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Thermal conductivity of Tetryl by modulated differential scanning calorimetry

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Abstract

An investigation of the use of modulated differential scanning calorimeter (MDSC) to measure thermal conductivity (κ) of the explosive Tetryl using isothermal and non-isothermal methods. Issues surrounding the use of silicone oil as a heat transfer aid are discussed. Using these methods the calculated isothermal and non-isothermal properties of specific heat capacity were observed to be 0.844 and 0.863 J/(g K) and the calculated thermal conductivity values were found to be 0.165 and 0.186 W/K. Calibration experiments using polystyrene indicate that the non-isothermal method is more reproducible but has a larger offset (35%) from the true value. Our corrected values for Tetryl fall in the middle of the considerable range of values reported in the literature.

Keywords: Thermal conductivity; Apparent heat capacity; Isothermal; Non-isothermal; MDSC

1. Introduction

Computational models to predict violent and non-violent reactions in high explosives are becoming increasingly important. Lawrence Livermore National Laboratory (LLNL) has developed computer codes and material models to simulate time temperature dependence of energetic materials to aid in the prediction for cook-off events [1]. These models need physical and kinetic properties that must be provided by experiment, two of which are specific heat capacity and thermal conductivity. The ease at which heat is transferred by a material has a major impact on the material's use, stability and ultimately its safety. High explosives generally do not conduct well and are often considered to be insulators. While insulators have thermal conductivities in the range of 0.2–2 W/(K m), conductors [2] typically have thermal conductivities in the range of 10–400 W/(K m). Poor heat conduction can allow hot spots to develop and grow catastrophically. Textbook and literature values are useful references to experimenters but are often given as single values at ambient temperatures. Information such as this does not always suffice for experiments such as thermal cook-off where a dynamic temperature range is involved. Here we quantify the specific heat capacity, C_p, and thermal conductivity, κ, of the energetic material, Tetryl.

2. Theory

The heat flux model can determine heat capacity, where Eq. (1) is the basic equation to derive C_p [3–7].

$$C_p = \lambda_{C_p} \left(\frac{Q_{amp}}{T_{amp}} \right) \left(\frac{\text{modulation period}}{2\pi} \right) \tag{1}$$

where C_p is the heat capacity (J/(g K)), λ_{C_p} the heat capacity calibration constant, Q_{amp} the heat flow amplitude (W/g) and T_{amp} is the temperature amplitude (K).

The enthalpy of a substance increases as its temperature is raised. The relationship between the increase in enthalpy and the increase in temperature depends on the conditions that are maintained, such as constant volume or constant pressure [8].

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In this experiment, heat capacity measured at constant pressure was used to relate the change in enthalpy to the change in temperature. The increase in enthalpy can be expressed as the heat supplied to a sample at constant pressure as,

$$q_\mathrm{p} = C_\mathrm{p}\,\Delta T \tag{2}$$

Eq. (2) shows us how to measure the heat capacity [8] of a sample, as it is quantitatively measured while heat is supplied under conditions of constant pressure and the temperature change is being monitored.

Thermal conductivity can be measured using several different instrumental techniques. The associated heat flow of a material permits the measurement of transitions that occur with respect to time and temperature. Eq. (3) calculates the observed thermal conductivity of the sample [9].

$$\kappa_\mathrm{o} = \left(\frac{8LC^2}{C_\mathrm{p}Md^2P}\right) \tag{3}$$

where κ_o is the observed thermal conductivity (W/(K m)), L the sample thickness (mm), C the apparent heat capacity (mJ/K), C_p the specific heat capacity (J/(g K)), M the specimen mass (mg), d the specimen diameter (mm) and P is the period of measurement (s).

These parameters are used to analyze Tetryl over a dynamic temperature range under isothermal and non-isothermal conditions. They were established to gather both non-isothermal and isothermal thermal conductivity in a time-effective manner.

3. Experimental

Physical heat transport measurements outlined by TA Instruments [3] was used in this study. Modulated differential scanning calorimetry (MDSC) [10] measures the difference in the heat flow between a sample and an inert reference measured as a function of time and temperature (see Eq. (1)). Both the sample and reference are subjected to a controlled environment of time, temperature, pressure and atmosphere. The instrument design used for making MDSC measurements in this work is the heat flux design, TA Instruments, New Castle, Delaware, Model 2920 [11].

