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High Pressure DSC on LLM-105 and other High Explosives

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Thermal Decomposition of Explosives Under Constant Pressure

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The purpose of this study is to establish an experimental setup to fundamentally understand the thermal decomposition of energetic materials as a function of pressure and to be able to model the reaction kinetics of explosive materials. These kinetic models in-turn could be applied to the aging and compatibility of these materials.

1.1 Introduction

The fundamental understanding of the thermal decomposition of energetic materials as a function of pressure is important in the prediction and modeling of their thermal cook-off behavior for aging and compatibility studies. The thermal decomposition studies of propellants as a function of pressure have been previously performed [1, 2], but little is known on the thermal decomposition of explosives as a function of pressure.

1.2 Experimental Apparatus

1.2.1 Overview

Differential Scanning Calorimetry (DSC) on explosives is most commonly measured at atmospheric pressure, but many stimuli that generate heat in explosives are mechanically driven and therefore occur at elevated pressure. Here we present a detailed study on the thermal decomposition of HMX, TATB, Explosive D, and LLM-105 as a function of pressure up to ~ 5 MPa using a High Pressure Differential Scanning Calorimeter (HPDSC).

1.2.2 Sample Holder – Pan Selection

In order determine which sample holder would be best suited for these high pressure DSC measurements, two types of sample holders were tested. One was a pinhole pan sample holder and the other was an open pan sample holder. Heating rates ranging from 0.5 to 10°C min^{-1} were used to monitor the thermal behavior of the explosive material. Figure 1 shows the two types of sample holders used in this study.

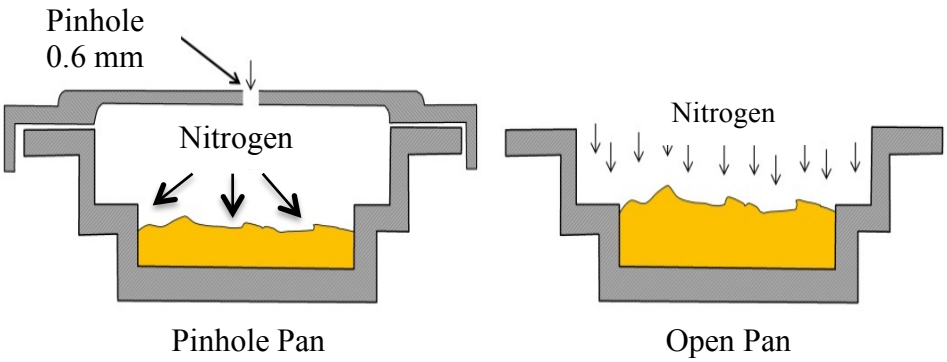

Figure 1. Schematic representation of the pinhole and open pans used in this study.

1.2.3 High Pressure Differential Scanning Calorimeter

The thermal behavior of four explosive materials was monitored using a TA Instruments Q2000 DSC with a high pressure attachment. The selected heating rate for these measurements was 1 °C min^{-1} and the pressure varied from 0.1 MPa to 5.8 MPa. The DSC with the high pressure attachment is shown in Figure 2.

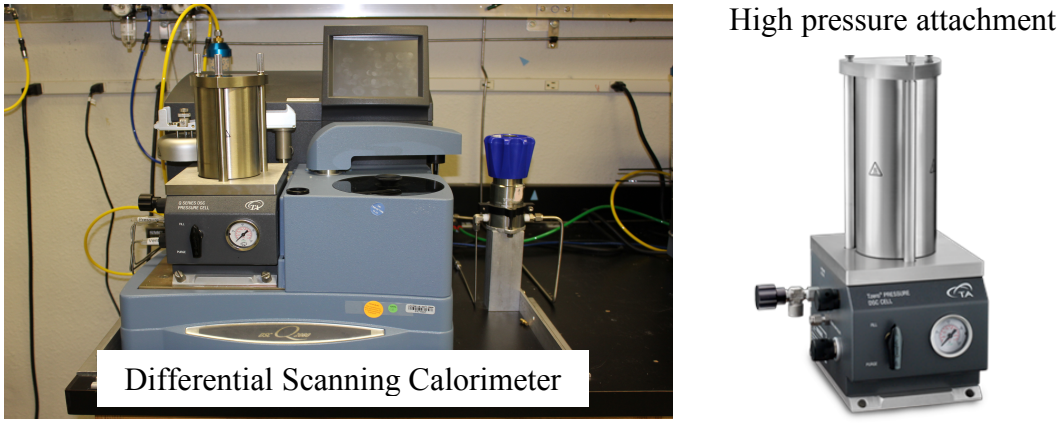

Figure 2. Images of the DSC and high pressure attachment used in this study.

