

## **THERMAL STABILITY AT ELEVATED PRESSURE – AN INVESTIGATION USING DIFFERENTIAL SCANNING CALORIMETRY**

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During laboratory scale development of a new chemical process which is to be operated at elevated pressure a material was found to undergo an unexpected thermal decomposition.

Initial DSC testing had indicated that melting appeared to be a pre-requisite for decomposition and based upon this and the fact that melting points are elevated at increased pressures the material had been expected to be thermally stable under the proposed operating conditions.

The unexpected thermal decomposition resulted in a more extensive investigation into the thermal stability of the material being performed. Work was carried out primarily at ambient pressure in order to obtain an understanding of the mode of decomposition. The work was then extended to pressures of up to 30 bar and although this gave us a further insight into the decomposition it failed to simulate the process conditions which could reach 600 bar. A collaboration with The University of Aberdeen has enabled DSC measurements to be carried out at 500 bar confirming predictions about the melting point behaviour but also giving an unexpected view of the thermal decomposition. A second collaboration with The University of Huddersfield provided a further insight into the thermal decomposition of the material.

### **INTRODUCTION**

The vast majority of solid materials handled within the Agrochemical industry have a generally predictable pattern for thermal decomposition. Typically they are stable up to the melting point and only start to decompose at elevated temperatures. The decomposition may or may not be accompanied by gas evolution. This has led to the erroneous belief from some quarters that if a melting point exists then the material will be thermally stable at all temperatures below this.

If the material is thermally stable up to the melting point then handling under normal conditions is relatively straight forward as, provided you ensure that the maximum heating medium temperature is limited to a temperature below the melting point, the risk of thermal decomposition is minimised. However, as chemicals become more complex we are starting to find that materials do not fit the general pattern and the erroneous view is being challenged.

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This paper highlights an investigation in to one such material in an unusual application.

## EXPERIMENTAL

Initial investigations in to the thermal stability of the material were carried out using a Mettler DSC821 ambient pressure DSC at 5 K/min over the temperature range 25–450°C with a gold plated high pressure crucible. Several runs were carried out on the material and all showed that reproducible results can be obtained. A typical thermogram is shown in Figure 1. These test results showed an endotherm in the range 123–152°C with an indicated melting point of ca 139°C, followed by a series of exothermic events which could be separated into an initial decomposition with a heat output of ca 610 J/g, followed by a second sharper exotherm with a heat output of around 750 J/g and a third broader event having a heat output of ca 1040 J/g. The total heat output was ca 2400 J/g.

When using an aluminium crucible at 10 K/min the melting point was ca 138.4°C and the initial exotherm was around 640 J/g, after this point although thermal data was obtained the thermogram shows a clear indication that the containment in the crucible has been lost Figure 2.

