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Thermal stability of a plastic bonded explosive

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Abstract

Data on the thermal stability of a plastic bonded explosive containing an oxidizer cyclotetramethylene tetranitramine (HMX), binder and plasticizer was required in order to satisfy the requirement of NAVORD OD 44811 and to obtain safety information for handling and use. The thermal stability of the PBX was determined by dynamic differential scanning calorimetry (DSC) in sealed/unsealed sample pans and by thermogravimetry (TG) in a nitrogen atmosphere using the variable heating rate method. Critical temperature for self-heating at various sample radii and the 500 day cookoff temperature were calculated. Thermal conductivity, specific heat and thermal diffusivity were determined at the critical temperatures in order to calculate the approximate time to explosion at these temperatures. A DSC self-heating half-life experiment was carried out to confirm that the overall decomposition of the PBX was first order. Published by Elsevier Science B.V.

Keywords: Plastic bonded explosive; Differential scanning calorimetry; Thermogravimetry

1. Introduction

Thermal characterization of explosives and propellants must be done in order to ensure that these materials are safe to compound and handle. Navy's munitions requirements require all energetics to be qualified for performance and safety in their manufacture, handling, storage and use. These test are described in OD4481 [1] and MIL-STD-1648 (AS) [2]. Since all energetic materials decompose exothermally, and the decomposition is faster the higher the temperature that they are subject to, the potential hazards associated with their thermal stability must be understood. Both the DSC and TG are used to measure decomposition kinetics and thermal flow properties which are used to calculate the temperature of 500 day cookoff, the time to explosion and the critical temperature of self-heating, which are some of the required information.

2. Experimental

2.1. Dynamic DSC

DSC samples were contained in unsealed sample pans with a pin-hole in the cover, in a 50 ml/min helium atmosphere. Heating rates used for kinetic analysis were 0.2, 0.5, 1.0, 2.0, 5.0, 10.0 and 20°C/min. A plot of the log heating rate versus the reciprocal of the absolute peak temperature was a straight line, which indicated that the mechanism of thermal decomposition over this temperature range did not vary. The activation energy was obtained from the slope of the line. The instrument's software based on ASTM E698-79 [3] was employed to calculate the kinetic constants. The DSC experiments were also

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Table 1
DSC and TG kinetic data for PBXW-11

Heating rate (°C/min)	DSC[a], peak temperature (°C)		TG derivative peak in nitrogen (°C)
	Unsealed pan in helium	Sealed pan	
0.2	242	237	241
0.5	253	254	258
1	267	266	266
2	279	271	279
5	283	278	286
10	286	286	291
20	293	291	297
E_a[b] (kcal/mol)	46.9	42.7	45.5
A[c] (s^{-1})	10.8×10^{15}	0.33×10^{15}	4.49×10^{15}

[a] Average value from DSC (unsealed)+TG: E_a=46.2±1.0 kcal/mol, $A=7.65\pm4\times10^{15}$ s^{-1}.

[b] Average value from all measurements: E_a=45.0±2.1 kcal/mol.

[c] Average value from all measurements: $A=5.21\pm5\times10^{15}$ s^{-1}.

carried out using sealed sample pans to determine if the decomposition gases generated had an effect on the decomposition reaction. Kinetic data are presented in Table 1.

2.2. Dynamic TG

The TG analyses in a nitrogen atmosphere of 50 ml/min were run at the same heating rates as the DSCs. In DSC, temperatures at the peak maximums were used for the kinetic analysis, while in TG it was the temperatures at constant degrees of conversion (i.e. 10–80% at 10% intervals) using the variable heating rate method for kinetic analysis. Straight line plots were obtained for log heating rate versus the reciprocal of the absolute temperature at constant degrees of conversion.

3. Results

3.1. Kinetic data

DSC peak temperatures and TG derivative peak temperatures at the various heating rates are given in Table 1. Activation energies and frequency factors are also listed. There was good agreement for the activation energy from all three measurements (45.0±2 kca/mol), but better agreement between DSC unsealed pan (in helium) and TG (in nitrogen) (46.2±1.0 kca/mol). The latter value of 46.2 kca/mol and an average frequency factor of 7.65×10^{15} s^{-1} were used in the calculation of the 500 day cookoff temperature. The main oxidizer in this explosive is HMX. Its accepted value for decomposition is 52.7±2 kcal/mol with a frequency factor of 5×10^{19} s^{-1} [4]. In this explosive mixture, the activation energy of HMX is lowered by 12% from that of neat HMX.