1.3 Results and Discussion

1.3.1 Sample Holder - Pan Selection Results

Two types of sample holders were considered to determine which sample holder would be best suited for this study. HMX was tested on pinhole pan sample holders and open pan sample holders under a constant pressure (1.4 MPa) while varying the heating rate from 0.5 to 10°C min^{-1}. Figure 3 shows comparison plots of the thermal behavior of HMX at a constant pressure and varying heating rate.

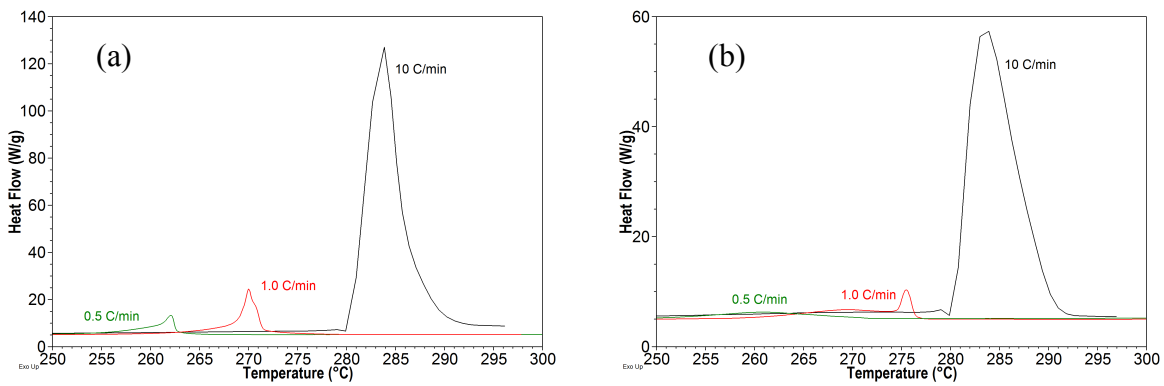

Figure 3. Thermal behavior of HMX under a constant pressure of 1.4 MPa and various heating rates using a pinhole pan (a) and an open pan (b) setup.

Figure 3 shows that the exotherm peaks from the open pan setup (b) are broad in comparison to the exotherm peaks from the pinhole pan setup (a) particularly at low heating rates (0.5 °C min^{-1}). It should be noted that as the sample decomposes in the open pan setup, the material is released to a 0.5 L volume; therefore, as the sample reacts and releases energy in the form of heat, some of that heat is lost to the entire volume and some is capture by the instrument. In contrast, when the sample in the pinhole pan setup decomposes, the energy (heat) is captured in a much smaller volume (0.02 L), which allows for a stronger heat flow signal.

Our sample holder – pan selection results demonstrated that we are able to obtain better signals particularly at low heating rates from sample holders with pinholes than from the sample holders with open pans; therefore from herethereafter our measurements will only include loading our materials into sample holders containing pinhole pans.

1.3.2 High Pressure Differential Scanning Calorimeter Results

The thermal behavior of HMX (a) and TATB (b) collected at 1 °C min^{-1} and various pressures is presented in Figure 4. It is observed that as the applied pressure increases, the exotherm peak shifts to lower temperatures, such behavior depicts that the ignition sensitivity increases as the pressure increases.