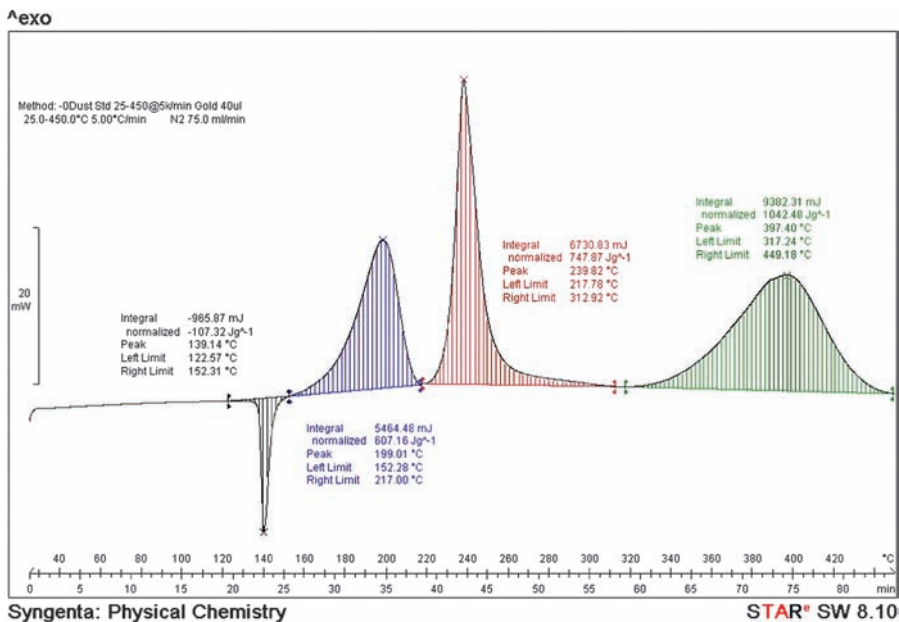
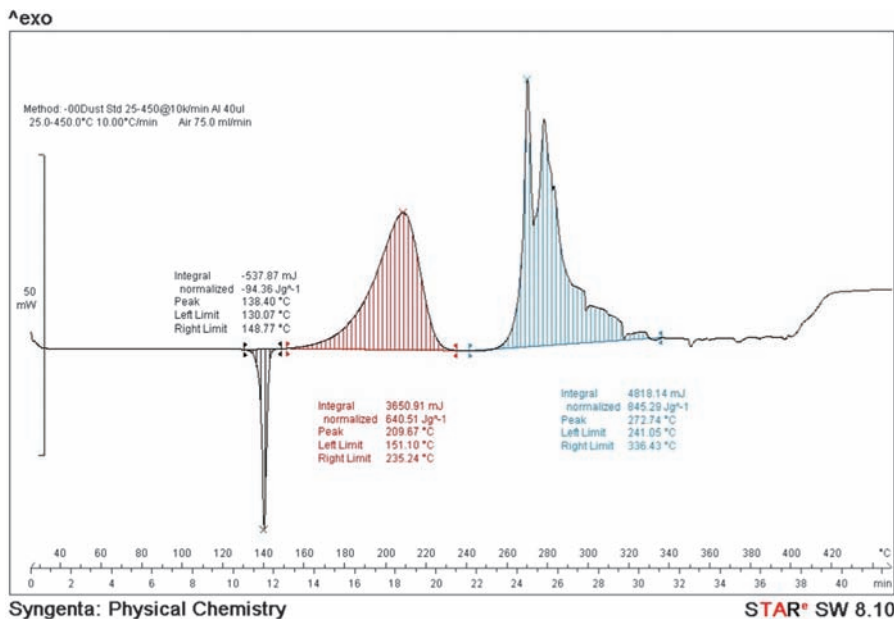


Figure 1. DSC scan from 25°C to 450°C at 5 K/min in a HP gold plated crucible



**Figure 2.** DSC scan from 25°C to 450°C at 10 K/min in an aluminium crucible ex Syngenta

Subsequent investigations were then carried out using a Mettler 27HP DSC Figure 3 and an open gold plated stainless steel crucible at 3-bar nitrogen pressure. This showed a melting endotherm around 140°C followed by two thermal events the first having a heat output of ca 290 J/g and the second around 270 J/g. When using an aluminium crucible similar results were obtained.

Further work was carried out at Aberdeen University using a Perkin Elmer Pyris Diamond DSC at ambient pressure from 20–400°C (Figure 4) then at 500 Bar over the range 20–200°C (Figure 5).

At ambient pressure a melting peak occurred at ca 139.3°C, two separate exothermic peaks were then apparent with respective heat outputs of ca 620 J/g and ca 180 J/g, with evidence that integrity of the crucible is lost sometime after the first exotherm.

Under 500 bar pressure two separate runs showed melting points in the range 152–153°C but no evidence of thermal activity up to 200°C (Figure 5).

TG/DTG work carried out at Huddersfield University showed that on heating at a rate of 10 K/min three separate thermal events were apparent. The first from 145°C to 226°C resulting in 17.3% mass loss, the second from 226°C to 309°C with 60% mass loss and the final event from 309°C to 445°C resulting in 7.3% mass loss. In parallel to this thermal microscopy showed that the first event resulted in significant gas evolution which appeared to stop on exceeding ca 220°C.

