

Research on the Specific Heat Capacity of PBX Formulations Based on RDX

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ABSTRACT: The experimental results of specific heat capacity of 2 plastic bonded explosives formulations based on 1,3,5-trinitroperhydro-1,3,5-triazine, using differential scanning calorimetry thermal analysis, and the theoretical ones calculated with the specific heat capacity and mass fraction of individual compounds are compared for a temperature range between 340 and 410 K. Apart the filler, the plastic bonded explosives composition includes the binder based on hydroxyl-terminated polybutadiene, the plasticizer bis (2-ethylhexyl) sebacate and the curing agent isophorone diisocyanate. The experimental and theoretical results showed a better approach when no curing agent is added. Without curing agent, the specific heat capacity of plastic bonded explosives increases linearly with temperature. When plastic bonded explosive is cured, the specific heat capacity is nearly constant until 380 K and decreases linearly for higher temperature values. These results suggest that phase change requires adjusting parameters to different heating rates in order to describe adequately the experimental data.

KEYWORDS: Heat capacity, DSC, RDX, HTPB, DOS, IPDI.

INTRODUCTION

Energetic materials (EM) must be safe during handling, transport or storage; thereby it is important to know their behaviour under potential thermal scenarios, like cookoff. In order to predict the thermal behaviour of EM the specific heat capacity is a fundamental property that allows assessing the energy storage progress by the effect of temperature increasing. Not only this property but also others, such as the activation energy, pre-exponential factor, kinetic model, heat of reaction and thermal conductivity, are used in thermal simulation of EM and must be obtained free from errors caused by incorrect setting or sample effects, allowing to perform efficient kinetics computations (Vyazovkin *et al.* 2014; Zhang *et al.* 2014). Many methods can be used for thermal analysis, such as differential scanning calorimetry (DSC), thermogravimetry (TG), dilatometry (DIL) or thermomechanical analysis (TMA) (Hemminger and Cammenga 1989; Cuimei *et al.* 1991; Fiala and Šesták 2000; Höhne *et al.* 2003; Ehrenstein *et al.* 2004; Magoń *et al.* 2015). Thermoanalytical curves analysis requires careful interpretation and should be compared with literature data but these are not available for all materials or used conditions, despite the significant amount of information available on materials science (Schindler *et al.* 2015).

In this study it was used a well-established method (Speyer 1993) based on DSC technique to measure the specific heat capacity of 2 plastic bonded explosives (PBX) formulations based on 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and their individual compounds. This experimental technique (DIN 51007:1994) has the advantage of using a baseline, which allows a better accuracy and enables specific heat capacity values with less scatter at high temperatures.

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The main objectives of this study are to compare these results of specific heat capacity for a temperature range from 340 to 410 K with those obtained by other authors for RDX and similar PBX at room temperature (Rogers 1975; Tarver *et al.* 1978; Dobratz 1981; Jones and Parker 2004; Xue *et al.* 2010) as well as to evaluate the difference between the specific heat capacity value of a PBX based on RDX and the results obtained by calculation based on the mass fraction of individual compounds figures.

MATERIALS AND METHODS

The individual compounds were selected in order to be representative of potentially useable species in PBX. The main charge was RDX, also named 1,3,5-trinitro-1,3,5-triazacyclohexane, the binder was hydroxyl-terminated polybutadiene (HTPB), the plasticiser was bis (2-ethylhexyl) sebacate (DOS) and the curing agent was isophorone diisocyanate (IPDI). Two compositions were studied:

- PBX RH8515 — RDX and HTPB, with a weight ratio of 85/15, respectively.
- PBX RHDI8515 — RDX, HTPB, DOS and IPDI, with a weight ratio of 85/10.46/3.49/1.05, respectively.