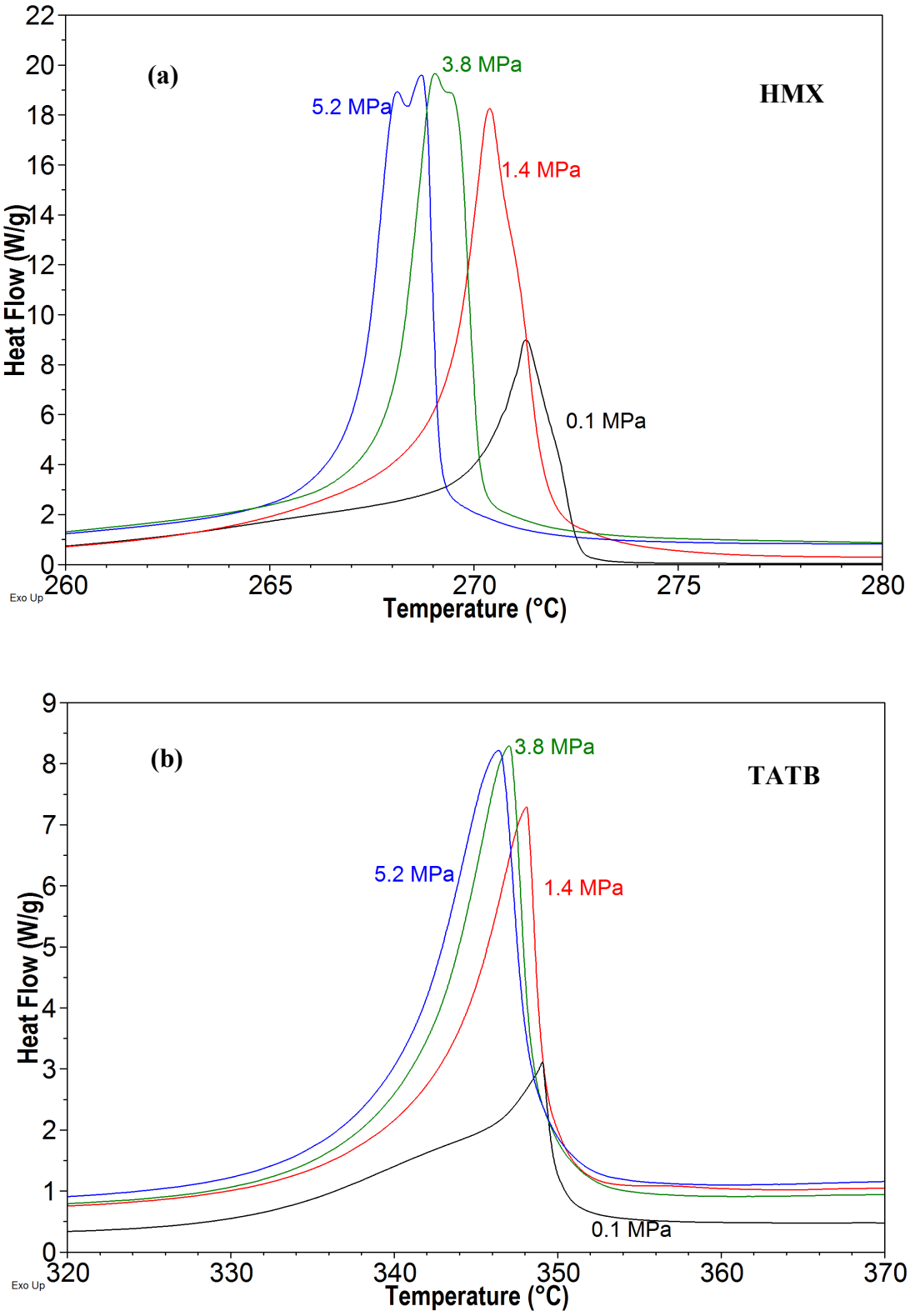

Figure 4. Thermal behavior of HMX (a) and TATB (b) as a function of pressure.

In contrast, the thermal behavior of Explosive D (a) and LLM-105 (b) collected at 1 °C min^{-1} and various pressures presented in Figure 5 shows that the exotherm peak shifts to higher temperatures as the pressure increases, this suggests that the ignition sensitivity decreases as the pressure increases.