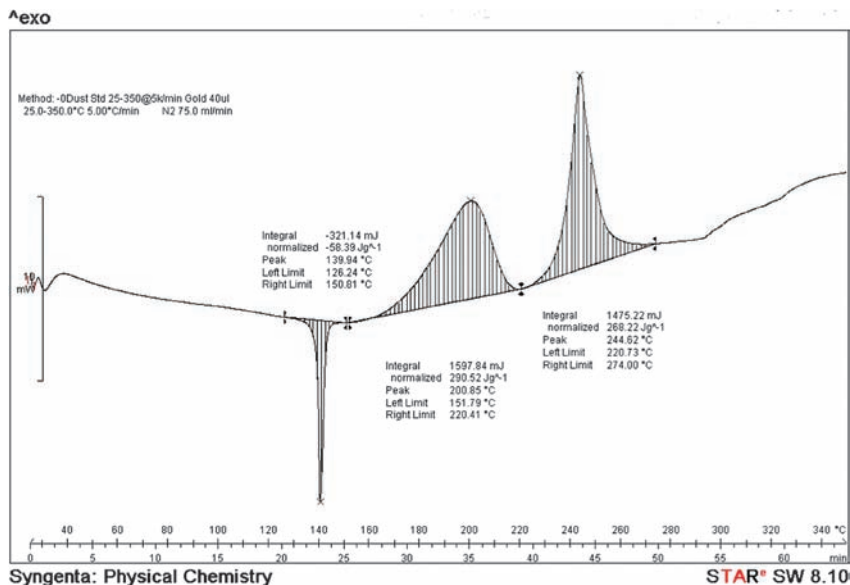


Figure 3. DSC scan from 25°C to 450°C at 5 K/min in an open HP gold plated crucible under 30 bar pressure

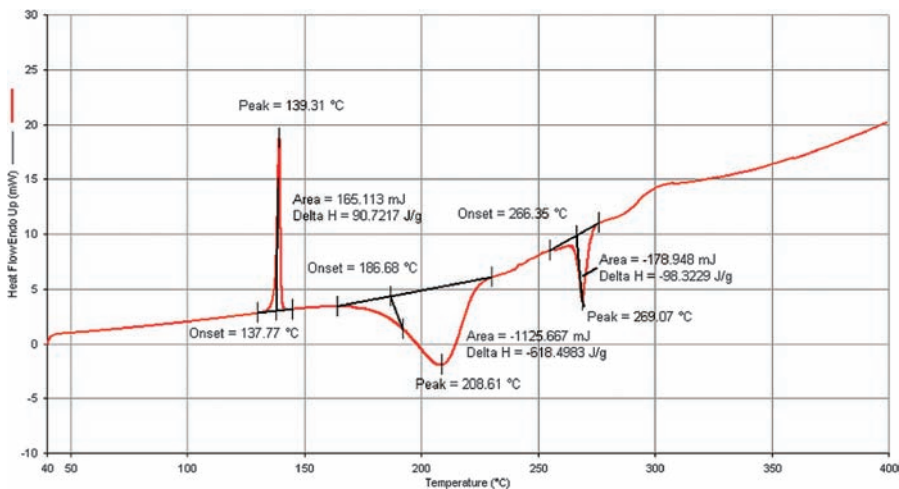
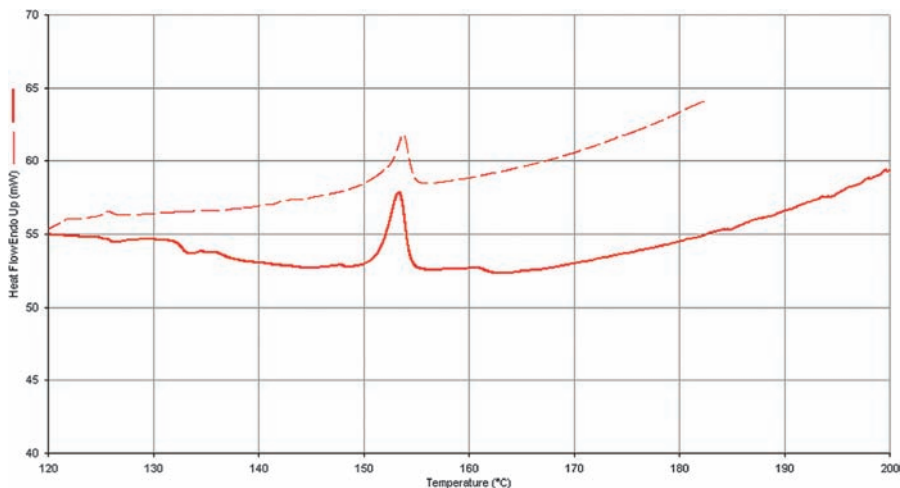