The measurements were carried out using a simultaneous TGA/DTA (Rheometric Scientific STA 1500) thermal analyser. The test conditions were: sample masses in the range of 20 – 30 mg; temperature range of 298 – 420 K; linear heating rates of 2.5 and 10 K·min⁻¹ and inert atmosphere. The samples were carefully loaded into alumina crucibles, and a dry nitrogen purge flow of 50 mL·min⁻¹ at 0.1 MPa (absolute pressure) was used in all the measurements. The specific heat capacity calculation was based on the difference between the DSC heat flow signals of the sample and a reference standard material (Sapphire). Both curves were corrected by a zero line or baseline correction experiment, whereby 2 empty crucibles were placed in the furnace and the system signal drift was measured under identical experimental conditions. The procedure was carried out following the 3 steps for standard specific heat capacity according to the German standard DIN 51007:1994.

The specific heat capacity is then calculated by Eq. 1 (Speyer 1993):

$$C_{p, \text{sample}} = \frac{m_{\text{reference}}}{m_{\text{sample}}} \frac{\Delta T_{\text{sample-zero}}}{\Delta T_{\text{reference-zero}}} C_{p, \text{reference}}$$

where: $\Delta T_{\text{sample/reference-zero}}$ is the temperature difference between the sample (or reference material) and the empty crucible during the operating range; m is the mass of the sample or reference.

A minimum of 3 runs were carried out for each sample and the relative difference between replicates in the range of 340 – 410 K was lower than 2.0%. This difference is due to the unavoidable sample heterogeneity and potential slight adsorption of water coming from the air captured in the vessel during sample preparation.

RESULTS AND DISCUSSION

The accuracy of experimental results may be influenced by material factors, such as weight, sample geometry and thermal diffusivity (Vyazovkin *et al.* 2014). The most fundamental factor is the baseline stability, which will depend largely on the apparatus employed. In order to obtain precise measurements, a very good baseline stability should be guaranteed and needs to be checked at regular intervals. With the same objective it is fundamental to reduce the unfavourable factors that may include: (a) variation of sample preparation including mixing, storage or curing conditions; (b) change the positioning of crucibles in relation to the heat flux sensor; (c) poor cleaning of the crucible for each new sample; (d) change the positioning and thickness of the sample on the crucible. Samples with very low or high mass are not suitable. Although the sample mass increase allows improving the measurement accuracy it also causes effects on temperature gradients and self-heating of the explosive, which in turn may lead to deviations in performance and equipment damage. Since the measurements were performed at temperatures below the beginning corresponding to the variation of mass loss, there was no risk of damage to the equipment and the sample mass was between 20 and 30 mg.

Figure 1 shows the specific heat capacity results of individual compounds used for the PBX studied. Within the temperature range of 340 – 410 K, the specific heat capacity of RDX is almost constant. In the same temperature range, the specific heat capacity of IPDI decreases slightly, while the HTPB and DOS decrease significantly. Table 1 shows, for the temperature range of 340 – 410 K, the specific heat capacity and standard deviation obtained with RDX and IPDI and the representative equations obtained to describe the specific heat capacity of HTPB and DOS as a function of temperature. The square correlation coefficient (R^2) for both equations is higher than 0.995.

The specific heat capacity of RDX available in literature data for 298 K (Table 2) is between 1.005 and 1.226 kJ·kg⁻¹·K⁻¹. Our measurement compared with these results shows a difference of 6.8% with the highest value and of 12.5% with the lowest one. These differences are significant when compared with the relative standard deviation (RSD), which can be relevant in thermal simulation studies.

Figure 2 shows the results of specific heat capacity within the temperature range of 340 – 410 K for a PBX RH8515 just with binder and a PBX RHDI8515 fully cured, both based on RDX. When the HTPB binder is added to RDX, the specific heat capacity is increased and shows a linear dependence with the temperature. When the plasticiser and curing agent are added, the specific heat capacity of PBX has no linear dependence with temperature being

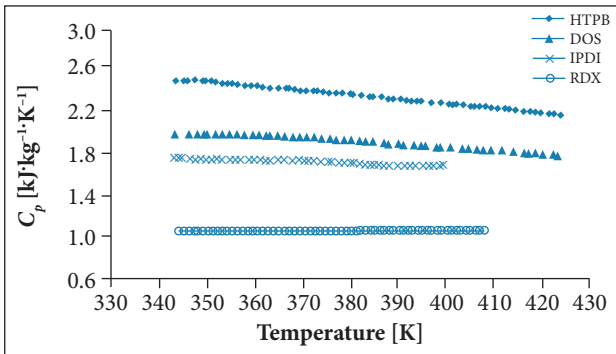


Figure 1. Specific heat capacity of RDX, HTPB, DOS and IPDI as a function of temperature.

