. The impact would of course be over a much shorter time period than the 60 seconds in the PVT apparatus, as desired. It may be necessary in this case to allow for some loss of energy during impact.

8. Conclusions

- Two methods of obtaining thermal property data in the melt state at elevated pressure have been investigated.
- The DSC method can provide specific heat data up to about 7 MPa.
- The DSC work did not show any significant variation of specific heat with pressure.
- A compression heating method has been investigated which can operate up to 160 MPa.
- It was found that the time scale of the application of pressure in the PVT equipment was of the same order as the rate of cooling.
- Two different models of the compression heating experiment were developed which attempted to take into account of heat transfer from the sample to its surroundings.
- One model gave specific heat values higher than expected at high pressure (20 to 160 MPa) and lower than expected at lower pressures (20 to 80 MPa).
- A second model consistently gave specific heat and thermal conductivity values about 50% lower than expected.
- To overcome the difficulties of modelling heat losses it is recommended that an instrumented falling weight apparatus be investigated to carry out the compression over a much shorter time period.

9. Acknowledgements

Funding for this work from the Department of Trade and Industry (EID), through the MPM programme, is gratefully acknowledged. The authors would like to acknowledge Elena Arranz for assistance with the DSC measurements, Simon Chorley who assisted with early modelling work and David Hills for suggesting the model in Appendix A.