Figure 4. DSC scan from 40°C to 400°C at 10 K/min in a double Al DSC pan ex Aberdeen



**Figure 5.** DSC scans from 120°C to 200°C at 10 K/min in an aluminium crucible

## DISCUSSION

Development work highlighted the potential for a new application involving formulating the material in to a plastic which is extruded at elevated temperature and pressure. This was a new area for both the manufacturing procedure for this material and also in terms of the work required to define safe operating parameters for the formulation.

During the development of the AI only a limited amount of work was carried out to investigate the thermal stability of the material using DSC and as no exothermic effects were observed below the melting point it was concluded that it would be thermally stable up to this temperature (ca 139°C). Therefore if the 'rule' that the material will be stable up to the melting point is assumed no issues would be expected in operating up to say 120°C. However, if the material were to melt and decomposition occurred then the overall temperature rise under adiabatic conditions would be >1400 K. Experimental work using other techniques has shown that the decomposition would be accompanied by the evolution of copious quantities of gas and this would clearly be a problem on a plant scale, leading to the possibility of a catastrophic vessel failure.

The initial test work did not provide an accurate simulation of the process situation therefore further testing was carried out using a Mettler 27HP DSC which allowed a back pressure of nitrogen to be applied to the sample.

At first glance the overall profiles of the thermograms obtained with and without applied pressure are similar (Figures 1 & 3). However on closer inspection it is apparent that under pressure the melting point has increased by ca 0.8 K and the first exotherm has reduced from ca 610 J/g to around 290 J/g. Whilst the minor change in the endothermic

peak could be due to sampling the significant difference in the first exothermic peak could not be explained in such a way. Re-calibration of the 27HP DSC followed by repeat runs confirmed that the effects were genuine.

There was also no appreciable difference between results obtained in aluminium or gold plated crucibles. This indicates that catalytic effects due to the material of construction of the crucibles were not an issue.

The applied back pressure was only ca 5% of the pressure that would be exerted in the extrusion process and given the difference between the two thermograms extrapolation to the process conditions was not thought to be advisable.

Further work was then carried out in collaboration with University of Aberdeen who have developed a method based upon a Perkin Elmer Pyris Diamond DSC which can be operated at pressures of up to 5000 Bar over the range 20–300°C. It should be noted that the data obtained from a Perkin Elmer DSC is typically displayed with exothermic effects shown as negative inflexions, ie, the inverse of the Mettler data representation.

The equipment developed at Aberdeen is described in detail in the reference paper<sup>1</sup> and a brief description is provided here for clarity.

The HP-DSC operates on the power compensation principle, using a Perkin Elmer Pyris Diamond DSC. This is equipped with an autoclave which can be pressurised by means of a hand operated spindle pump. The pump is filled with a silicone oil which acts as the pressurising medium. The HP-DSC head consists of two self-contained silver furnaces in ceramic housings which closely fit inside the autoclave.

A branched chain silicone oil is used as the pressurising medium, this particular oil having a usable temperature range of 20 to 300°C (cf. operating range of the DSC instruments used up to 50 bar of 25–450°C) over the pressure range 50–500 MPa (500–5000 bar).

In order to provide a comparison with the previous work a thermogram was produced under ambient pressure conditions using a Perkin Elmer DSC (Figure 4).

Consideration of these two thermograms show good agreement with the enthalpy of fusion being 90.7 J/g and 94.4 J/g respectively and the actual melting point peak differing by <1K. The initial exotherms are also in very close agreement, at 618 J/g and 640 J/g. Subsequent exothermic behaviour does however differ, with both thermograms showing evidence of loss of containment. This deviation is related to crucible type and mode of operation and was not felt to be significant in this application. It was therefore concluded that there was a very good comparison between data generated on different instruments in different locations. After some discussion it was agreed that work at a pressure more representative of the pressure that would be encountered in the extrusion process would be carried out.