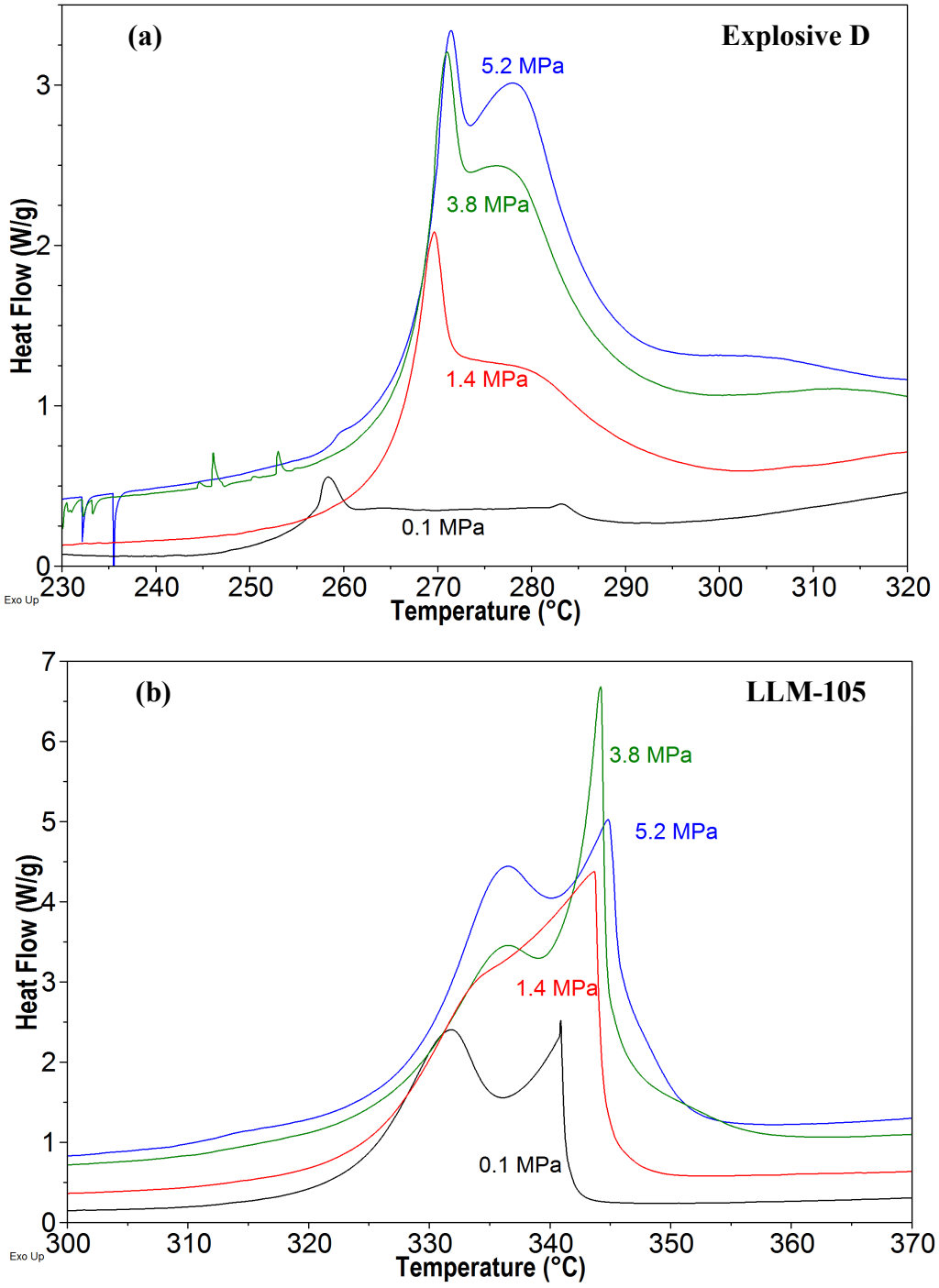

Figure 5. Thermal behavior of Explosive D (a) and LLM-105 (b) as a function of pressure.

1.3.3 Reproducibility of High Pressure Differential Scanning Calorimeter Results

Duplicate measurements were performed to check the reproducibility of the data. A similar exotherm peak shift behavior was observed in all four explosive materials as in the first set of data, but some differences were observed that need to be addressed. For instance, the duplicate measurements of HMX show that the maximum exotherm peak shifts to lower temperatures as pressure increases. Such behavior was also observed on the first set of data, but the magnitude of the peak shift is larger on the duplicate data than on the first set of data. Figure 6 shows a comparison of high pressure DSC data of HMX.