Table 1. Specific heat capacity of RDX, HTPB, DOS and IPDI in the temperature range of 340 – 420 K.

EM	C_p [kJ·kg ⁻¹ ·K ⁻¹]
RDX	1.148 ± 0.010*
HTPB	$-1.9408E-05 \times T^2 + 0.0121 \times T + 0.0116$ $R^2 = 0.9960$
DOS	$-0.0043 \times T + 3.9973$ $R^2 = 0.9987$
IPDI	1.726 ± 0.032**

*Temperature range of 340 – 410 K; **Temperature range of 340 – 400 K.

Table 2. Specific heat capacity of RDX available in literature for 298 K.

Reference	Specific heat capacity [kJ·kg ⁻¹ ·K ⁻¹]
Dobratz (1981)	1.226
Tarver <i>et al.</i> (1978)	1.004
Rogers (1975)	1.087
Jones and Parker (2004)	1.005

close to the specific heat capacity of RDX main charge. Specific heat capacity of PBX RHDI8515 is almost constant until 380 K, decreasing after that due to the phase transition based on the crosslink (cure) of DOS and IPDI compounds with HTPB and RDX, showing lower values than RDX (Fig. 2).

The average value and the polynomial fit functions representative of specific heat capacity of PBX dependence with temperature, based on least squares method, are shown in Table 3. The specific heat capacity of PBX RH8515 is well-described by a linear fit with $R^2 = 1$. The specific heat capacity of PBX RHDI8515 within the temperature range of 343 – 379 K is 3.1% lower than that of RDX. As the specific heat capacity is an indirect measurement of the molecular mobility, the crosslinking effect of the curing agent is the main responsible for the decrease in specific heat capacity of PBX when compared with the RDX alone (Vyazovkin *et al.* 2014).

For the same temperature range, despite the gap between the results, a similar behaviour of specific heat capacity with the temperature is observed for PBX RH8515 and the other 2 PBX (PBXN 109 and PBX 9407) both based on RDX (with 64 and 95 wt%) cited in the literature (Table 4).

Taking into account the mass fraction of the individual compounds of the PBX, the theoretical specific heat capacity

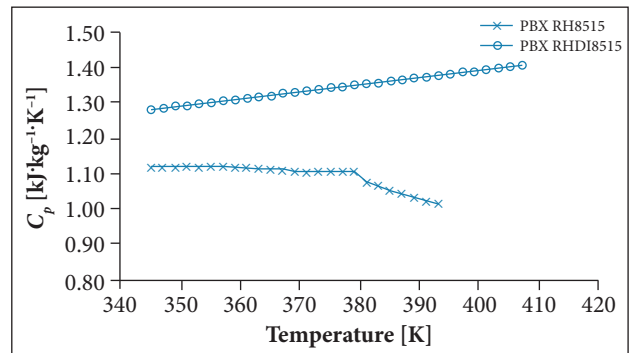


Figure 2. Specific heat capacity of PBX RH8515 and PBX RHDI8515 within the temperature range of 340 – 410 K.

Table 3. Specific heat capacity of PBX based on RDX within a temperature range.