Our particular area of interest is 30–60 MPa (300 to 600 Bar), this is at the lower end of the operating range for the high pressure differential scanning calorimeter. It was agreed that in order to validate the technique investigations would be carried out at a pressure of 50 MPa.

Two separate experiments carried out at Aberdeen are shown in Figure 5, both show endothermic activity with a melting point around 152–153°C, but neither shows any appreciable exothermic activity.

During safety reviews concern was expressed as to the affect that applying very high pressures to a material could have on its thermal stability. During the initial investigations it was not known if melting was a pre-requisite for decomposition to occur. If melting is a pre-requisite then elevation of melting point would not be a problem as the sample could tolerate higher temperatures before decomposition would occur. If melting is not a pre-requisite for decomposition then this is potentially more hazardous as decomposition could be apparent below the melting point of the material, ie, decomposition would occur during the formulation process.

It is well known that applying pressure to a material can increase its melting point. The phenomenon of melting point elevation under pressure was first reported in 1826 by Perkins<sup>2</sup>, yet it was not until 1849 that a theoretical and experimental investigation was carried out<sup>3,4</sup>, Clausius then put the work on a sound theoretical basis in 1850<sup>5</sup>. Numerous other investigators examined the phenomenon however the most successful work is by Simon and Glatzel<sup>6</sup> who derived what is now known as the Simon equation.

The degree of melting point elevation depends upon the structure of the material but typically this amounts to a 1–3 K rise for every 100 Bar increase in pressure. A more accurate determination can be obtained using the basic version of the Simon equation as follows:

$$\frac{P - P_{tp}}{a} = \left( \frac{T_m}{T_{m,1atm}} \right)^b - 1 \quad (1)$$

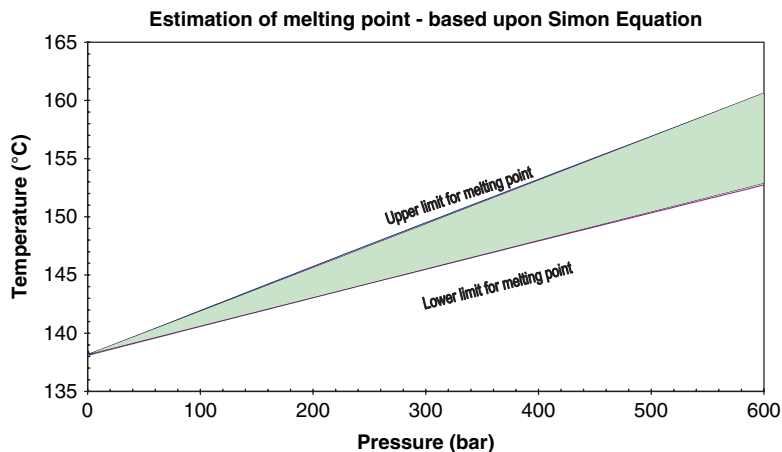
Where  $P$  = pressure  
 $P_{tp}$  = triple point pressure  
 $T_m$  = equilibrium melting point at  $P$   
 $T_{m,1atm}$  = melting point at 1 atm  
 $a$  &  $b$  = constants related to structure

$P_{tp}$  can normally be neglected as it is much smaller than  $P$ .

Although specific values for  $a$  &  $b$  for the material being studied were not available, values were available for compounds with some structural similarities<sup>7,8</sup>. Taking these values allowed a range of melting points to be calculated which are shown in Figure 6 and Table 1, the shaded area in the graph representing the expected melting point limits at any given pressure from 0–600 bar.

The calculations indicate that at 500 bar the melting point would be expected to be in the range 150.3°C to 156.9°C, the experimental values obtained were 151.9°C and 153.1°C respectively. It can therefore be concluded that the melting point elevation seen experimentally is in good agreement with the theoretical prediction.

The DSC results indicate that increasing the pressure reduces the exotherm that occurs after melting and it could therefore be concluded that increasing the pressure is therefore making the process safer. It was unclear as to why the exotherm had been reduced by almost 50% when applying 30 bar and disappears completely when 500 bar pressure is



**Figure 6.** Estimation of melting point using Simon equation

applied. As a number of adiabatic calorimeters designed to operate under pressure are known to experience a loss in sensitivity as pressure increases it was suggested that the cause could be related to the equipment. This was discussed with the manufacturers (Mettler Toledo) who indicated that whilst the possibility of this occurring could not be completely discounted any error introduced from this source would be limited to a few %.