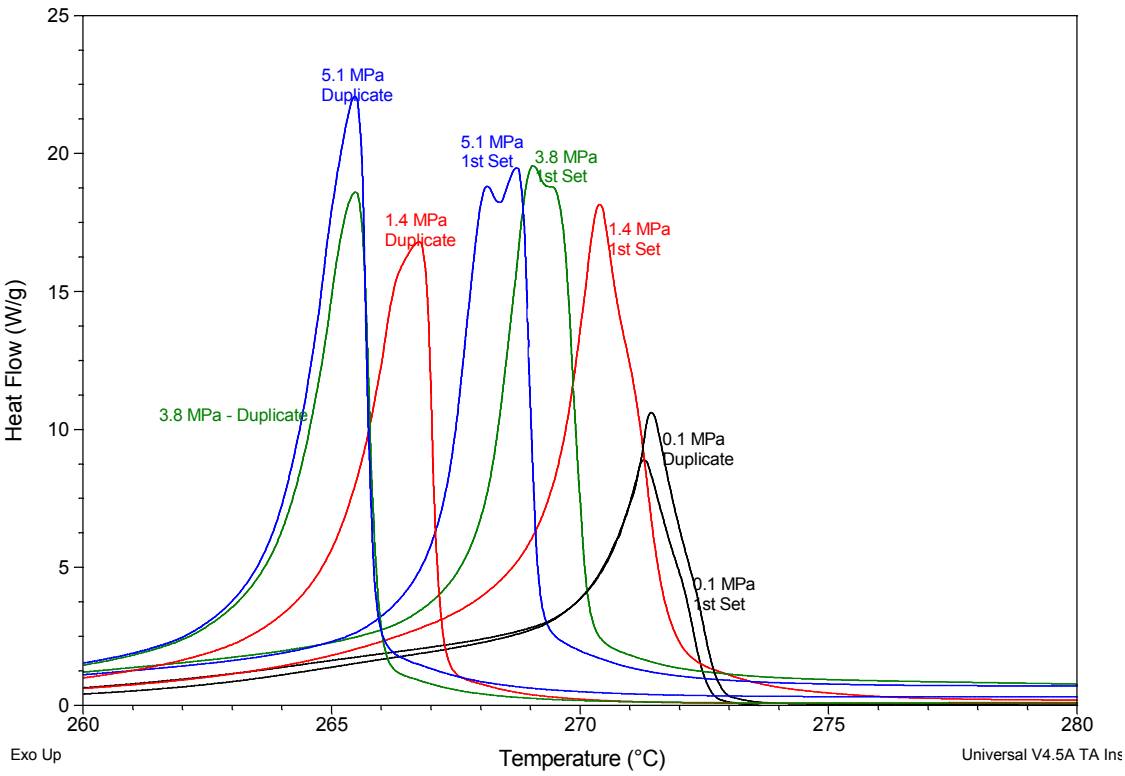

Figure 6. Comparison of high pressure DSC data on HMX as a function of pressure.

Moreover, the duplicate data on LLM-105 shows the similar tread as the data collected in the first set. The maximum exotherm peaks in the duplicate data shift to higher temperatures as pressure increases. Although the data is similar, an abnormality was found on the duplicate data at 1.4 MPa. Figure 7, shows that the maximum exotherm peak at 1.4 MPa is higher than the exotherm peaks from the 3.8 and 5.1 MPa.