3.2. 500 day cookoff temperature

Pakulak (NWC TP 6118, 6686, 6765) [5–7] made use of two equations to calculate the 500 day cookoff temperature for a MK 84 2000 lb general purpose bomb. Cookoff should not occur in <500 days at 180°F (82°C).

The first equation is

$$\ln(1-F) = -tk$$

where F is fraction or the amount reacted during the warm-up period in an isothermal cookoff test; values found are usually 0.06±0.02, t is time to cookoff; 4.32×10^7 s (500 days).

Solving for k

$$k = \frac{-\ln[1-F]}{t} = \frac{-\ln[0.94]}{4.32\times10^7} = 1.43\times10^{-9}$$

k is the Arrhenuis rate constant during the warm-up period.

The rate constant together with the Arrhenius frequency factor (A) and activation energy (E_a) are needed in the second rate equation in order to calculate the 500 day cookoff temperature.

The second equation is:

$$\ln k = \ln A - \frac{E_a}{RT}$$

where k=1.43×10^{-9} s^{-1}, A=7.65×10^{15} s^{-1}, E_a= 46,200 cal/mol, R=1.987 cal/(mol K), T=temperature (K) for 500 day cookoff.

Substituting these values into the equation and solving for the temperature (K), a value of 408 K=135°C was calculated.

3.3. Thermal flow properties

In order to calculate the critical temperature for self-heating, time to explosion, etc.; the thermal conductivity, specific heat, and thermal diffusivity of the explosive must be known. We modified the standard DSC cell to permit accurate thermal conductivity values to be determined [8].

The Fourier heat flux equation was employed where

$$K = \frac{QL}{A\Delta T}$$

where K is the thermal conductivity, Q the heat flux (mW), L the length of the sample, A the cross-sectional area, ΔT the temperature difference between the bottom (hot side) and top (cold side) of the sample.

Corning pyrex 7740 rods of various lengths were used as standards. An air blank was also run. The experiment was carried out at isothermal temperatures as a function of time. A minimum of 30 min was needed to achieve steady-state conditions. Heat capacity was determined using the new modulated DSC procedure [9]. Fig. 1 shows a plot of C_p versus temperature. The equation of the straight line is C_p (J/g °C)=1.328+0.0033T. Where T is the temperature in °C. In this direct method of determination, calibrations employing indium and alumina are carried out. Thermal diffusivity (α) is calculated from the equation:

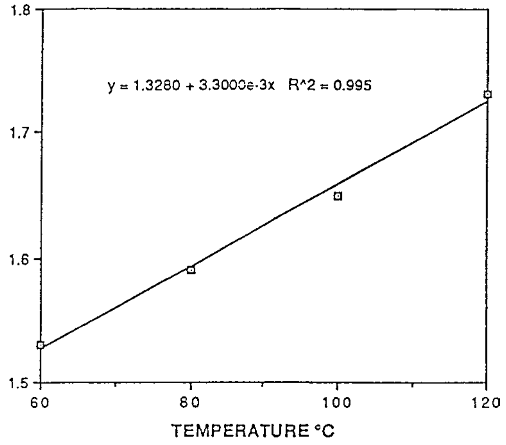

Fig. 1. MDSC specific heat capacity plot for PBXW-11 as a function of temperature.

$$\alpha = \frac{K}{C_p d}$$

where C_p is specific heat capacity (J/g °C), d the density (1.80 g/cc).

Table 2 list the thermal conductivity, heat capacity and thermal diffusivity.