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Ref NPL Report MATC(A)25v16

11. Figures

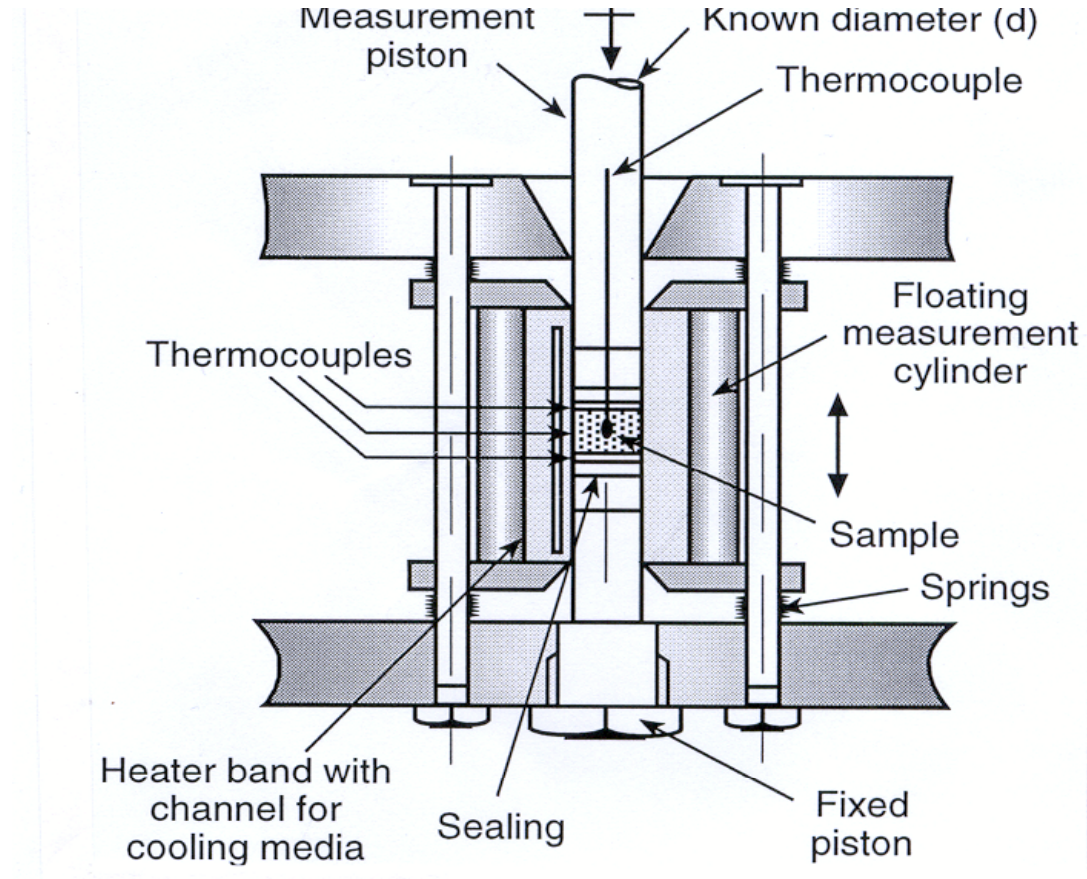


Fig. 1: Diagram of the compression heating PVT apparatus

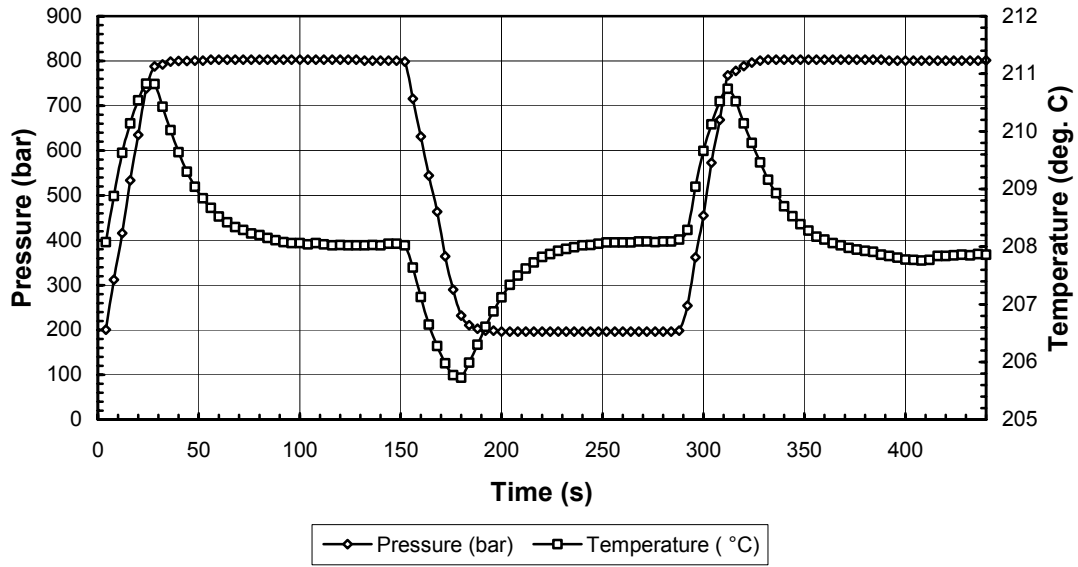


Fig. 2: Plot of centreline temperature and applied pressure (cycling from 20 MPa to 80 MPa) against time for Polyethylene HGH-800.

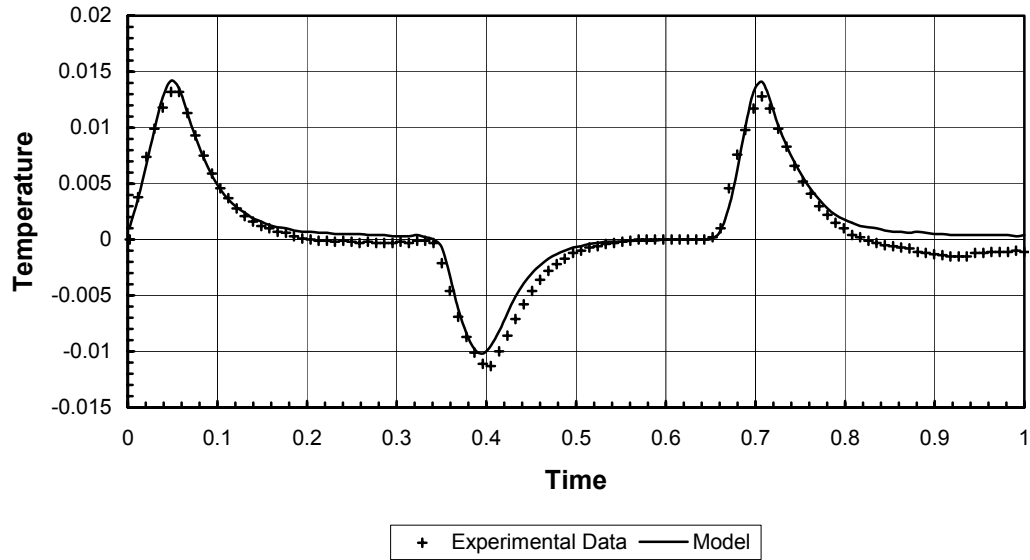


Fig. 3: A comparison of the dimensionless centreline temperature $[(T-T_0)/T_0]$ against normalised time $[(t-t_0)/(t_f-t_0)]$ for the two parameter model of Appendix B with experimental data. Pressure was cycled between 20 MPa and 80 MPa for Polyethylene HGH-800 .

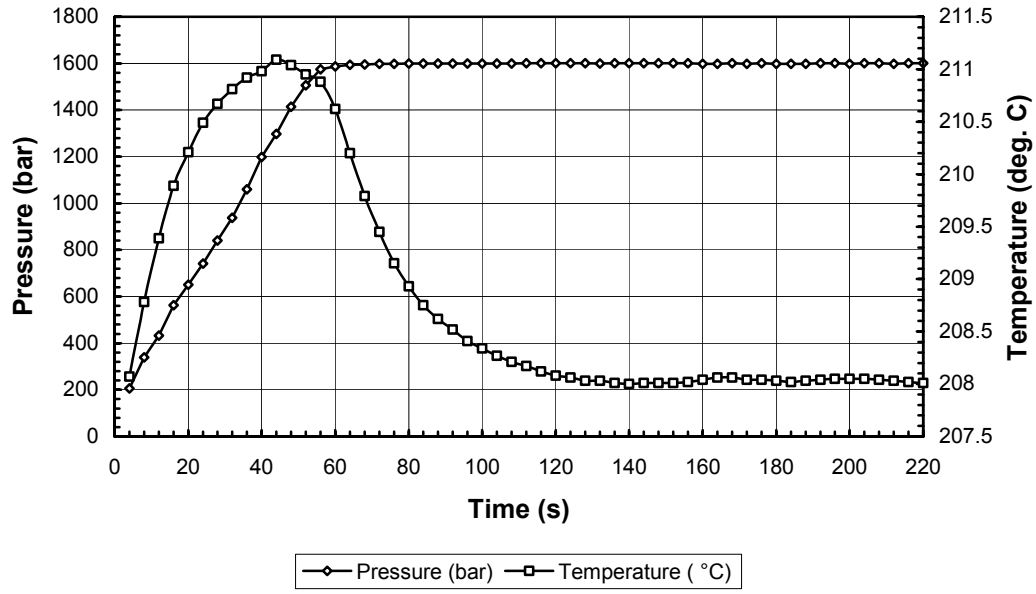


Fig. 4: Plot of centreline temperature and applied pressure (increased from 20 MPa to 160 MPa) against time for Polyethylene HGH-800.

