

Latent Heat of Polymers Crystallised Under Pressure

Milestone 7 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

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ABSTRACT

Heat transfer of polymers is affected by latent heat. In industrial processing high pressures take place, therefore it is desired to characterise the effect of pressure on latent heat. Two measuring techniques are described. Three commercial polymers, PP, HDPE and PET have been tested. It has been found that the latent heat of crystallisation of the polyolefins investigated does not vary greatly with pressure over the range studied, 0.1 to 160 MPa. However, in the case of PET, the effect of pressure was more significant.

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1 INTRODUCTION

In order to create reliable models, polymer processing simulators need accurate data [1]. Data accuracy improves when measurements are taken under pressure conditions comparable to industrial processes, as values may differ from those measured at normal pressure. Significant pressure effects on thermal conductivity have already been reported [2].

It is known that pressure diminishes the rate of spherulitic growth and shifts the temperature range of crystallisation to higher values [3]. More evidence of the effect of pressure on crystallisation temperature can be found in [4].

Since latent heat is the amount of heat per unit mass of material given out during crystallisation, or the amount of heat per unit mass absorbed during melting, latent heat data are very significant in terms of accurate modelling of cooling times. For instance, it has been shown [7] that inclusion of latent heat in the simulation of the injection moulding of a HDPE cylinder changed the predicted cooling time by 13 % compared with ignoring latent heat. For the above reasons an investigation of the effect of pressure on latent heat is warranted.

Measurement of latent heat is relatively simple using Differential Scanning Calorimetry (DSC). The latent heat of crystallisation and melting are determined from the areas of the trough and peak on DSC plots recorded in cooling and heating respectively [6]. The difficulty arises when measurements have to be taken at high pressures. Elevated pressure DSC apparatus is limited to pressures of 70-150 bar [8], not quite representative of the pressures involved in most industrial processes [5], thus there is a need for another method capable of producing measurements at much higher pressures.

A technique to measure the effect of pressure on latent heat has been developed which makes use of PVT (Pressure, Volume, Temperature) equipment to crystallise the polymer under pressure and DSC equipment to measure the latent heat. Three commercial materials, PP, HDPE, and PET have been tested using this technique. In addition, latent heat of HDPE has been calculated at normal and elevated pressure using the elevated pressure DSC apparatus.

This report is part of the MPM1.5 project on heat transfer in polymer processing. It combines deliverables D1 and D3 of milestone 7.

2.2 COMBINED PVT/DSC METHOD

Samples of materials crystallised under pressure were obtained using PVT-100 equipment manufactured by SWO. This PVT apparatus normally measures the pressure (P), volume (V) and temperature (T) during cooling of polymer melts. Polymer pellet was melted in the cylindrical cell of diameter 7.73mm. The desired pressure, up to 1600 bar, was applied through a piston. Then the polymer was cooled at the selected rate, up to 100 °C/min. The result is a moulded cylinder cooled under pressure.

The apparatus is capable of recording the volume changes that occur through the cooling process. This allows the calculation of the temperature range of crystallisation as the onset of crystallisation is characterised by a sharp decrease in specific volume.

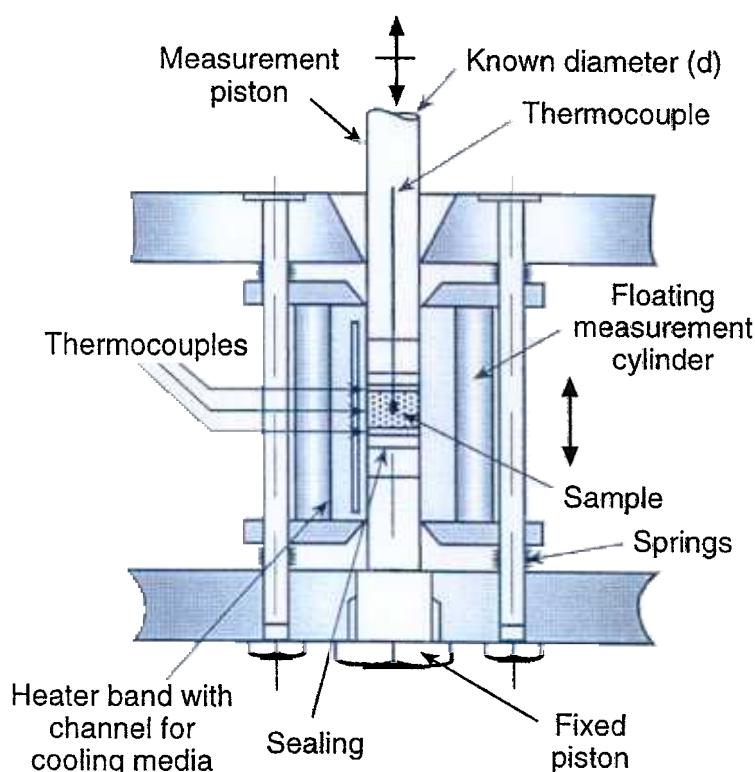


Figure 2. Diagram of PVT apparatus.

Cylinders of HDPE, PP and PET were manufactured under different pressures and cooling rates. Samples were cut off the edge of the cylinders and heated at 10 °C/min in normal pressure DSC. The latent heat of melting observed during heating reflects the latent heat of melting of the crystals formed during cooling under pressure.

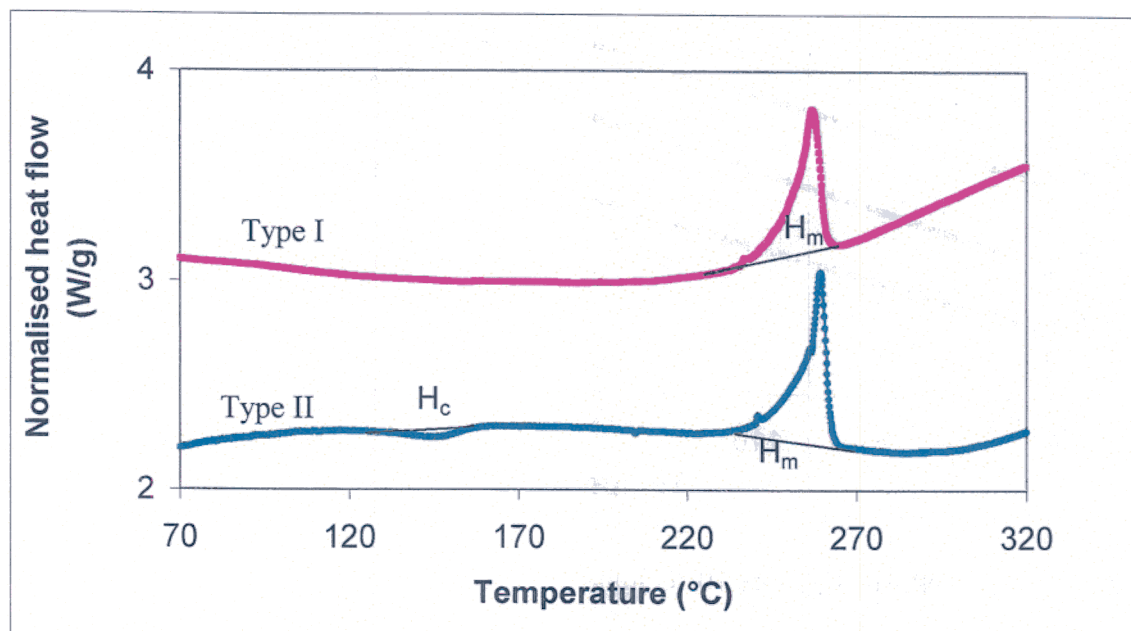
The possibility of energy being stored in the cylinders during compression and then released together with the latent heat during heating in the DSC was also investigated. In order to do so cylinders from an amorphous material, PS, were cooled under pressure. Then they were heated in the DSC. The DSC plot was examined in search of peaks around the T_g indicative of energy being released in the form of heat.