EM	C_p [kJ·kg ⁻¹ ·K ⁻¹]	Temperature range (K)
PBX RH8515	$0.5914 + 2 \times 10^{-3} \times T$ $R^2 = 1$	343 – 407
PBX RHDI8515	1.112 ± 0.007 $3.0094 - 5.1 \times 10^{-3} \times T$ $R^2 = 0.9957$	343 – 379 380 – 393

of the PBX was estimated and it was established a correlation with the experimental result. Table 5 compares the specific heat capacity result obtained by theoretical calculation with the experimental one and the relative deviation (RD) in relation to the experimental results. Without curing agent, the theoretical results of specific heat capacity of PBX are lower than the experimental ones. When the curing agent is added, the theoretical results of PBX are always higher than the experimental ones and show a significant relative deviation.

The accuracy of the specific heat capacity is relevant on cookoff simulation, since a variation of 20% causes considerable differences in the results of time and temperature of runaway (Góis *et al.* 2004). Thus, within the temperature range studied, the specific heat capacity measurement with this DSC method was more reliable, providing a suitable reference data for thermal simulation.

CONCLUSIONS

Using a well-established kinetic method based on ICTAC recommendations (Vyazovkin *et al.* 2014) and DIN 51007:1994 standard, the specific heat capacities of RDX, HTPB, DOS and IPDI (individual compounds of 2 PBX), as well as of 2 plastic bonded explosives formulations, PBX RH8515 and PBX RHDI8515, were measured in the temperature range of 340 – 410 K to complete the limited set of data required for thermal modelling. The results of specific heat capacity of these different materials are comparable with those available in literature data.

Theoretical values of specific heat capacity of PBX calculated with the specific heat capacity and mass fraction of the correspondent individual compounds were compared with the experimental results. This comparison showed better approach between theoretical and experimental results for PBX without cure. Nevertheless, the relative deviations between theoretical and experimental results

Table 4. Specific heat capacity of PBX based on RDX used for comparison.

Reference	Material	Temperature range (K)	Specific heat capacity [$\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$]
McClelland <i>et al.</i> (2001)	PBXN 109	-	$1.086 + 3.223 \times 10^{-3} \times T$
Cooper (1996)	PBX 9407	310 – 440	$1.009 + 3.223 \times 10^{-3} \times T$

Table 5. Comparison of experimental and theoretical values of specific heat capacity of two PBX (cured and not cured) based on RDX as a function of the temperature.

PBX RH8515	Experimental	Theoretical	RD (%)	PBX RHDI8515 *	Experimental	Theoretical	RD (%)
T (K)	C_p [$\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$]			T (K)	C_p [$\text{kJ}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$]		
298.15	1.1877	1.2599	6.1	298.15	1.1120	1.2868	15.7
340	1.2714	1.2581	-1.0	340	1.1120	1.2793	15.0
345	1.2814	1.2572	-1.9	345	1.1120	1.2779	14.9
350	1.2914	1.2562	-2.7	350	1.1120	1.2764	14.8
355	1.3014	1.2550	-3.6	355	1.1120	1.2748	14.6
360	1.3114	1.2536	-4.4	360	1.1120	1.2732	14.5
365	1.3214	1.2522	-5.2	365	1.1120	1.2714	14.3
370	1.3314	1.2505	-6.1	370	1.1120	1.2695	14.2
375	1.3414	1.2488	-6.9	375	1.1120	1.2675	14.0
380	1.3514	1.2469	-7.7	380	1.1120	1.2654	13.8
385	1.3614	1.2448	-8.6	385	1.0459	1.2632	20.8
390	1.3714	1.2426	-9.4	390	1.0204	1.2609	23.6
395	1.3814	1.2402	-10.2	395	0.9949	1.2586	26.5
400	1.3914	1.2377	-11.0	400	0.9694	1.2561	29.6

*Cured PBX.

are higher than the relative standard deviation of experimental data, thus it is not recommended to use the specific heat capacity based on theoretical calculation to perform thermal simulation.

Methods used to measure specific heat capacity from the DSC curves are accurate and faster than those using

microcalorimetric measurements, since the relationship between the specific heat capacity and the temperature can be obtained only in a single test, and the amount of sample used is small. These methods may be also applied to powders, liquids and mixtures.