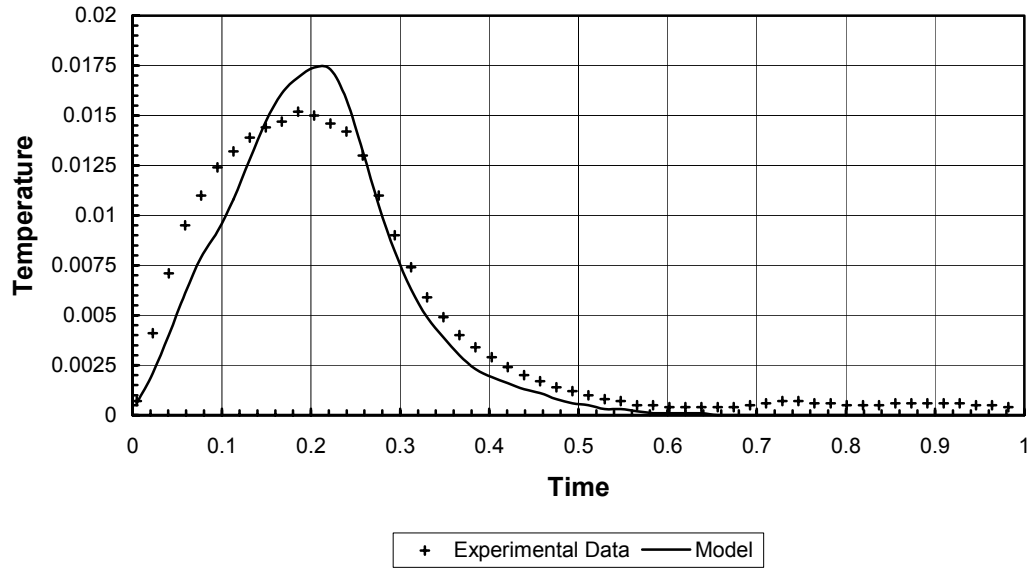


Fig. 5: A comparison of the dimensionless centreline temperature $[(T-T_0)/T_0]$ against normalised time $[(t-t_0)/(t_f-t_0)]$ for the two parameter model of Appendix B with experimental data. Pressure was increased from 20 MPa and 160 MPa for Polyethylene HGH-800.

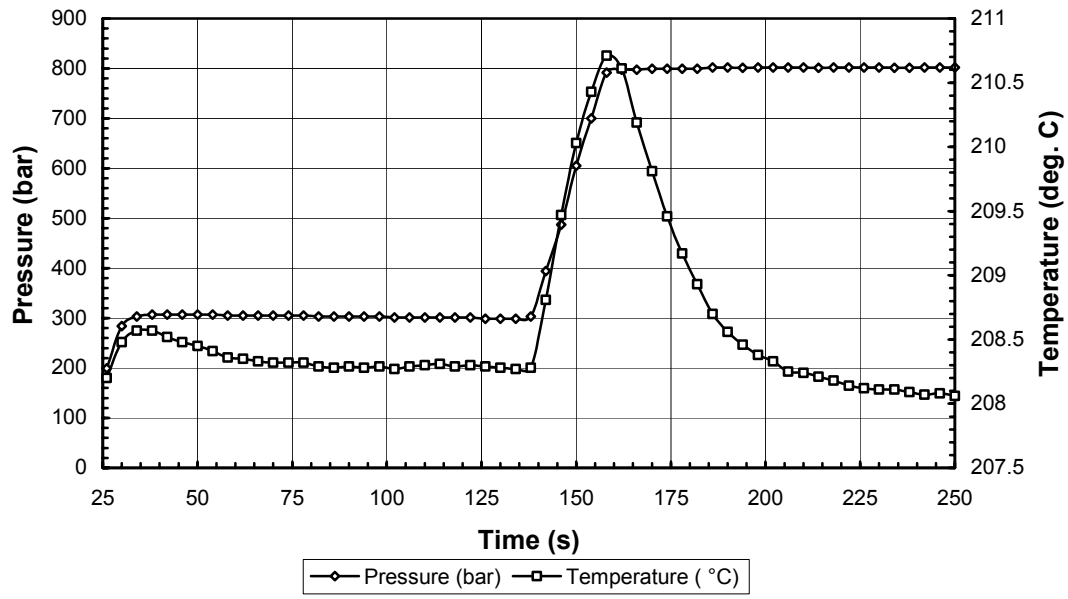


Fig. 6: Plot of centreline temperature and applied pressure (increased from 20 MPa to 30 MPa to 80 MPa) against time for Polyethylene HGH-800.