3.4. Critical temperature for self-heating

According to Rogers [10], the critical temperature of an energetic material is the lowest constant surface

Table 2
Thermal flow property data for PBXW-11

Temperature (°C)	Thermal conductivity		C_p (cal/g °C)	α (cm^2/s)
	[cal/(cm s °C)]×10^{-4}	W/(m °C)		
130	11.8	0.496	0.419	0.00156
100	8.4	0.353	0.396	0.00118
80	7.3	0.306	0.380	0.00107
60	5.2	0.217	0.365	0.00084

temperature above which the material will self-heat to explosion. It may be calculated from the Frank–Kamenetskii equation.

$$T_c = \frac{E}{R}\ln\left[\frac{da^2QAE}{kRT_c^2\delta}\right]$$

where T_c is the critical temperature (K), R the gas constant=1.987 cal/(mol K), d the density=1.80 g/cc, a the radius (cm) of a sphere, cylinder, or the half-thickness of a slab, Q the heat of reaction for the self-heating process ~500 cal/g, A the frequency factor=7.65×10^{15} s^{-1}, E the activation energy=46,200 cal/mol, k the thermal conductivity=7.3×10^{-4} cal/(cm s °C) at 80°C, δ the shape factor=2.00 for cylinders.

Rogers and Pakulak have found fair to good agreement between calculated and experimentally determined critical temperatures, usually within 10°C. Substituting experimental values into the Frank–Kamenetskii equation it was found:

$$T_c = \frac{10109}{(26.04 + \log a^2 - \log T_c^2)}$$

Next the equation may be solved for T_c at different values for the radius. For a 1-in. diameter, radius=1.27 cm and T_c=10,109/(26.248−log T_c^2).

Now a trial and error procedure for calculating T_c is employed whereby an approximate value (pick-T_c) is inserted on the right side of the equation for T_c and the equation is solved for T_c on the left. This process is repeated until the value does not change significantly.

Pick-T_c	Calc-T_c
450 K	483 K
483 K	484 K

Therefore, T_c=484 K=211°C.

In a similar manner, values for T_c may be calculated at other radii. Critical temperature data are presented in Table 3. As the radii increases the critical temperature for self-heating decreases. A plot of log radius versus the reciprocal of the absolute temperature for self-heating is a straight line plot as seen in Fig. 2. The equation for the line is:

$$\log r = 9.914 + 4850\left(\frac{1}{\mathrm{K}}\right)$$

where K is Kelvin.

Table 3
Critical temperature for self-heating data for PBXW-11

Cylinder diameter (in.)	Cylinder radius (cm)	Critical temperature (°C)
1	1.27	211
2	2.54	197
4	5.08	184
8	10.16	171
16	20.32	159

3.5. Approximate time to explosion

Pakulak calculated the time to cookoff relationship from the equation:

$$\tau = \frac{a^2}{\alpha}$$

where τ is the thermal time constant, a the radius (cm), α the thermal diffusivity (cm^2/s).

The time to explosion is when $\tau_e/\tau=1$ where τ_e is the time to explosion. When $\tau_e=\tau$ then $\tau_e=a^2/\alpha$. Now the time to explosion may be calculated for cylindrical samples of PBXW-11, whose radii and critical temperatures are listed in Table 3. The thermal diffusivity values at these critical temperatures were unknown. Therefore, they were calculated using the equation of the line of thermal diffusivity versus temperature. Approximate time to explosion data for cylindrical samples of PBXW-11 at selected radii and critical

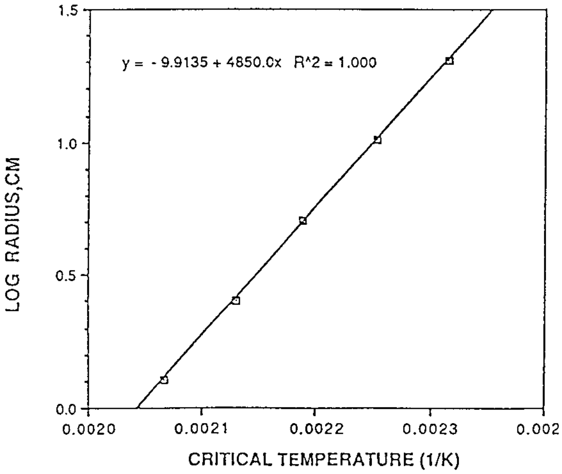

Fig. 2. Critical temperature for self-heating plot for PBXW-11 as a function of cylinder radius (cm).

Table 4
Approximate time to explosion data for PBXW-11

Cylinder diameter (in.)	Critical temperature (°C)	Thermal diffusivity (cm^2/s)	Time to explosion (min)
1	211	2.34×10^{-3}	11
2	197	2.20×10^{-3}	48
4	184	2.07×10^{-3}	207
8	171	1.94×10^{-3}	884
16	159	1.82×10^{-3}	3772

temperature are given in Table 4. A log time to explosion versus critical temperature plot is shown in Fig. 3. The equation for the line is:

$$\log \tau_e = 11.316 - 0.04882T_c$$

where T_c is the critical temperature.