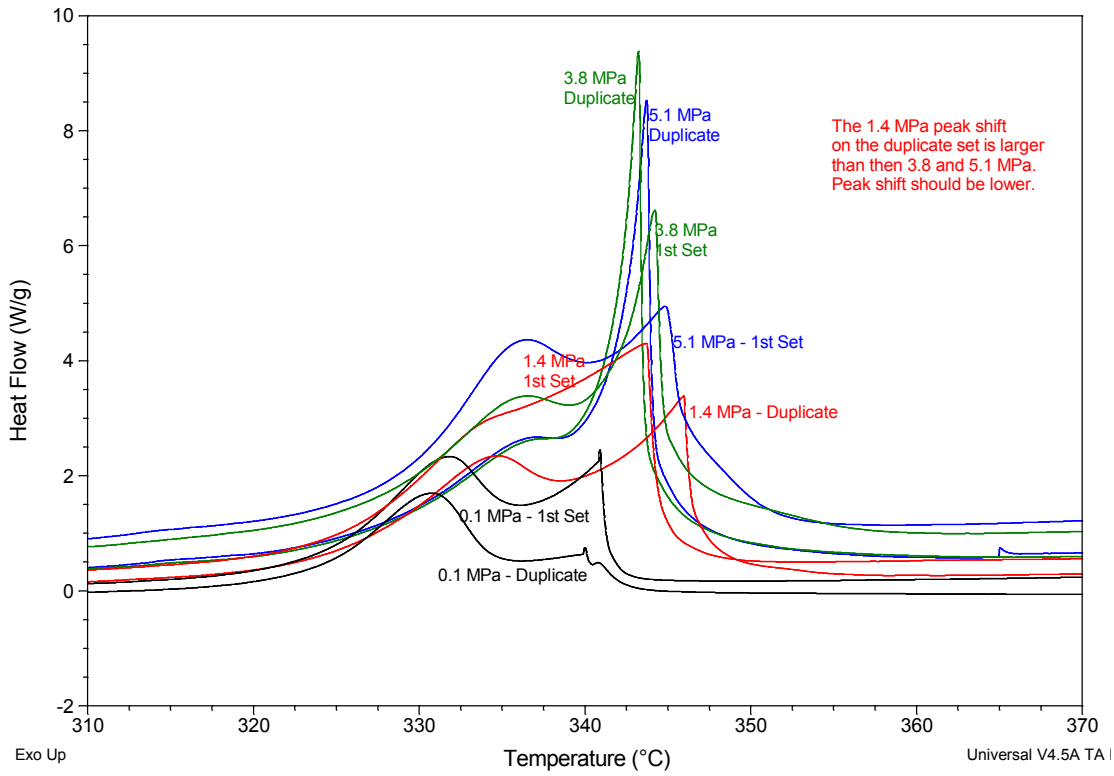

Figure 7. Comparison of high pressure DSC data on LLM-105 as a function of pressure.

1.4 Future Work

Duplicate data on all four explosives verified that the general thermal behavior is reproducible, but some abnormalities were found and need to be addressed. For instance, HMX shows a similar thermal behavior as a function of pressure, but the peak shift is larger on the duplicate data than in the first set of data. Further studies are necessary to determine the origin of these abnormalities. There are several steps that could be taken to assist with this task.

1. The exotherm peak shift in most of the data is narrow due to the limited capabilities of the instrument. We are currently applying pressures in increments of tenths of MPa. It will be beneficial if we can apply pressures in increments of 10s of MPa.
2. The present configuration of the instrument makes it difficult to maintain a constant pressure while making measurements. We are in the process of purchasing an automated system that will allow us to maintain a constant pressure throughout the measurement.
3. We are also in the process of collaboration with a Canadian laboratory to make these measurements at 10s of MPa. These measurements will be used as seed results to vet a high pressure DSC instrument for our laboratory.

1.5 Conclusions

Understanding of the thermal decomposition of energetic materials as a function of pressure may help in the prediction and modeling of their thermal cook-off behavior. A short study was conducted to determine the type of sample holder to use for these measurements. It was found that sample holders with a pinhole pan provide the best heat flow signal. Therefore, all high pressure DSC measurements were performed using pinhole pans. Moreover, high pressure DSC measurements showed that the ignition sensitivity of HMX and TATB increases as pressure increases. In contrast, the ignition sensitivity of Explosive D and LLM-105 decreases as pressure increases.

1.6 References

1. W. Zheng; et al., Propellants, Explosives, Pyrotechnics 2007, 32, (6), 520-524.
2. J. H. Yi; et al., Journal of Hazardous Materials 2009, 165, (1-3), 853-859.