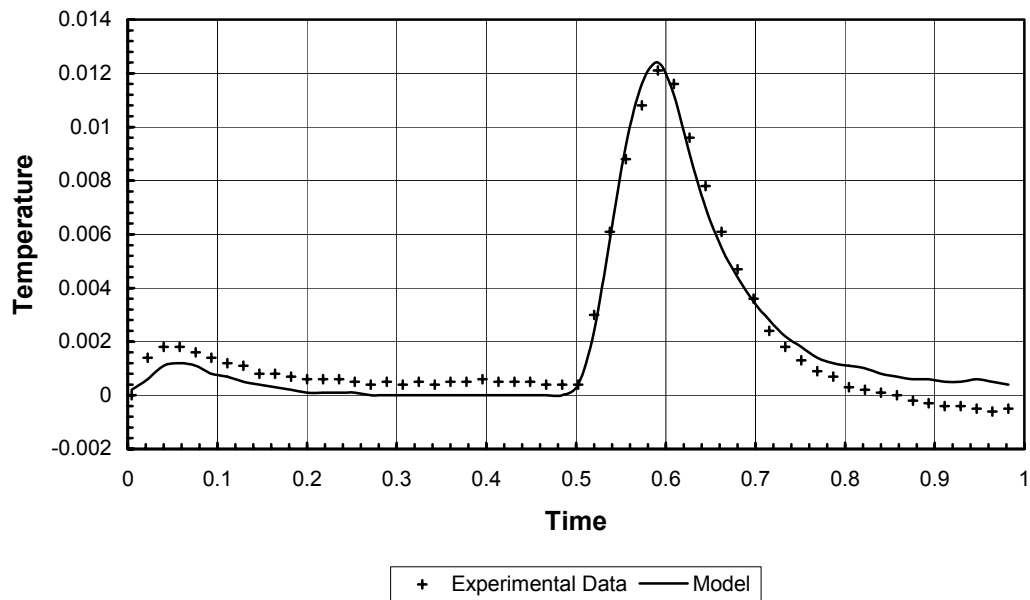


Fig. 7: A comparison of the dimensionless centreline temperature $[(T-T_0)/T_0]$ against normalised time $[(t-t_0)/(t_f-t_0)]$ for the two parameter model of Appendix B with experimental data. Pressure was increased from 20 MPa to 30 MPa to 80 MPa for Polyethylene HGH-800.

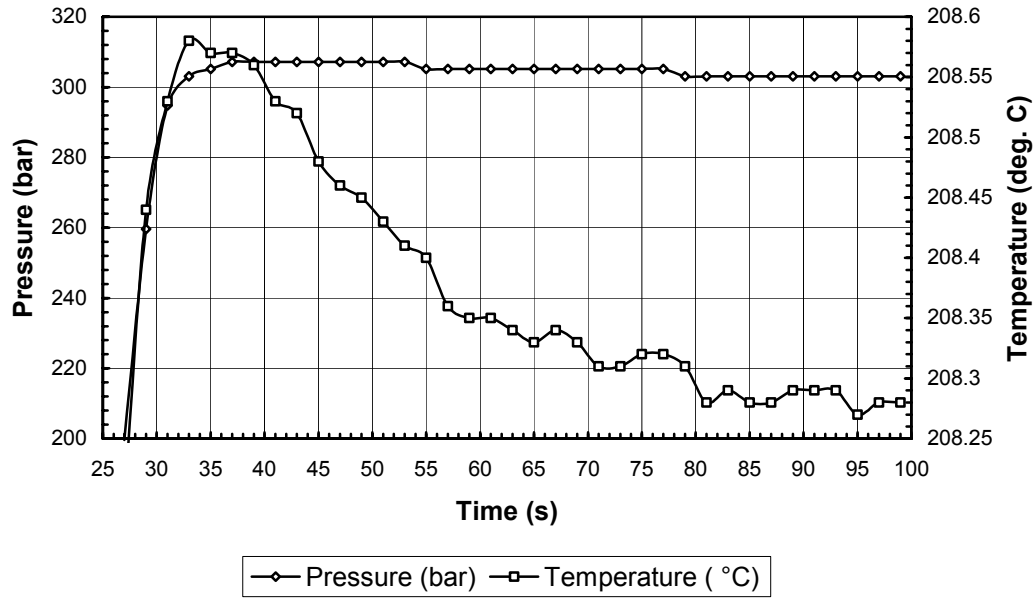


Fig. 8: Plot of centreline temperature and applied pressure (increased from 20 MPa to 30 MPa) against time for Polyethylene HGH-800.