3.6. Half-life determination

Assuming a first-order decomposition, the equation to determine the half-life is: $t_{1/2}=0.693/k$. For a half-life time of 60 min the rate constant is 0.693/60=0.01155. Substituting into the equation:

$$\log k = \log\ A - \frac{E_a}{2.3RT}$$

the value of k=0.01155 min^{-1}, $A=4.59\times10^{17}$ min^{-1}, E_a=46,200 ca/mol, R=1.987cal/(mol K) and solving for temperature, it was found to be 515 K=243°C. Now at a heating rate of 2°C/min the enthalpy for decomposition is 1989 J/g while at 5°C/min it is 2049 J/g (Fig. 4) using unsealed sample pans with a pin-hole in the cover in a helium atmosphere. To check the goodness of the kinetic constants for the decomposition the PBXW-11 was held isothermally at 243°C for 60 min, cooled to room temperature and then heated at 5°C/min through decomposition. For a first-order decomposition reaction the enthalpy should decrease to 50% of its original value [(1989+2049)/2] to ≈1009 J/g. A value of 1006 J/g was found (Fig. 5). This is in excellent agreement with the predicted enthalpy for half-life and confirms that the overall decomposition of PBXW-11 is first order.

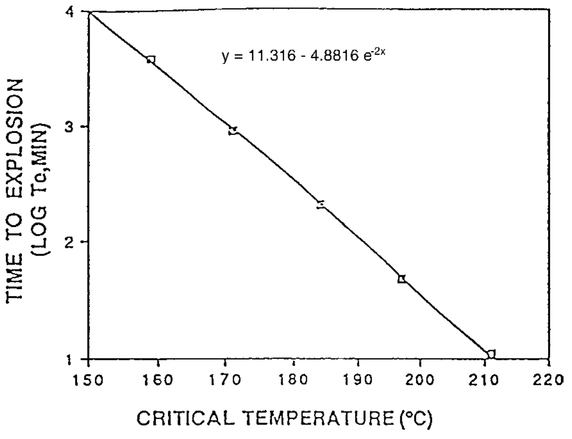

Fig. 3. Time to explosion plot for PBXW-11 as a function of critical temperature.

4. Conclusion

The thermal stability of PBXW-11 was determined by differential scanning calorimetry (DSC) and thermogravimetry (TG) by a variable heating rate method based on ANSI/ASTM E698-79. DSC runs were carried out in sealed and unsealed pans in helium while TG was in nitrogen. Activation energies and frequency factors for decomposition were calculated. In order to determine the 500 day cookoff temperature, it was also necessary to determine the thermal flow properties such as thermal conductivity, specific heat, and thermal diffusivity. These thermal flow values were used to calculate the critical temperatures for self-heating at various explosive diameters and approximate times to explosion at the critical temperatures.

The results of this study were:

- 500 day cookoff temperature was 135°C;
- kinetic constants for decomposition were an activation energy of 46.2 kcal/mol and a frequency factor of 7.65×10^{15} s^{-1};
- thermal flow properties are given in Table 2;