**Table 1.** Calculated values for melting point derived from the Simon Equation

| Pressure( bar) | Melting point limit 1 (°C) | Melting point limit 2 (°C) |
|----------------|----------------------------|----------------------------|
| 1              | 138.1                      | 138.1                      |
| 10             | 138.3                      | 138.5                      |
| 50             | 139.3                      | 140.0                      |
| 100            | 140.6                      | 141.9                      |
| 150            | 141.8                      | 143.8                      |
| 200            | 143.0                      | 145.7                      |
| 250            | 144.3                      | 147.6                      |
| 300            | 145.5                      | 149.5                      |
| 350            | 146.7                      | 151.4                      |
| 400            | 147.9                      | 153.2                      |
| 450            | 149.1                      | 155.1                      |
| 500            | 150.3                      | 156.9                      |
| 550            | 151.5                      | 158.7                      |
| 600            | 152.7                      | 160.6                      |



We are therefore dealing with a real issue rather than an artefact of the experimental method.

By this time a small scale laboratory trial had been carried out on the extrusion process and this yielded unexpected results. It was found that it was necessary to heat the carrier polymer to around 120°C in order to ensure that it was sufficiently free flowing and also ensure that the other components of the formulation were uniformly distributed throughout the final product. Given the thermal data no issues would be anticipated on the scale proposed nor would chemical interactions between the components be expected to be a problem. However, on exiting the extruder instead of the desired product – long spaghetti like strands – a foamy material of variable diameter and density was formed. It was suggested that this was as a result of poor mixing in the extruder but this did not seem to be a plausible explanation and even after pre-milling the components the foaming effect was still apparent.

It was still unclear why the exothermic peak in the DSC disappears under pressure. It is known from other experimental investigations that at elevated temperatures the test material will decompose with the evolution of copious quantities of gas. Work by Bogdanov et al<sup>9</sup> describes transformations of solid organic material under high pressure. Of particular note is work carried out on benzyl peroxide which can undergo up to 73% decomposition simply by applying pressure and altering the stress and shear deformation, however no thermal data is reported. Previous unpublished work by Priestley had observed that applying pressure to materials such as oxalates can under certain conditions result in the evolution of CO<sub>2</sub>. In addition to this a literature search highlighted an application in which microcellular foam can be formed by the action of a gas on a thermoplastic in an extruder<sup>10</sup>.

Taking this information into account, a scenario was postulated in which decomposition is occurring at elevated pressure however as the decomposition produces gas the application of pressure suppresses either the reaction itself or simply leads to any gases produced dissolving in the reaction mass. At elevated pressures the gases remain in solution and on extrusion through a die the dissolved gases are rapidly released due to the pressure drop leading to the foamy texture in the extruded material.

This scenario does not provide a complete explanation as there does not appear to be a valid thermochemical reason as to why no heat is evolved. It is unlikely that the heat of solution of decomposition gases in the reaction mass would be sufficiently endothermic to offset a heat of decomposition of the order of 600 J/g.

A more likely although as yet unproven explanation is that the application of pressure does in fact suppress the decomposition of the material up to a temperature of ca 200°C, however as the material exits the die head it is still hot (ca 120°C) and the rate of cooling is not rapid enough to prevent the sudden gas evolving decomposition of the material suspended in the semi-molten plastic. For this scenario to be valid it would mean that the material was decomposing below its melting point at ambient pressure.

In order to provide some supporting evidence for this latest hypothesis two parallel work programmes were carried out.

- 1) In house investigation in to the thermal stability of the material below the melting point at ambient pressures.

- 2) An investigation of the properties of the material using reflected light thermomicroscopy and TG/DTG carried out by Professor Charsley and The Centre for Thermal Studies at Huddersfield University.

Extensive in-house work using a variety of techniques has clearly shown that the material can undergo thermal decomposition at temperatures below the melting point with decomposition occurring from as low as 95°C after extended isothermal hold periods. The work has also highlighted that the overall decomposition mechanism is apparently auto-catalytic and further investigation of this is currently being carried out in order to gain a more complete understanding of the mechanism for decomposition.