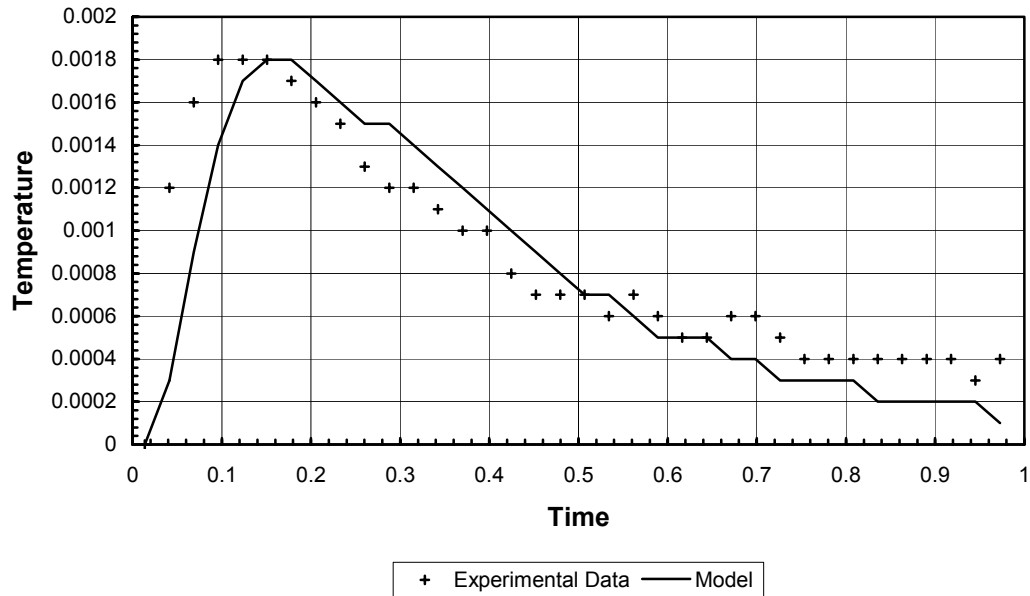


Fig. 9: A comparison of the dimensionless centreline temperature $[(T-T_0)/T_0]$ against normalised time $[(t-t_0)/(t_f-t_0)]$ for the two parameter model of Appendix B with experimental data. Pressure was increased from 20 MPa and 30 MPa for Polyethylene HGH-800.

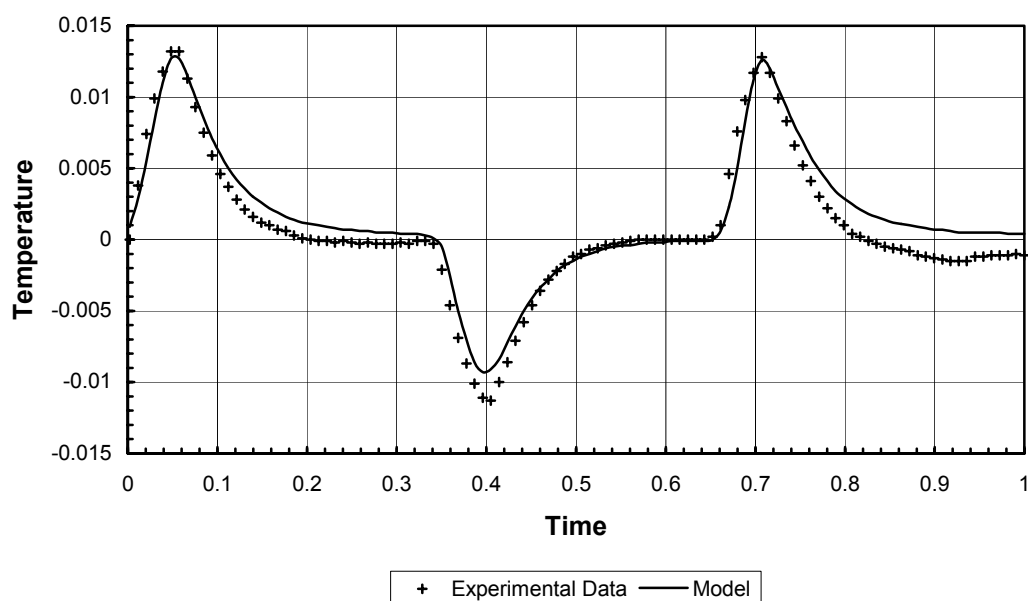


Fig. 10: A comparison of the dimensionless centreline temperature $[(T-T_0)/T_0]$ against normalised time $[(t-t_0)/(t_f-t_0)]$ for the one-parameter model of Appendix B with experimental data. Thermal diffusivity was set at $k = 1.4 \text{ m}^2\text{s}^{-1}$ and pressure was cycled between 20 MPa and 80 MPa for Polyethylene HGH-800.