As a result of rapid cooling, a significant temperature gradient is expected from within the centre to the edge of the samples. In order to minimise this problem, samples for DSC tests were carefully cut off the edge of the cylinders.

DSC Results

Two types of DSC plot were obtained, type I with one peak and type II with one peak and one trough. The latent heat of further crystallisation (H_c) and the latent heat of melting (H_m) are calculated from the area of the trough and the peak respectively. Type I corresponds to a material that does not crystallise further in heating in the DSC but melts (peak). This means that the material had already reached maximum crystallisation during cooling in the PVT apparatus. Type II represents a material that in heating crystallises further (trough) prior to melting (peak). The subtraction $H_m - H_c$ is believed to be the best measure of the latent heat of crystallisation under pressure.

See appendix for details of measurement of the latent heat in the DSC.

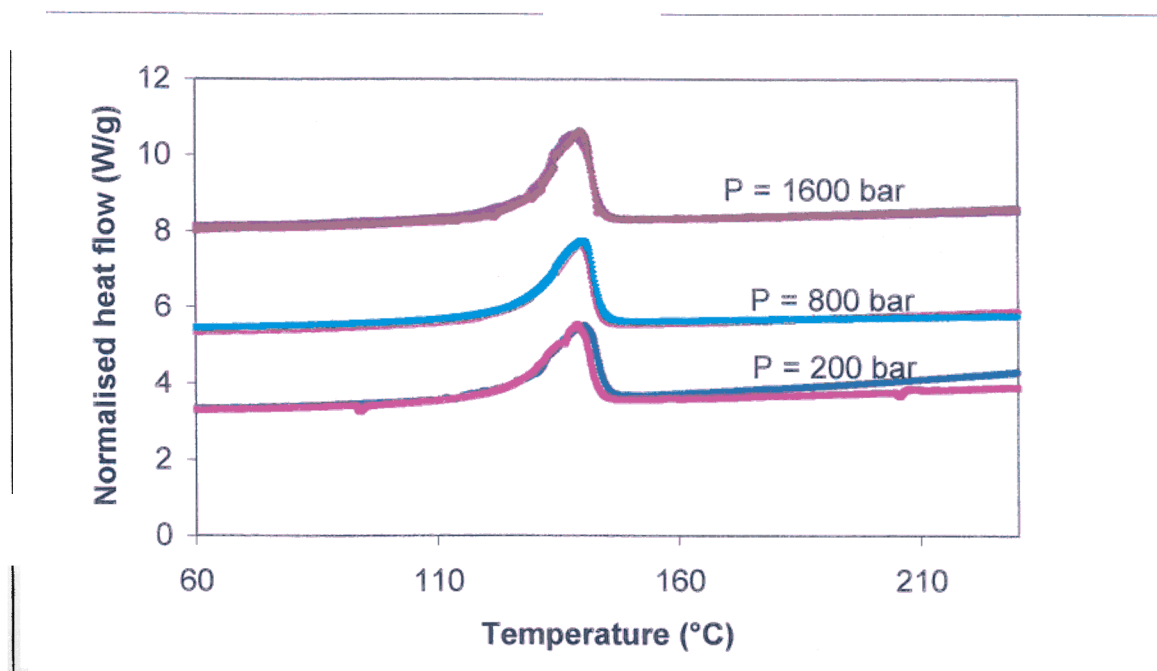


Graph 1. The two types of DCS curves obtained.

PP polypropylene

No further crystallization of PP occurred during heating in the DSC (Graph 2), which indicates that the materials had reached their maximum crystallinity before they were heated in the DSC.

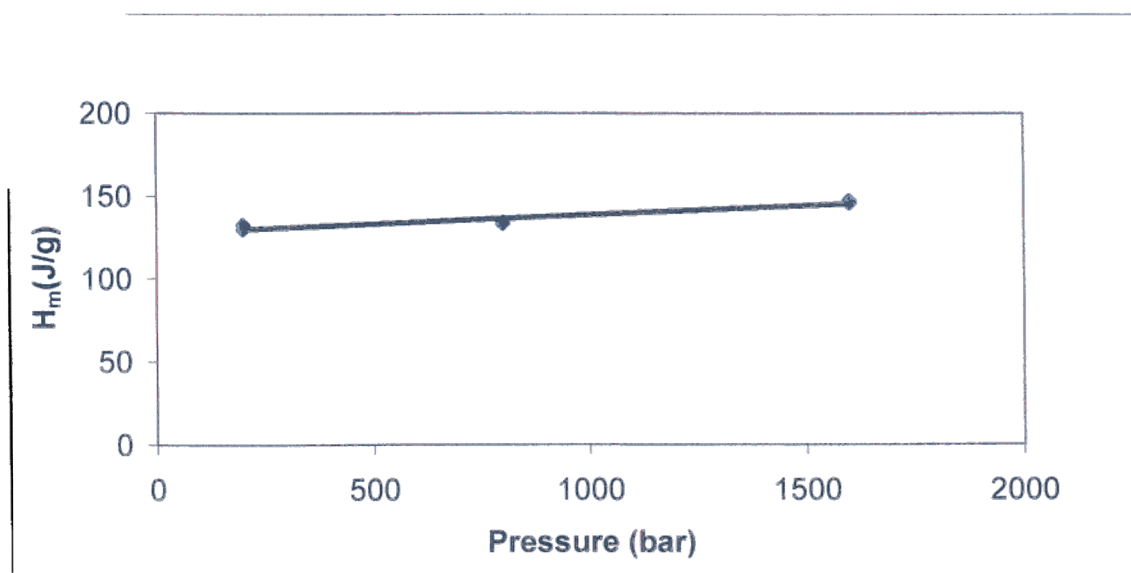
Values of the latent heat of melting (Table 5) did not vary with the pressure history of the material.



Graph 3. DSC Plots for HDPE. Heating rate 10 °C/min.

Table 6. Measured latent heat of melting for high density polyethylene.