Temperature and heat flow calibrations were carried out as outlined [3] using indium, tin, lead and zinc metals along with sapphire standard reference materials. Thermal conductivity calibration was performed using two polystyrene disks. The thin sample weighed approximately 14.90 mg, was approximately 0.5 mm thick and had a diameter of approximately 6.38 mm. The thick sample weighed approximately 117.81 mg, had a thickness of approximately 3.53 mm and had a diameter of approximately 6.38 mm. The two sample thicknesses are used based on the premise that the thin sample obtained equilibrium, the thick sample did not reach equilibrium and the difference is related to thermal conductivity [12]. The specific heat capacity C_p, apparent heat capacity C and the thermal conductivities κ_o were obtained using standard MDSC procedures [3] and ASTM E 1952–98 [13].

All samples were pressed from powder using a cold steel die of approximately 6.4 mm in diameter. A maximum press pressure of 208 MPa, was used for all samples. For this method two Tetryl sample sizes were needed. One of approximately 15–20 mg is used to carry out specific heat capacity measurements and the other sample of approximately 250 mg is used for the apparent heat capacity. All samples were pressed into approximately right cylindrical disks. (See Appendix A for sample masses and dimensions.)

Isothermal and non-isothermal analysis conditions were defined prior to all calibrations and analyses to optimize measurements and to minimize thermal lag [10]. For sapphire, the temperature range used was approximately 233–493 K, for polystyrene the temperature range used was approximately 233–353 K.

Isothermal measurements of Tetryl were carried out over a temperature range of approximately 270–350 K. Analysis data was collected by cooling the sample, with a TA refrigerated cooling unit, RCA, to a sub ambient temperature of 250 K. Once the temperature was achieved the computer program held the temperature isothermally 20 min. After each 20-min isotherm the temperature was increased at 3 K/min, stepping in intervals of 10 K until a maximum temperature of 350 K was reached. A modulated temperature program with modulation amplitude of ±0.5 K over a 100 s period was maintained throughout.

Non-isothermal measurements of Tetryl were carried over a temperature range of approximately 233–353 K using a linear heating ramp rate of 3 K/min, with a modulation amplitude of ±0.5 K over a 100 s period.

In this study, the thermal conductivity of Tetryl was evaluated at 270, 290 and 320 K using isothermal and non-isothermal conditions. These temperatures were chosen to represent the dynamic temperature range of this experiment. (See Appendix A for non-isothermal and isothermal sample masses and dimensions and Appendix B for apparent heat capacities.)

4. Results and conclusions

MDSC is generally not the best method to measure thermal conductivities. However, we used MDSC here to measure thermal conductivity because it was an available resource that shows promise for specialized situations. We show how to obtain measurements within the range of other methods.

Tables 1 and 2 compare non-isothermal and isothermal polystyrene values obtained by MDSC with literature values. The % variation values show the accuracy and the precision of these thermal conductivity measurements. The results shown in Table 1 have a bias of approximately 0.05–0.06 W/(K m) between the observed values and the literature values. This corresponds to an average error of approximately 34.7% and a standard deviation about that average of approximately 1.2%.

Table 1
Comparison of non-isothermal thermal conductivities of polystyrene ($W K^{-1} m^{-1}$) without correction

Temperature (K)	κ_o (W/(K m))	Literature value (W/(K m))	% Deviation between measured and literature values
270	0.2012	0.1499	34.2
290	0.2039	0.1523	33.9
320	0.2121	0.1558	36.1

Table 2
Comparison of isothermal thermal conductivities of polystyrene (W/(K m)) without correction

Temperature (K)	κ_o (W/(K m))	Literature value (W/(K m))	% Deviation between measured and literature values
270	0.1696	0.1499	13.1
290	0.1646	0.1523	8.1
320	0.1593	0.1558	2.2

Table 1 compares the non-isothermal thermal conductivity of polystyrene without corrections. Table 2 compares the isothermal thermal conductivity of polystyrene without corrections. The offset is more constant for the non-isothermal method than the isothermal method. On the other hand, the accuracy is distinguishably worse than for the isothermal method.

Table 3 compares measured specific heat capacities with literature values and the % variations. The % variations range from approximately 10.0% for the isothermal to 0.9% for the non-isothermal over a dynamic temperature of 270–320 K.

There are two prominent areas for errors. First, the thin sample was encapsulated in the aluminum pan and was believed to be in good thermal contact with sample and furnace. However, this is not the case for the large sample. The large sample sits on a silicone oil drop and a thin aluminum disk. These two samples are therefore analyzed under different heat transfer conditions. Second, silicone oil is applied to the DSC furnace with the intention of providing a good thermal conduction pathway. One important aspect that is overlooked is the solubility of silicone with the substrate, in this case Tetryl. The solubility of silicone oil with Tetryl probably had a direct effect on the apparent heat capacity measurements. The Tetryl samples looked dark and wetted at the furnace sample interface where the silicone oil was applied. This indicates a change in the physical aspects of the Tetryl sample. (This was not observed in the polystyrene samples.) The assumption that the silicone oil had a constant effect on the calibration and sample specimens is at best a crude assumption.