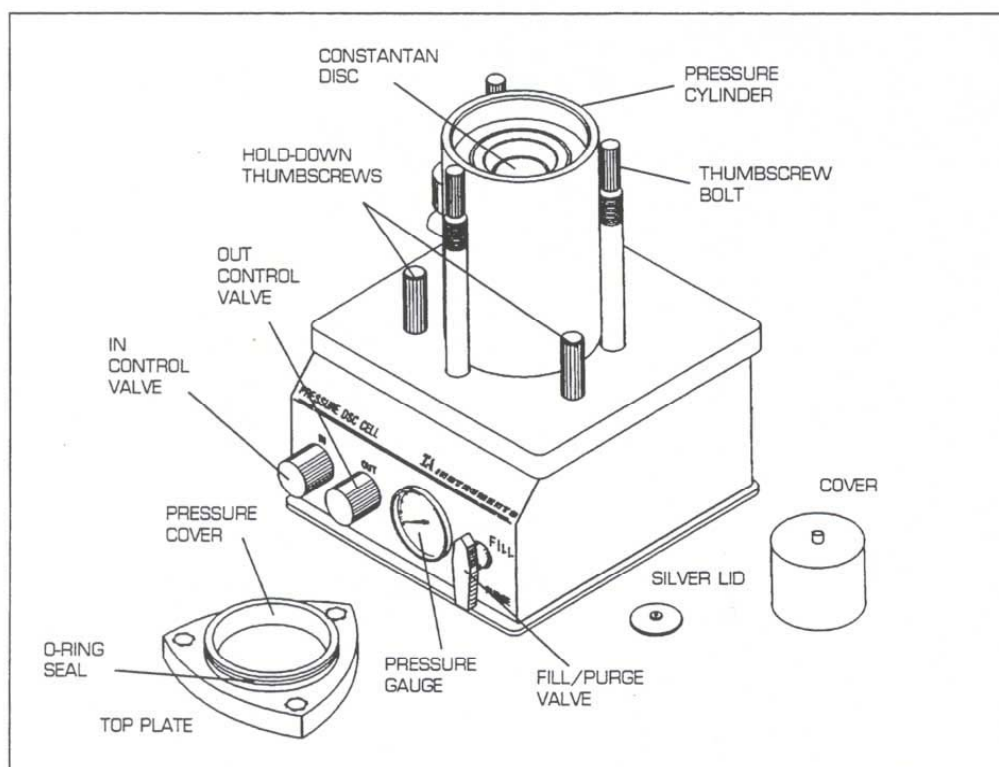


Fig. 11: Overall construction of the high pressure DSC courtesy of TA instruments.

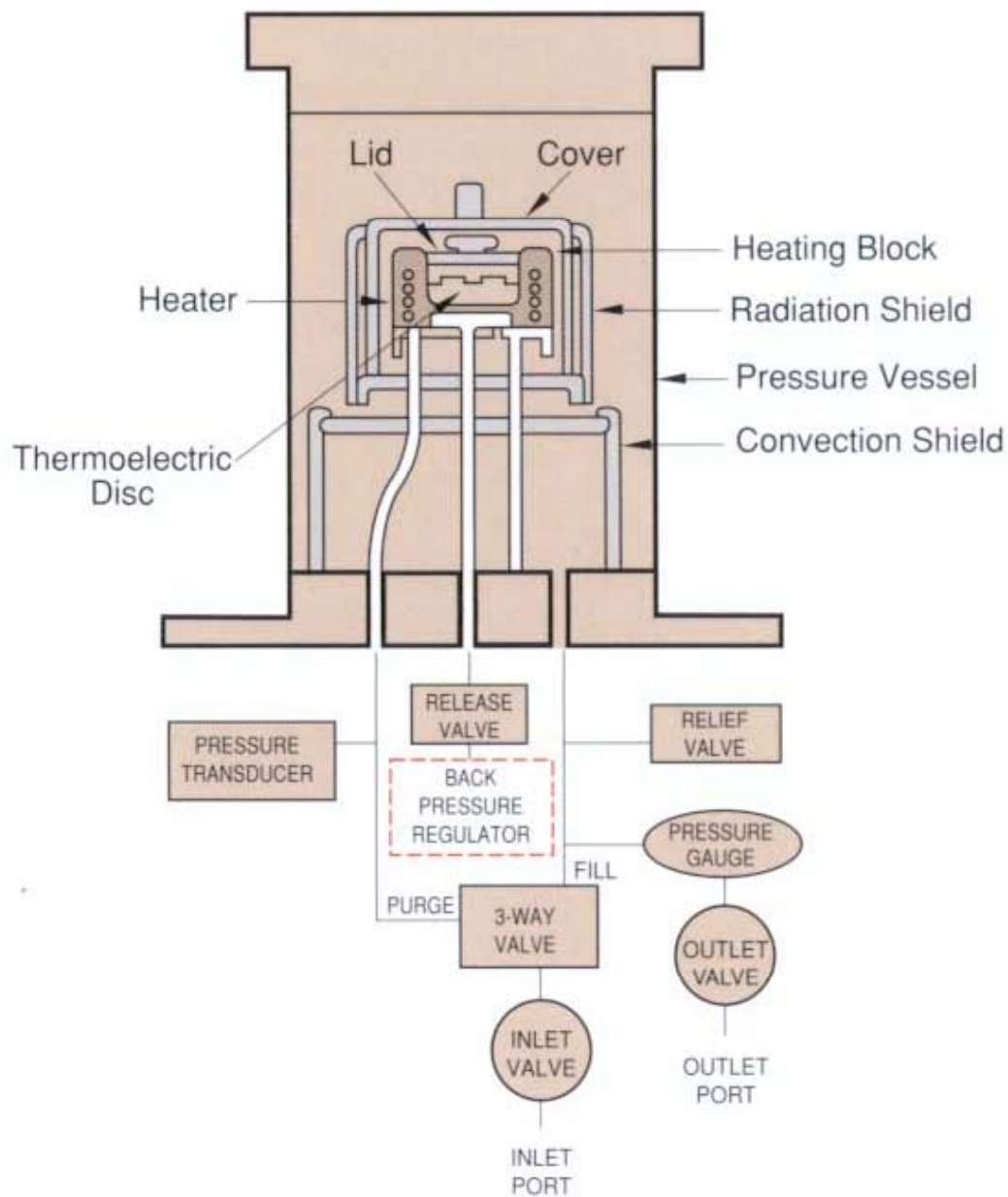


Fig. 12: Pressure cell schematic courtesy of TA instruments.