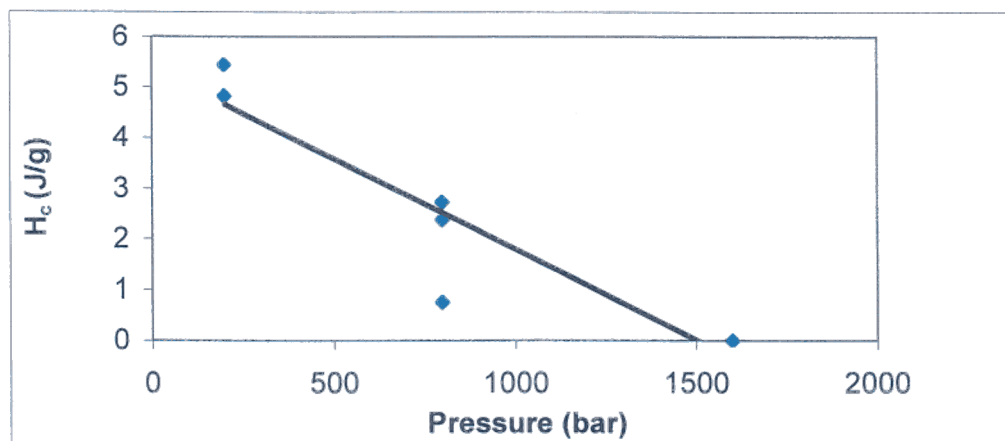
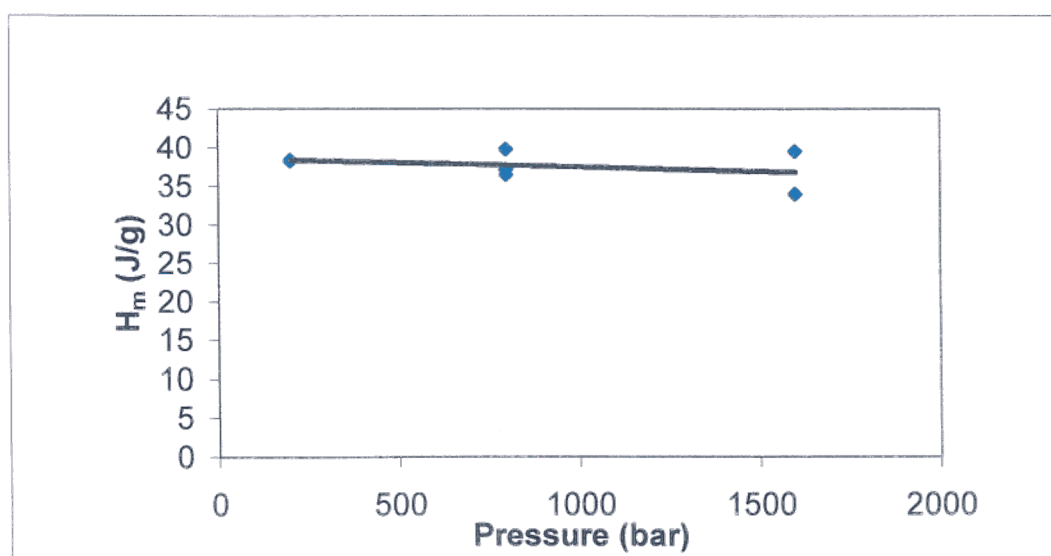
Sample ID	Pressure (bar)	Average H_m (J/g)
HGH801	200	131
HGH805	800	134
HGH806	1600	147

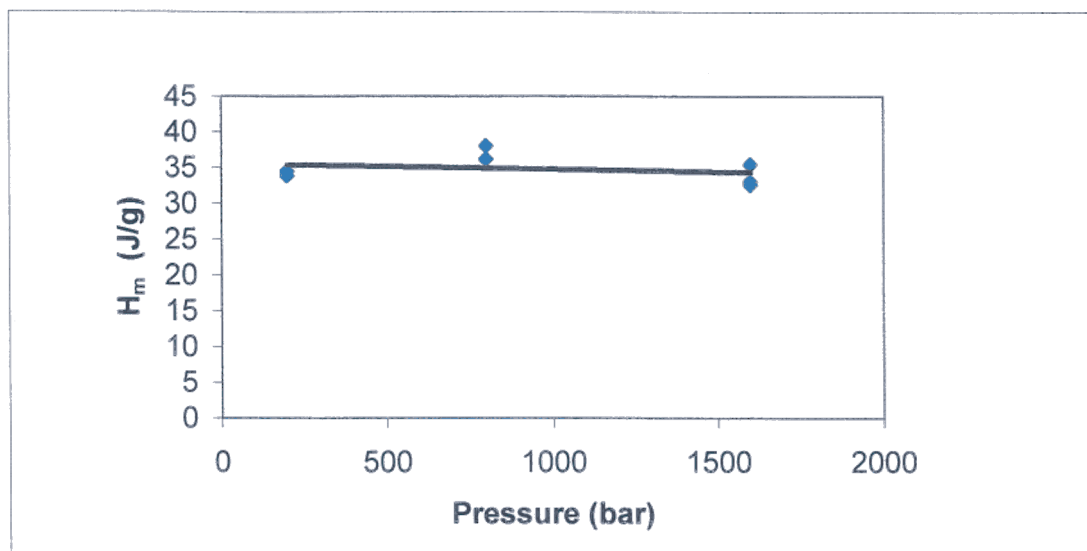


Graph 4. Effect of pressure on latent heat of melting for high density polyethylene.

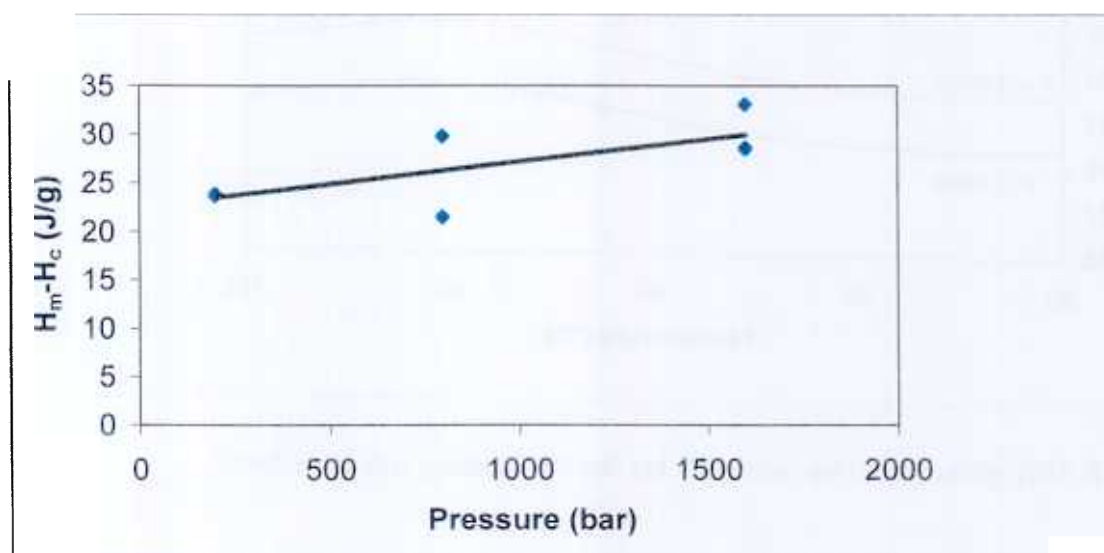
Table 9. Measured latent heat values for PET cooled at 50 °C/min.