The work at Huddersfield University showed that on heating the material started to undergo some minor transformations from temperatures as low as 70°C. On melting gas evolution was apparent immediately and this continued up to ca 226°C at which point it stopped abruptly even though heat evolution was still occurring. Comparison with the thermoanalytical data (Figure 7) shows that this temperature is coincident with the completion of the first exotherm and the start of the second. This suggests a complex mechanism for decomposition with the first part involving the generation of both heat and gas and the second heat only. This evidence also provides a possible explanation of why there is a

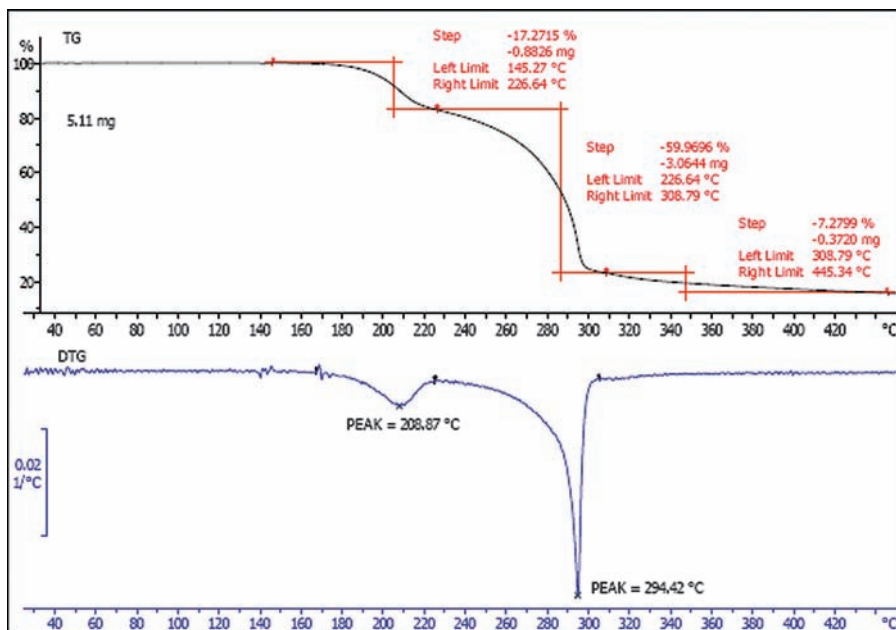


Figure 7. TG/DTG curve heating rate 10 K/min

reduction in heat output on applying pressure, as following Le Chateliers principle, if the evolution of gas is suppressed then the degree of conversion of the starting material will also be suppressed, hence the amount of heat produced will decrease.

Work by Miller et al<sup>11,12</sup> carried out on the decomposition of the explosive HMX and also nitromethane at elevated pressures showed that for a unimolecular mechanism the application of pressure will significantly decreased the rate of the decomposition. This suggests that the mode of decomposition of our material may in part be due to a unimolecular process, further investigation will however be necessary to confirm this.

Our work has clearly identified that the material can undergo thermal decomposition below its melting point.

From a safety viewpoint due to the construction of the extruder decomposition of the material whilst it is contained within the equipment would not be a problem. Discharging the material at elevated temperatures but ambient pressure has been shown to result in decomposition. The effect of pressure on the decomposition is not fully understood however from the insight obtained so far it has been possible to provide guidance to the Formulation development team to enable them to develop an extrusion process which does not result in decomposition of the material during production.

## CONCLUSIONS

1. Under pressure the melting point of the material in question increases. The experimentally determined high pressure melting point is in good agreement with theoretical calculations.
2. Applying moderate pressure suppresses the initial decomposition.
3. At an applied pressure of 500 bar no exothermic effects are observed below 200°C.
4. At ambient pressure the material can undergo a gas evolving thermal decomposition below its melting point.
5. The mode of decomposition of the material is complex and requires further investigation in order to provide a complete understanding of its nature.
6. Notwithstanding the 'unusual' mode of decomposition a safe method for extruding the material can be defined.

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