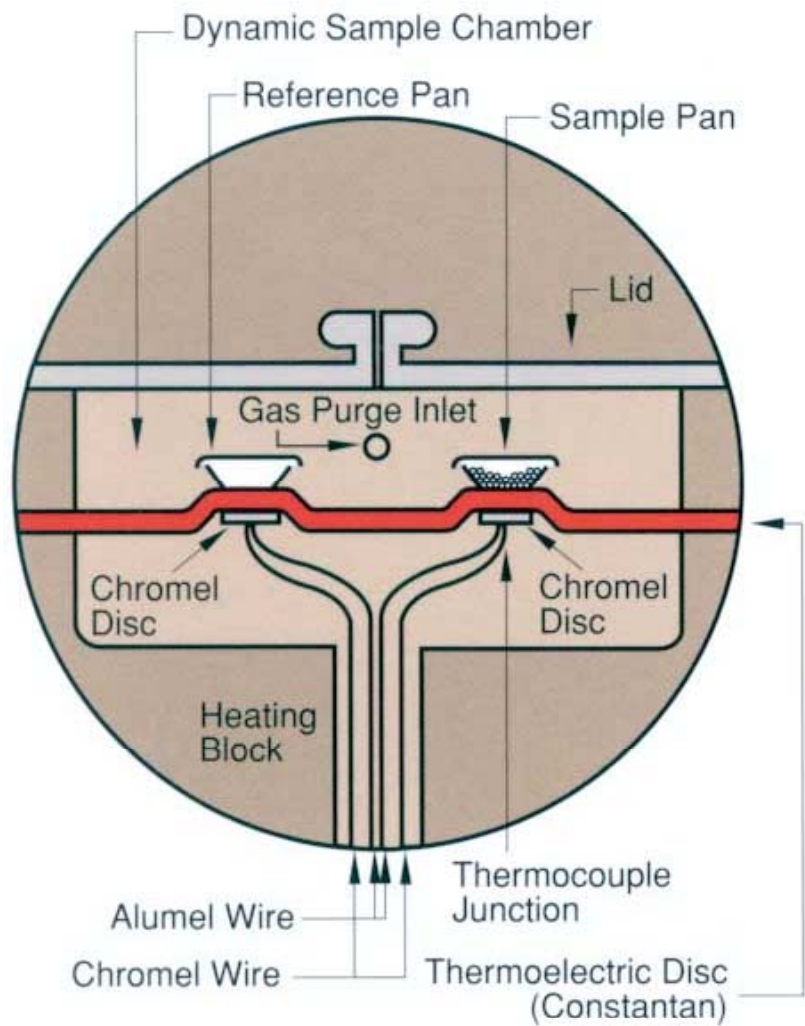


Fig. 13: Pressure cell cross-section courtesy of TA instruments.