Sample ID	Pressure (bar)	Average H_c (J/g)	Average H_m (J/g)	Average $H_m - H_c$ (J/g)
NEH105C	200	5	38	33
NEH109C	800	2	38	36
NEH110C	1600	0	37	37

**Graph 7.** Effect of pressure on latent heat of further crystallisation, H_c , for PET cooled at 50°C/min.**Graph 8.** Variation with pressure of the latent heat of melting in heating, H_m , for PET cooled at 50 °C/min.



Graph 11. Effect of pressure on the latent heat of melting in heating, H_m , for PET cooled at 100 °C/min.

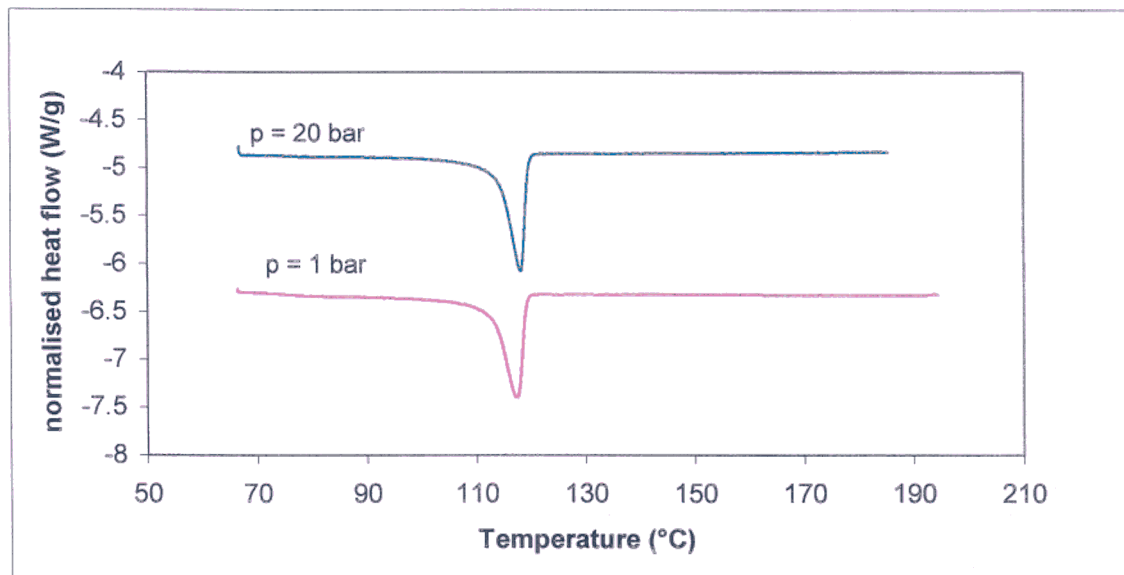


Graph 12. Variation of the latent heat of crystallisation under pressure, $H_m - H_c$, for PET cooled at 100 °C/min

Table 11. PET cooled at 50 °C/min and PET cooled at 100 °C/min. Comparison of $H_m - H_c$ values.

	PET 50 °C/min	PET 100 °C/min	
Pressure (bar)	Average $H_m - H_c$ (J/g)	Average $H_m - H_c$ (J/g)	% difference between both PETs cooled at 50 °C/min and 100 °C/min
200	33	24	27 %
800	36	26	27 %
1600	37	30	19 %

Graph 14 shows the DSC plots of two HDPE samples cooled under 20 bar pressure and at normal pressure.



Graph 14. DSC plots in cooling at normal and elevated pressure for HDPE. Cooling rate 2 °C/min.

4. DISCUSSION

DSC/PVT Method

DSC plots revealed that the latent heat of melting of PP at this cooling rate did not vary with pressure. In the case of HDPE the latent heat increased slightly with pressure. This increase seems to be real although it could be due to sample variability (cuts from different depth and position of the cylinders) or baseline fitting (see appendix). These results were expected because materials like PP and HDPE crystallise readily even at high cooling rates, thus it is not surprising that pressure does not alter the degree of crystallinity.

In contrast, PET shows further crystallisation (H_c) when heating in the DSC. H_c values decreased significantly with pressure, reaching zero at 1600 bar (see graph 7). The latent heat of crystallisation in cooling, represented by $H_m - H_c$, increased by 10 % and by 21 % with pressure for PET cooled at 50 °C/min and 100 °C/min respectively. The effect of pressure on latent heat of crystallisation seems to be greater the higher the cooling rate, where the degree of crystallinity of the sample cylinder made in the PVT machine is lower.

Tables 11 and 12 show the effect that cooling rate has on both latent heat of further crystallisation in heating (H_c) and the latent heat of crystallisation on rapid cooling under pressure ($H_m - H_c$). This suggests that cooling rate is a much more significant parameter than pressure in influencing the latent heat.

The DSC plots of PS in heating did not indicate any energy locked in during cooling under pressure in the PVT apparatus.

- The DSC plot in heating of PS did not reveal evidence of any energy being released as a result of stresses locked in during cooling under pressure.

7 APPENDIX: REPEATABILITY OF DSC VALUES

The software used by the DSC instrument calculates the latent heat by measuring the area enclosed by the melting endotherm (or freezing exotherm) and a straight line constructed by connecting two points chosen manually (Figure 1).