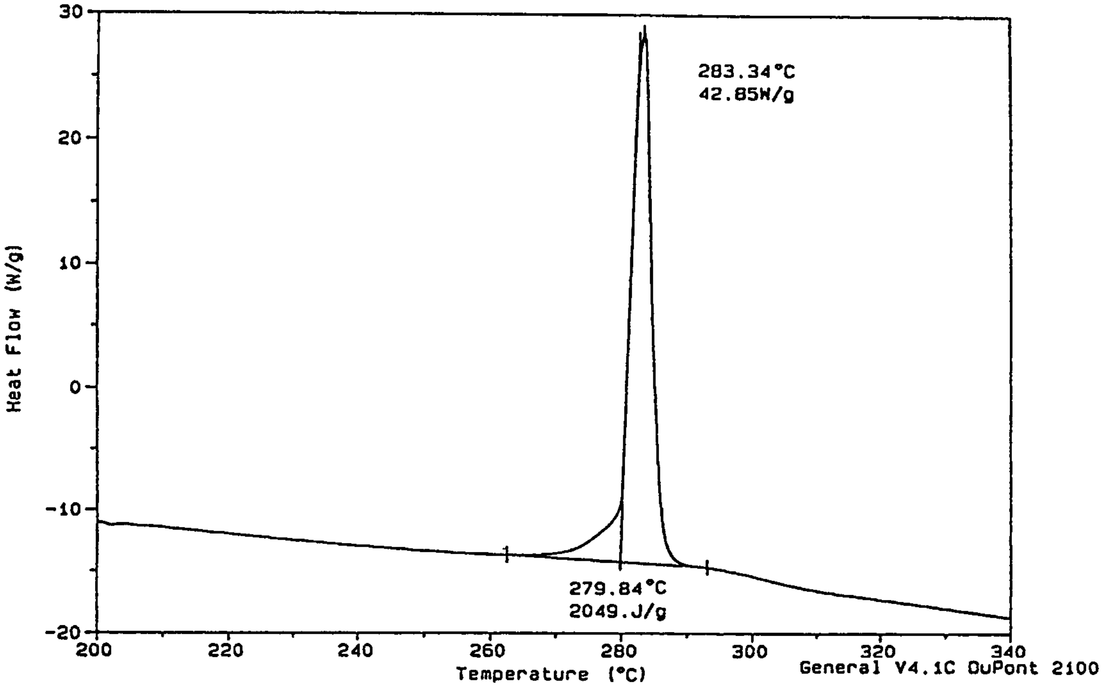

Fig. 4. DSC curve of PBXW-11 at 5°C/min in helium.

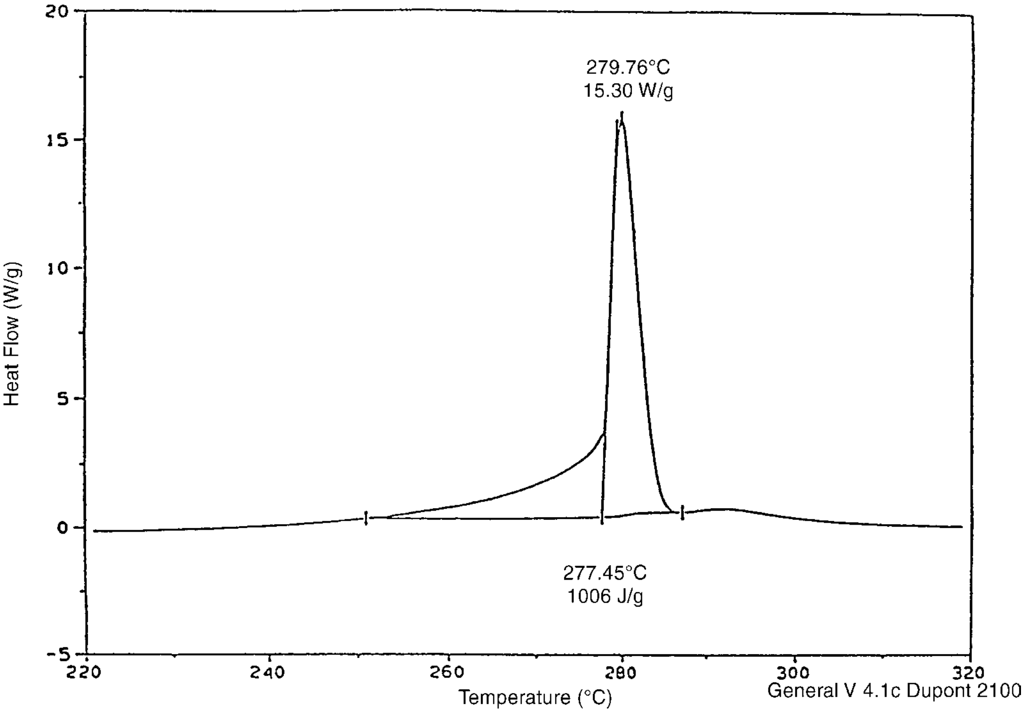

Fig. 5. DSC half life curve of PBXW-11 after 60 min at 243°C.

- critical temperatures are presented in Table 3;
- approximate times to explosion at various critical temperatures are given in Table 4; and
- half-life experiment confirmed that the overall decomposition of PBXW-11 is first order.

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