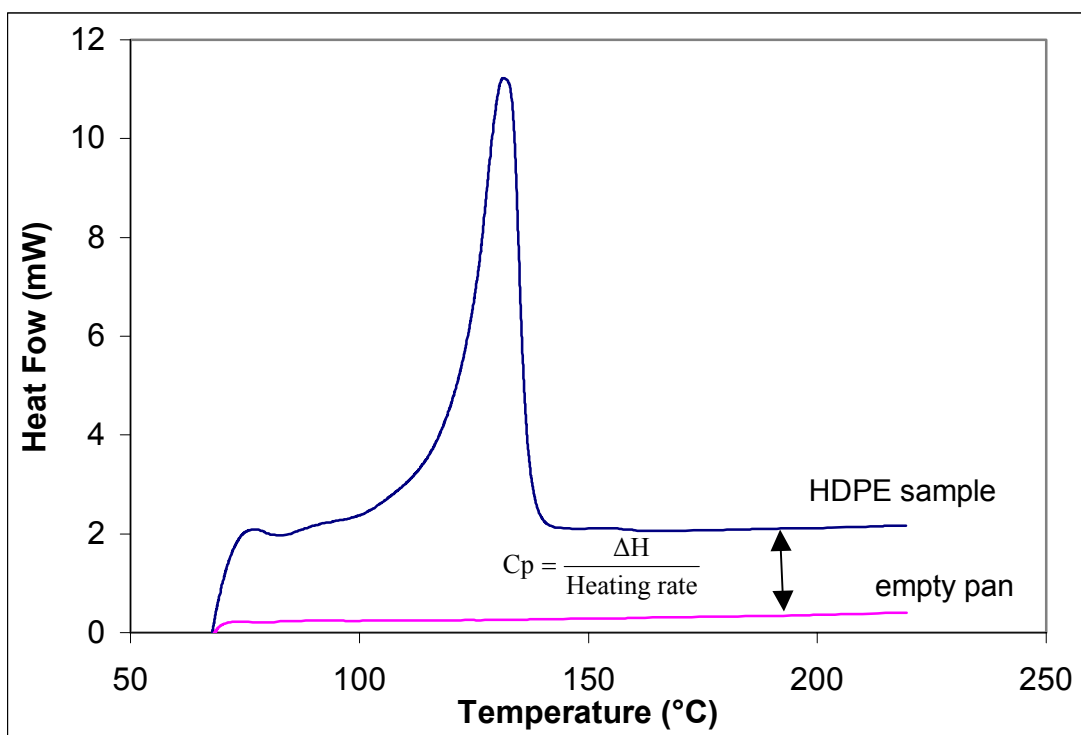


Fig. 14: DSC plot showing the calculation of C_p

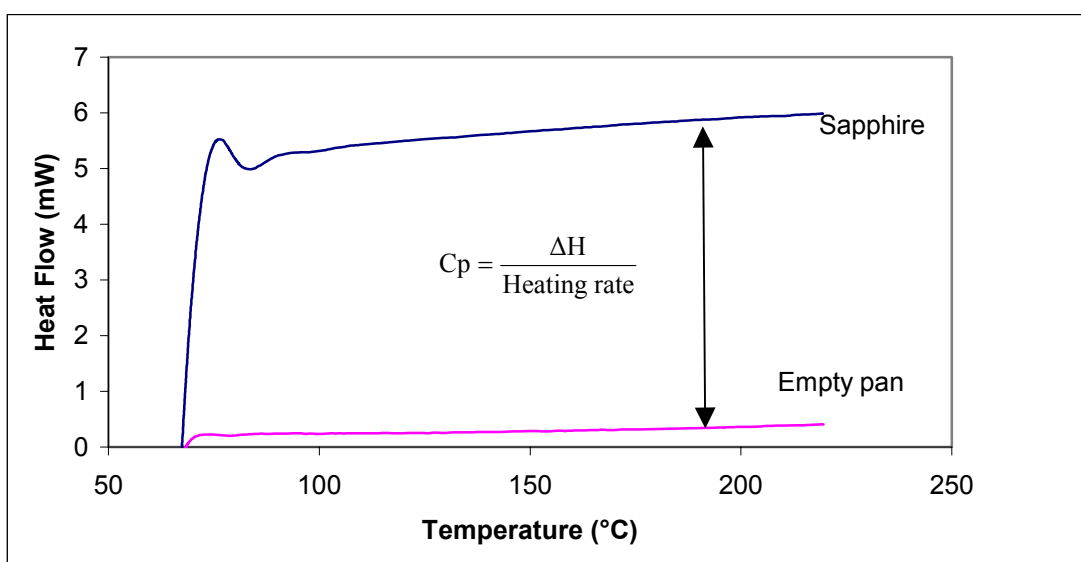


Fig. 15: DSC plot showing the calculation of the specific heat of sapphire

12. Appendix A

Approximate method to estimate the specific heat of a cylindrical sample using compression heating

Calculation of the average temperature rise of the sample

It is assumed:

1. Temperature distribution is axi-symmetric.
2. The sample surface temperature is the same as the wall temperature.

Assume the approximate temperature rise of the sample θ at a radius r under compression heating is given by the “trial function”

$$\theta = \theta_{r=0} \left[1 - \left(\frac{r}{r_0} \right)^2 \right], \quad (1)$$

where $\theta_{r=0}$ is the temperature rise “measured” by the centre thermocouple (i.e at $r = 0$) and the sample radius is defined as r_0 . The average temperature rise of the whole sample $\bar{\theta}$ may be calculated from (1)

$$\bar{\theta} = \frac{\theta_{r=0}}{\pi r_0^2} \int_0^{r_0} 2\pi r \left[1 - \left(\frac{r}{r_0} \right)^2 \right] dr. \quad (2)$$

Evaluating (2) gives

$$\bar{\theta} = \frac{\theta_{r=0}}{2}. \quad (3)$$

Calculation of the specific heat

The specific heat ρ of the sample may be estimated from the average temperature rise in the sample using

$$\rho = \frac{W}{m\bar{\theta}} = \frac{2W}{m\theta_{r=0}}, \quad (4)$$

where W is the work done on heating and m is the mass of the sample. Equation (4) ignores any heat loss (e.g. through the thermocouple), so for a more accurate estimation of the specific heat of the material a correction factor for the heat loss must be added.

Estimation of the fractional heat loss from the sample during heating

It is assumed:

1. The heat flows are linear functions of temperature or temperature gradient.
2. The temperature field is “similar” in heating and cooling.

From “Newton’s law of cooling” the heat balance over the heating and cooling period is

$$W = N \int_0^T \theta_{r=0}(t) dt, \quad (5)$$

where T is the time taken for the sample to heat and then cool and N is the constant of proportionality for Newton’s law of cooling. Using assumption (2) above, if the sample is heated for a time t_1 then the fractional heat loss L may be estimated from

$$L = \frac{\int_0^{t_1} \theta_{r=0} dt}{\int_0^T \theta_{r=0} dt}, \quad (6)$$

which is independent of N . The value of L may be assessed from experimental graphs.

Expression for the corrected specific heat

Adjusting for the fractional heat loss on the sample the corrected specific heat ρ_c would now be

$$\rho_c = \frac{2W}{m\theta_{r=0}}(1-L). \quad (7)$$

From experimental plots the fractional heat loss may be estimated as $L = 1/3$. From (7) the best estimate of the specific heat of the sample is at $t = t_1$, which may be written as

$$\rho_c = \frac{4}{3} \frac{W}{m\theta_{r=0,t=t_1}}. \quad (8)$$

where $\theta_{r=0,t=t_1}$ is the measured centre line temperature at the end of the heating period.

13. Appendix B

A Model for Axisymmetric Heat Transfer within a Polymer Subjected to Work Heating.