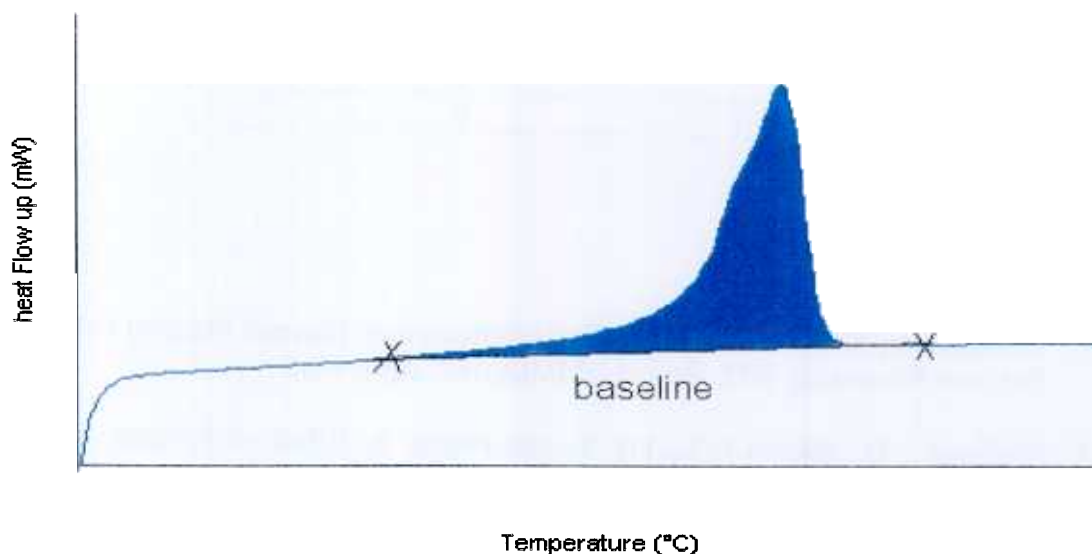
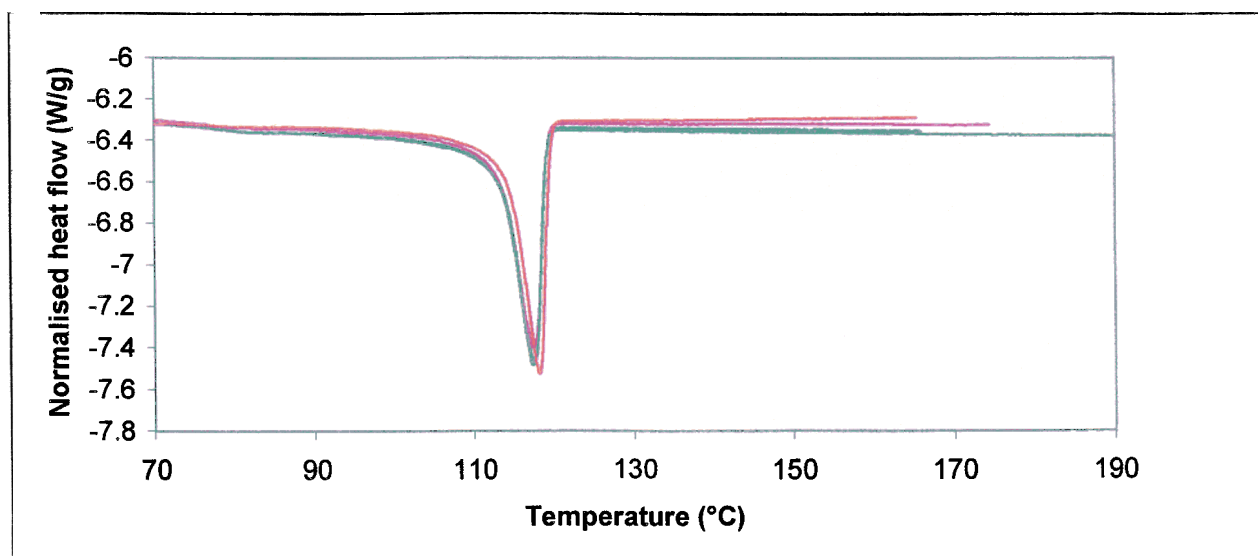


Figure 1. Area from which the latent heat is calculated.

The choice of points used to draw the straight baseline introduces errors in the calculation of the latent heat. In order to quantify this error four HDPE samples were tested in the DSC in cooling at a rate of 2 °C/min (graph 1). For each sample three different baselines were chosen to calculate the latent heat of crystallisation. The measured variability was $\pm 6\%$ (Table 1).



Graph 1. DSC cooling runs for HDPE at 2 °C/min**Table1. Effect of baseline fitting on latent heat for four samples of HDPE**

	Latent heat of crystallisation (J/g)		
	Baseline 1	Baseline 2	Baseline 3
Test 1	160	170	151
Test 2	163	173	152
Test 3	164	169	150
Test 4	161	168	149
AVERAGE	161		
STDEV	9		
% VARIABILITY	6		

8 REFERENCES

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The experimental results do not show a significant enough a trend to warrant a detailed mathematical model of the effect of pressure on latent heat, though graphs 7 and 10 indicate a relationship, in PET, between the latent heat of further crystallisation on heating (H_c) and the pressure applied during cooling.

DSC testing presented several difficulties like the problem of sample contamination. This occurred because the DSC samples were cut from the edge of the cylinders, where contamination during manufacture and handling is more likely. Also these samples were cut by hand using a scalpel and although great care was taken, it is not possible to ensure that they all originated from exactly the same position and depth of the cylinder and thus have the same cooling history. (The edge will cool at a higher rate than the centre). Another complication is the impossibility of previously melting the DSC samples to ensure good contact with the base of the DSC.

Elevated Pressure DSC Method

This method is simpler and more accurate as measurements of latent heat are made directly on the sample under pressure. However, measurements are limited to a maximum pressure of 70 bar, and thus there is a need for the combined PVT/DSC method to give an indication of latent heat values at much higher pressures that are experienced in industrial polymer processing.

5 GUIDELINES ON EXTRAPOLATION TO INDUSTRIAL PROCESSING

The effect of pressure on latent heat does not appear to be large in the conditions relevant to industrial processing. In the case where pressure has the greatest effect (in PET) it is in the polymer's tendency to crystallise on reheating. This effect may have some industrial significance. During bottle manufacture PET pre-forms are injection moulded under pressure and then reheated to blow the bottles. It appears from this work that the application of high pressure (e.g. 1600 bar) during cooling can suppress crystallisation on reheating, which is desirable as this crystallisation causes problems during blow moulding. It may thus be possible to slightly reduce the time the pre-form is in the mould if high pressure can be applied during cooling.

6 CONCLUSIONS

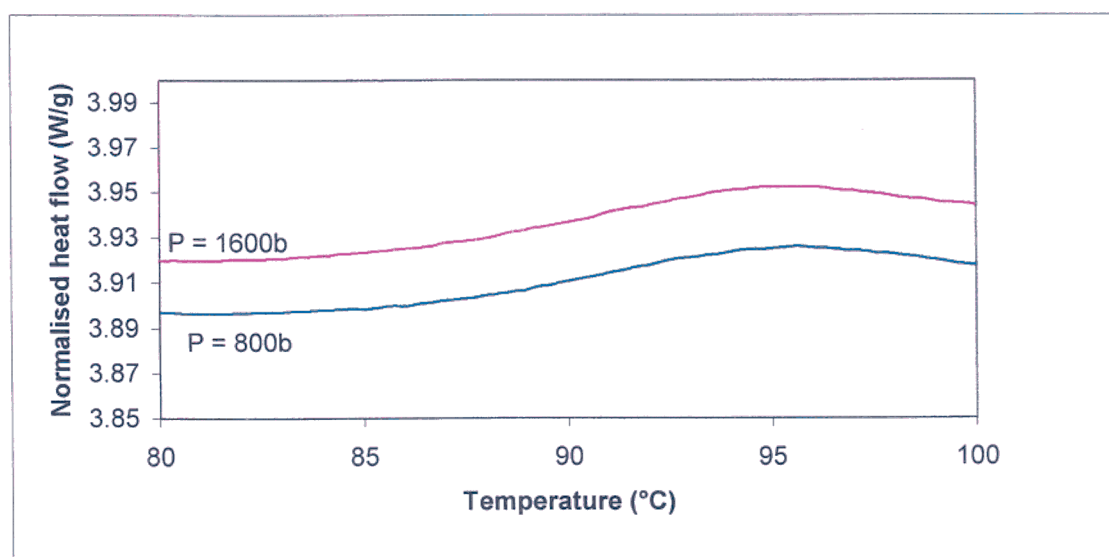
- Two methods of measuring the effect of pressure on latent heat have been investigated.
- For PP and HDPE the effect of pressure was not large.
- For PET the pressure during cooling reduces the polymer's tendency to crystallise further on reheating. This observation may have some significance for blow moulding of bottles.
- For PET the latent heat of further crystallisation was found to be a function of the pressure during the initial crystallisation in the PVT apparatus.
- The effect of pressure appears to be most significant at high cooling rates where the degree of crystallinity is low.