Table 4
Comparison of corrected Tetryl thermal conductivities (W/(K m))

Temperature (K)	K (W/(K m)), non-isothermal	K (W/(K m)), isothermal	% Variation
270	0.171	0.186	8.2
290	0.165	0.186	13.8
320	0.154	0.189	18.6

Table 5
Comparison of corrected Tetryl thermal conductivities (W/(K m)) at 290 K and reported literature values (W/(K m))

Material	This work	Literature [14,16–19]
Tetryl (non-isothermal)	0.165	0.084–0.286
Tetryl (isothermal)	0.186	0.084–0.286

In principle the losses of heat through the sides and the top of the polystyrene samples, as well as the imperfect heat transfer at the sample–pan interface are accounted for with the calibration constant D that is used for thermal conductivity calculations of subsequent samples of interest [2,14,15]. Eq. (4) calculates the D-cell calibration constant for the sample to correct for heat loss due to sample configuration [9].

$$D = (\kappa_o \times \kappa_r)^{0.5} - \kappa_r \tag{4}$$

where κ_o is the uncorrected thermal conductivity and κ_r the reference thermal conductivity.

The D cell constant is typically within the range of 0.02–0.05 W/(K m). The D cell constant value may then be substituted into Eq. (5) to obtain the unknown material thermal conductivity. Eq. (5) was used to calculate the corrected value for thermal conductivity [9].

$$\kappa = \frac{[\kappa_o - 2D + (\kappa_o^2 - 4D\kappa_o)^{0.5}]}{2} \tag{5}$$

Tetryl was analyzed by both isothermal and non-isothermal methods. Listed in Table 4 are the observed non-isothermal and isothermal corrected values of Tetryl. Table 5 is a comparison of the experimentally observed thermal conductivities of Tetryl and a range of literature thermal conductivity values [14,16–19].

Simon and McKenna [20] have shown different solutions to the calculated thermal conductivities of Marcus and

Table 3
Comparison of literature values and experimentally observed non-isothermal and isothermal specific heat capacity of Tetryl (J/(g K))

Temperature (K)	C_p, non-isothermal	C_p, isothermal	Literature	% Variation non-isothermal	% Variation isothermal
270	0.812	0.800	0.889	8.7	10.0
290	0.863	0.844	0.905	4.6	6.7
320	0.939	0.910	0.931	0.9	2.3

Blaine [2] and have addressed the problem of the use of a large sample not encapsulated in the same manner as the thin sample. Merzlyakov and Schick [21] report considerable evidence that agrees with Simon and McKenna. Merzlyakov and Schick report measured polystyrene and poly(methylmethacrylate) (PMMA) thermal conductivities that had variations of 10.3 and 8.4%. We observed similar errors in polystyrene and PMMA of 8–12% as Merzlyakov and Schick using the method of Marcus and Blaine.

Literature values for thermal conductivities of Tetryl span a range of 0.084–0.286 W/(K m). This variation may be the result of many factors such as density, purity and analysis method to name a few. Table 5 is a comparison of the experimentally observed thermal conductivities of Tetryl and a range of literature thermal conductivity values [14,16–19]. Measured thermal conductivities by both non-isothermal and isothermal methods values fall approximately in the middle of the cited literature values. Thus, the comparison of non-isothermal versus isothermal values described here appears to provide accuracy and precision at least equivalent to other reported works that measure insulator type materials without the expense for a specialized apparatus.

The purpose of this work was to lay a path for more works of this type. In the comparison of non-isothermal analysis versus isothermal analysis the isothermal analysis reported higher thermal conductivities.

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Appendix A. Masses, thicknesses and diameters of non-isothermal and isothermal Tetryl samples

Sample	Mass (mg)	Thickness (mm)	Diameter (mm)
Thin (non-isothermal)	19.8	0.4	6.3
Thick (non-isothermal)	249.3	4.6	6.3
Thin (isothermal)	19.4	0.4	6.3
Thick (isothermal)	248.9	4.6	6.3

Appendix B. Observed non-isothermal and isothermal apparent heat capacity of Tetryl (mJ/K)

Temperature (K)	*C* (non-isothermal) (mJ/K)	*C* (isothermal) (mJ/K)
−3	69.40	66.32
17	70.76	66.98
47	72.79	68.53

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