REFERENCES

- Cooper PW (1996) Explosive engineering. Weinheim: Wiley-VCH.
- Cuimei Y, Ziru L, Gangle W, Chengyan W (1991) Determination of heat capacity of explosives and related materials by DSC. Proceedings of the 17th International Pyrotechnics Seminar; Beijing, China.
- Dobratz B (1981) LLNL Explosives handbook – properties of chemical explosives and explosives simulants. Livermore: Lawrence Livermore Laboratory.
- Ehrenstein G, Riedel G, Trawiel, P (2004) Thermal analysis of plastics: theory and practice. New York: Hanser Gardner Publications.
- Fiala J, Šesták J (2000) Databases in materials science. Contemporary state and future. *J Therm Anal Calorim* 60(3):1101-1110. doi: 10.1023/A:1010100917679
- Góis JC, Chaves F, Simões P, Pedrosa L, Plaksin I, Mendes R, Ribeiro J, Portugal A, Campos J (2004) Cookoff test models and results. In: Branco PC, Schubert H, Campos J, editors. Defense industries: science and technology related to security: impact of conventional munitions on environment and population. Dordrecht: Springer Netherlands. p. 65-81.
- Hemminger W, Cammenga H (1989) Methoden der thermischen analyse. Heidelberg: Springer.
- Höhne G, Hemminger W, Flammersheim H (2003) Differential scanning calorimetry. Berlin: Springer-Verlag.
- Jones DA, Parker RP (2004) Simulation of cookoff results in a small scale test. Melbourne: Explosives Ordnance Division, Aeronautical and Maritime Research Laboratory, DSTO.
- Magoń A, Wurm A, Schick C, Pangloli P, Zivanovic S, Skotnicki M, Pyda M (2014) Heat capacity and transition behavior of sucrose by standard, fast scanning and temperature-modulated calorimetry. *Thermochim Acta* 589:183-196. doi: 10.1016/j.tca.2014.05.029
- McClelland MA, Tran TD, Cunningham BJ, Weese RK, Maienschein JL (2001) Cookoff response of PBXN-109: Material characterization and ALED3D thermal predictions. Proceedings of the 50th Joint Army-Navy-NASA-Air Force (JANNAF) Propulsion Meeting; Salt Lake City, USA.
- Rogers RN (1975) Thermochemistry of explosives. *Thermochim Acta* 11:131-139.
- Schindler A, Strasser C, Schmolzer S, Bodek M, Seniuta R, Wang X (2015) Database-supported thermal analysis involving automatic evaluation, identification and classification of measurement curves. *Journal of Thermal Analysis and Calorimetry* 123(3):2405-2414. doi: 10.1007/s10973-015-5026-x
- Speyer RF (1993) Thermal analysis of materials. New York, Basel: Marcel Dekker, Inc.
- Tarver C, McGuire RR, Lee EL, Wrenn EW, Brein KR (1978) The thermal decomposition of explosives with full containment in one-dimensional geometries. Proceedings of the 17th Symposium (International) on Combustion; Pittsburgh, USA.
- Vyazovkin S, Chrissafis K, Di Lorenzo ML, Koga N, Pijolat M, Roduit B, Sbirrazzuoli N, Suñol JJ (2014) ICTAC Kinetics Committee recommendations for collecting experimental thermal analysis data for kinetic computations. *Thermochim Acta* 590:1-23. doi: 10.1016/j.tca.2014.05.036
- Xue L, Zhao F, Xing X, Xu S, Pei Q, Gao Y, Hu R (2010) Evaluation of thermal hazard of composite modified double-base propellant by microcalorimetry method. *Chem Res Chinese Universities* 26(4):626-629.
- Zhang Y, Wu H, Xu K, Zhao F (2014) Nonisothermal decomposition kinetics, specific heat capacity, and adiabatic time-to-explosion of Zn(NH₃)₂(FOX-7)₂. *J Therm Anal Calorim* 116(2):817-823. doi: 10.1007/s10973-013-3589-y