Table 12. PET cooled at 50 °C/min and PET cooled at 100 °C/min. Comparison of H_c values.

Pressure (bar)	PET 50 °C/min	PET 100 °C/min	difference between both PETs cooled at 50 °C/min and 100 °C/min
	Average H_c (J/g)	Average H_c (J/g)	
200	5	10	50 %
800	2	11	82 %
1600	0	4	PET 50 °C/min did not crystallise further in heating

PS polystyrene

Graph 13 shows no evidence of heat being released around the T_g .

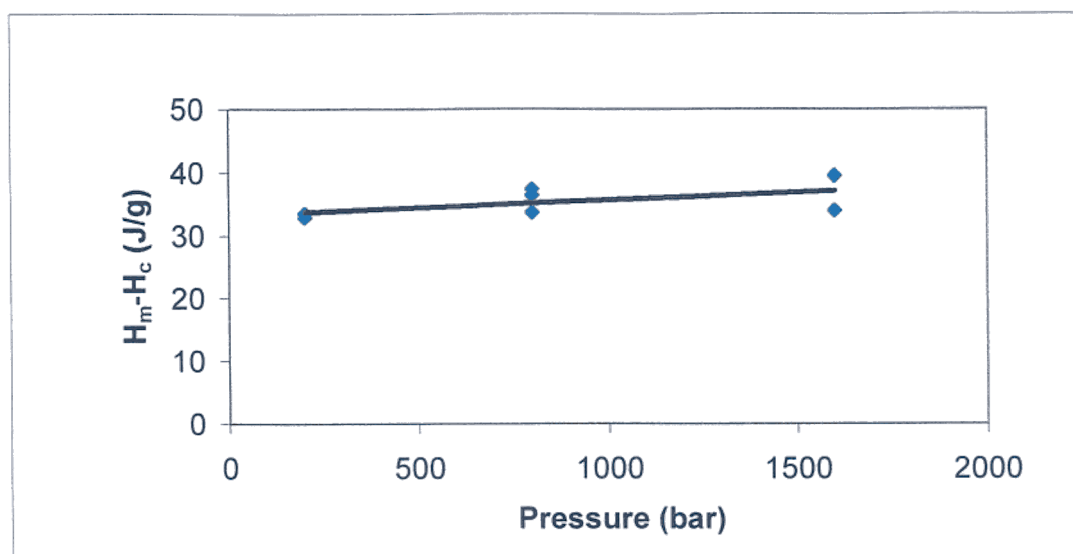
**Graph 13.** DSC plots at 800 bar and 1600 bar for PS. Heating rate 10 °C/min.

3.2 ELEVATED PRESSURE DSC RESULTS

Calculations of latent heat of melting were made using the same procedure as in the normal pressure DSC. The latent heat values obtained at normal and high pressure were found to be similar (Table 13).

Table 13. Latent heat values at normal and elevated pressure for HDPE

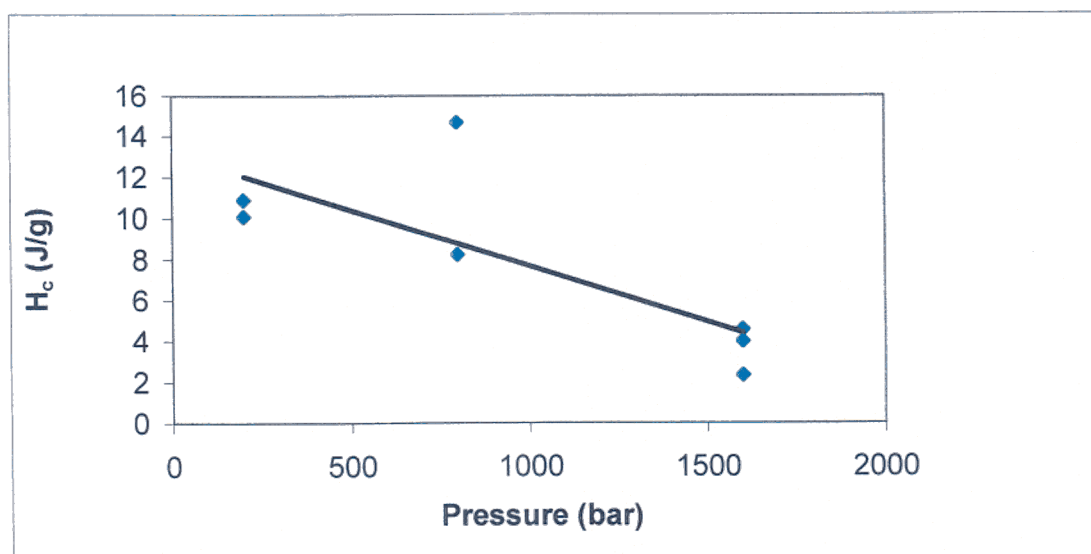
HDPE cooled from 200 °C down to 60 °C in elevated pressure DSC		
Sample ID	Pressure (bar)	Average H_m (J/g)
010913kb.002	1	160
010917kd.004	20	159



Graph 9. Variation of the latent heat of crystallisation under pressure, $H_m - H_c$, for PET cooled at 50 °C/min

Table 10. DSC values of latent heats for PET cooled at 100 °C/min.

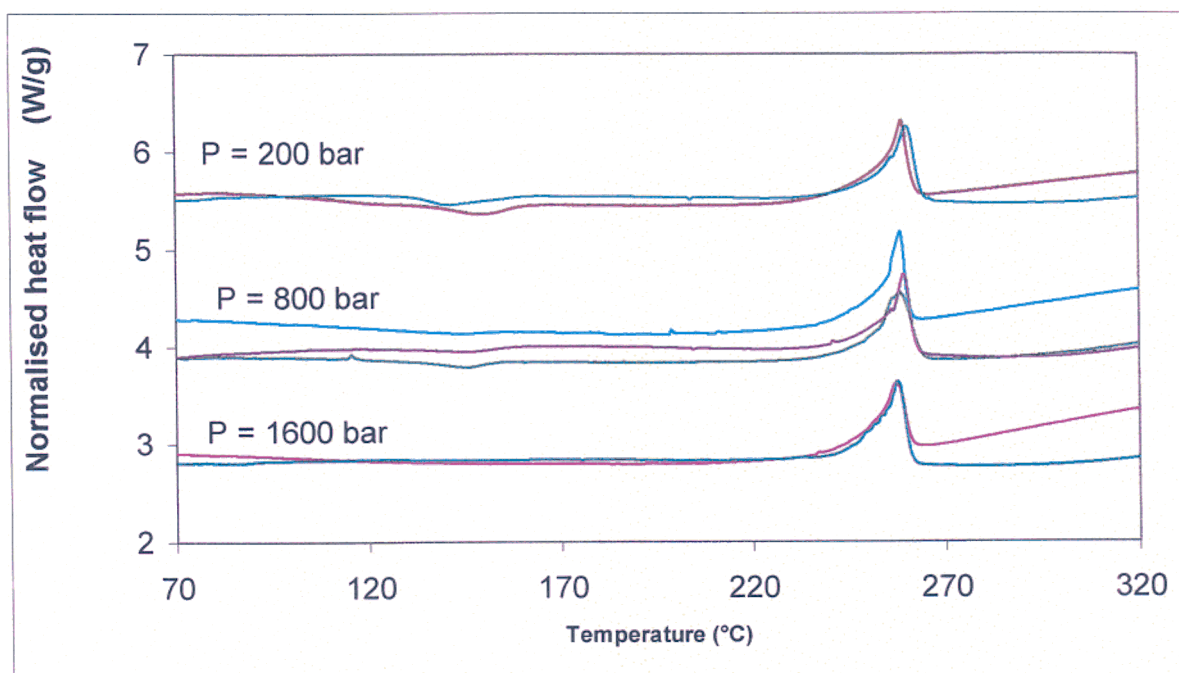
Sample ID	Pressure (bar)	Average H_c (J/g)	Average H_m (J/g)	Average $H_m - H_c$ (J/g)
NEH103C	200	10	34	24
NEH106C	800	11	37	26
NEH107C	1600	4	34	30



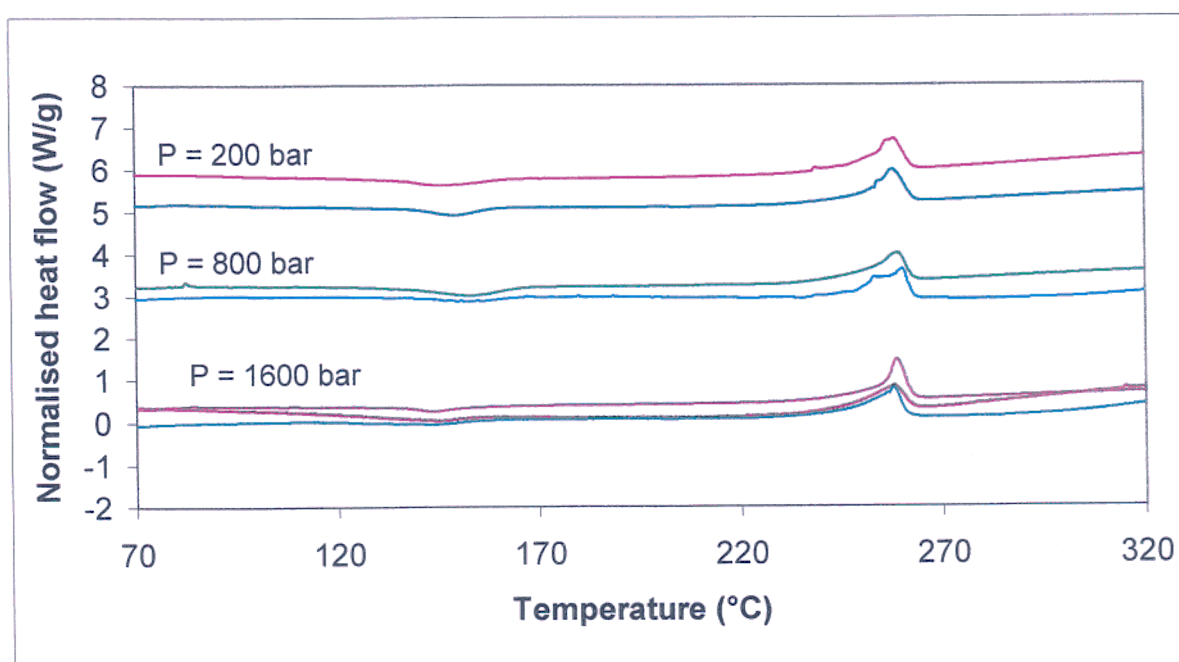
Graph 10. Effect of pressure on latent heat of further crystallisation, H_c , for PET cooled at 100 °C/min.

PET poly(ethyleneterephthalate)

Further crystallisation occurred on heating in the DSC in all cases except in the case where PET crystallised under 1600 bar at 50 °C/min (graphs 5 & 6). The latent heat of further crystallisation, H_c , decreased with pressure whereas the latent heat of melting, H_m , did not vary significantly. $H_m - H_c$ increased with pressure by 10 % and by 21 % for PET cooled at 50 °C/min and 100 °C/min respectively (graphs 7 -12, tables 9 & 10).



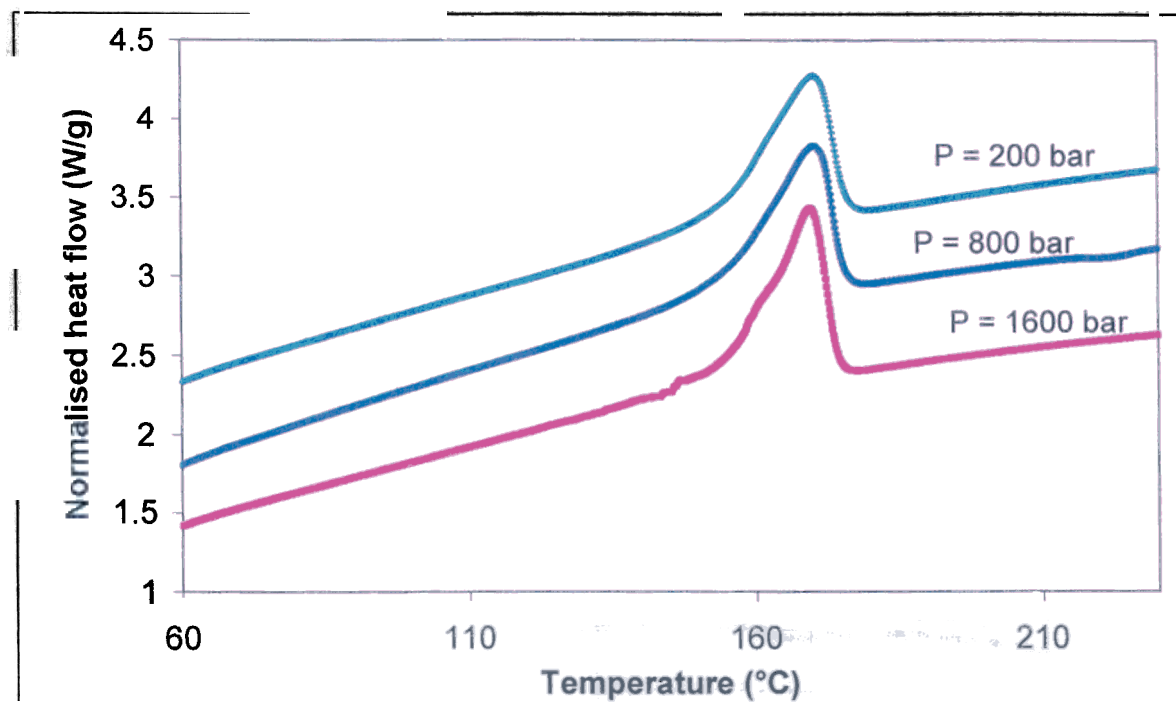
Graph 5. DSC runs for PET cooled at 50 °C/min. Heating rate 10 °C/min.



Graph 6. DSC runs for PET cooled at 100 °C/min. Heating rate 10 °C/min.

Table 5. Measured latent heat of melting for polypropylene.

Sample ID	Pressure (bar)	Average H_m (J/g)
HAQ006-200	200	79
HAQ006-800	800	78
HAQ006-1600	1600	78

**Graph 2.** DSC plots PP. Heating rate 10 °C/min.HDPE high density polyethylene

HDPE presented similar behaviour to PP in terms of no further crystallisation (graph 3), however, the latent heats of melting appeared to increase slightly, by about 10 %, from the minimum to the maximum pressure (graph 4, table 6).

3 RESULTS

3. COMBINED PVT/DSC RESULTS

Tables 1-4 summarise the different cylinder samples obtained from the PVT apparatus.

Table 1. PET cylinders

PET cooled from 240 °C down to -99.9 °C			
No. of repeat tests	Sample ID	Pressure (bar)	Cooling rate (°C/min)
2	NEH105C	200	50
3	NEH109C	800	50
2	NEH110C	1600	50
2	NEH103C	200	100
2	NEH106C	800	100
3	NEH107C	1600	100

Table 2. HDPE cylinders

HDPE cooled from 240 °C down to -99.9 °C			
No. of repeat tests	Sample ID	Pressure (bar)	Cooling rate (°C/min)
2	HGH801	200	100
2	HGH805	800	100
2	HGH806	1600	100

Table 3. PP cylinders

PP cooled from 220 °C down to -99.9 °C		
Sample ID	Pressure (bar)	Cooling rate (°C/min)
HAQ006-200	200	40
HAQ006-800	800	40
HAQ006-1600	1600	40

Table 4. PS cylinders

PS cooled from 240 °C down to -99.9 °C		
Sample ID	Pressure (bar)	Cooling rate (°C/min)
HAU005	800	100
HAU006	1600	100

2 MEASUREMENT METHODS

2.1 ELEVATED PRESSURE DSC METHOD

Tests were carried out using a TA Instruments TA2920 DSC cell enclosed within a steel cylindrical housing capable of operating at pressures up to 70 bar. The cell construction is similar to the standard DSC.

Samples of HDPE were melted in the DSC apparatus and then cooled under 20 bar pressure and at normal pressure at a rate of 2 °C/min.

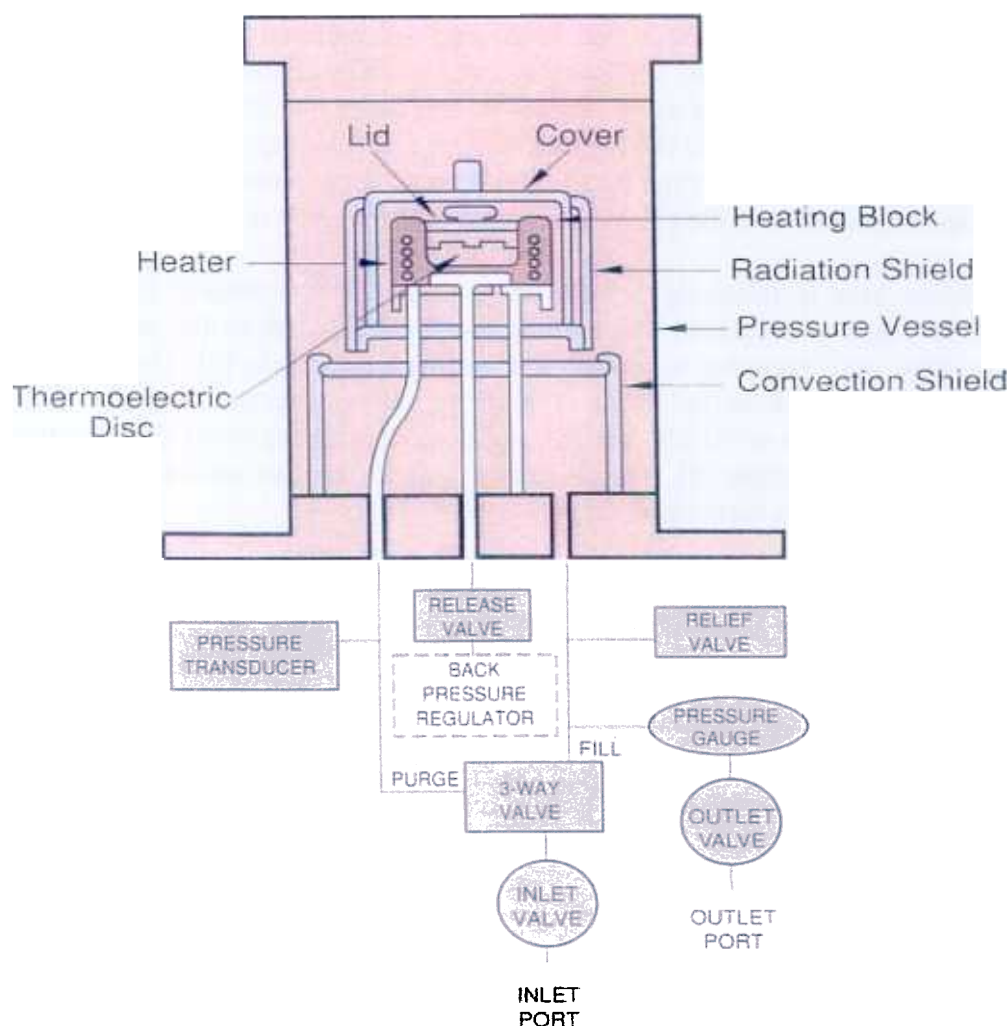


Figure 1. Schematic of apparatus. Courtesy of TA Instruments.



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ISSN 1473-2734

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