



Some Relationships Among Thermal Properties, Detonation Parameters and Sensitivity of Nitramine Fillers in Formex Based PBXs*

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Abstract. Thermal behavior and decomposition kinetics of formex-bonded PBXs based on some attractive cyclic nitramines (BCHMX, HMX, RDX and CL-20) were investigated by means of nonisothermal Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC). Besides, their detonation parameters have been calculated by EXPLO 5 code. It was found that the effect of formex polymer base on thermal decomposition of HMX is different from other cyclic nitramines, namely, the formex base could increase the activation energy of HMX while decrease that of others. Besides, the logarithm of volume heat of detonation for formex based explosives is linearly dependent on their time constant of initiation. Furthermore, on one hand, except for RDX, the heat of detonation decreases with the increase of activation energy, and the spark energy and impact energy of cyclic nitramine fillers decreases with the increase of the critical temperature of their PBXs. On the other hand, except for HMX, the rate constant of PBXs is linearly dependent on the impact sensitivity of their pure nitramine fillers.

Keywords: explosives, PBXs, detonation parameters

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1. INTRODUCTION

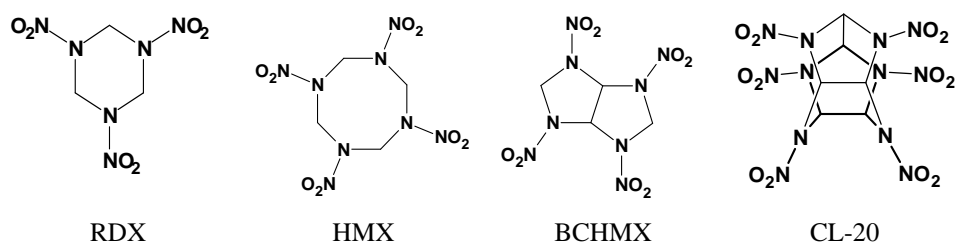
A polymer-bonded explosive or PBX is an explosive material in which explosive powder is bonded together in a matrix using typically 5-10% by weight of a synthetic polymer [1]. They are widely used in many military and civilian applications because of their high safety, processing ease and superior strength [2]. The next generation of PBX materials will be improved in terms of insensitivity and high energetic density combined with an enhanced mechanical integrity [3]. The development of energetic materials with improved detonation properties and low sensitivity is underway to meet superior performance requirements of PBXs, and they appear to be the future candidates to compete with the currently used high performance high energy materials such as 1,3,5-trinitro-1,3,5-triazinane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX). Actually, cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) are energy compounds of this kind [4-6].

In fact, thermal degradation of polymers plays an important role in the thermal response of many solid propellants and polymer bonded explosives [7, 8]. Felix et al. [9] have studied the effect of an addition of polymers, Kel F and Viton A, on the kinetics of the thermal degradation of a plastic bonded explosive. However, as one of prominent energetic candidates for RDX replacement, CL-20 and BCHMX have been used in many polymer based explosives [10-12], while still no data are available with regard to their thermal decomposition kinetics parameters. In particular, therefore, this paper will discuss some new findings with regard to the relationships among kinetic parameters, sensitivity and the detonation performance for PBXs containing BCHMX, HMX, RDX and CL-20. The calculations of the detonation parameters of all the samples were done by EXPLO 5 code [13].

2. EXPERIMENTAL

2.1. Preparation of Plastic explosives

BCHMX: cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (bicycle-HMX), which is a new polycyclic nitramine, was prepared by a continuous two step laboratory synthesis in our workgroup [6]. About 87% of BCHMX, HMX, RDX and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) by weight was bonded by 13% Formex matrix containing 25% styrene-butadiene rubber (SBR) plasticized by 75% oily material to form four new PBXs named as BCHMX-Formex, HMX-Formex, RDX-Formex and CL-20-Formex. The molecular structures of these cyclic nitramines are shown as scheme 1.



Scheme 1

2.2. Thermal properties

There are four kinds of samples used in the experiments which are BCHMX-formex, HMX-Formex, RDX-Formex and CL-20-Formex. They are studied with regard to the kinetics of thermal decomposition, using different heating rates Thermogravimetry (TG, Netzsch 209F3 instrument, Al_2O_3 crucible) and under a heating rate of 2.5, 5, 7.5 (with data collecting rate of 40 points per Kelvin) and $10^\circ\text{C}\cdot\text{min}^{-1}$ (with data collecting rate of 60 points per Kelvin). The test temperature range for TG was between $30\text{--}400^\circ\text{C}$, with the sample mass of about 1.35-1.45 mg under $30\text{ ml}\cdot\text{min}^{-1}$ dynamic nitrogen medium. Due to the length limit of this paper, the DSC and TG curves are not presented.

2.3. Sensitivity data

Impact and electric spark sensitivities data of the crystalline fillers of PBXs, i. e. RDX, HMX, BCHMX, HNIW and PETN, were taken from literature as presented in Table 1.

2.4. Detonation characteristics

The theoretical heats of detonation, Q_{det} , of the prepared samples of PBXs were calculated by the use of EXPLO 5 code [13]. In the case of EXPLO 5 code, the BKWS set of parameters for the BKW EOS was applied, these parameters are: $\alpha = 0.5$, $\beta = 0.298$, $\kappa = 10.50$, $\Theta = 6620$. The calculated Q_{det} values are (in kJ kg^{-1}) as follows [14]: for RDX-formex 5391, for HMX-formex 5465, for BCHMX-formex 5644, and for HNIW-formex 5726. Values of the experimental detonation velocity were taken from Ref. 14 and are presented in Table 1.

Table 1. A survey of results from VTS measurement and of data taken from the literature about detonation velocities and sensitivities of the explosives studied

PBXs	Equation of linearization			Experim. detonation velocity / density	Sensitivity of pure explosive filler			
	Slope k	intercept /kPa	R^2		Impact* / J		electric spark* / mJ	
RDX-formex	$0.0021 \pm 7.97E-6$	1.4344 ± 0.0012	0.9909	7711 / 1.56	5.58	[11]	216.4	[16]
RDX-formex	$0.0021 \pm 1.32E-5$	0.5770 ± 0.0020	0.9910	7711 / 1.56	5.58	[11]	216.4	[16]
HMX-formex	$0.0016 \pm 2.54E-5$	1.6863 ± 0.0039	0.9438	7986 / 1.61	6.37	[11]	236.4	[16]
HMX-formex	$0.0018 \pm 2.57E-5$	0.7478 ± 0.0039	0.9548	7986 / 1.61	6.37	[11]	236.4	[16]
BCHMX-formex	$0.0058 \pm 7.59E-5$	3.8295 ± 0.0115	0.9627	7922 / 1.59	2.98	[11]	148.7	[11]
BCHMX-formex	$0.0057 \pm 7.52E-5$	3.0915 ± 0.0114	0.9609	7922 / 1.59	2.98	[11]	148.7	[11]
HNIW-formex	$0.0009 \pm 8.63E-6$	2.0659 ± 0.0014	0.9532	8355 / 1.70	13.2	[15]	462.0	[17]
HNIW-formex	$0.0012 \pm 1.29E-5$	1.7394 ± 0.0021	0.9859	8355 / 1.70	13.2	[15]	462.0	[17]

Notes: Slope k in $\text{kPa g}^{-1} \text{min}^{-1}$; *, obtained from the references; Impact sensitivity is in J, electric spark in mJ, detonation in m.s^{-1} and density in g.cm^{-3} .

2.5. Calculation of kinetic parameters

In this paper, one of the most popular named modified Kissinger-Akahira-Sunose (KAS) equation [18] was used to calculate the activation energy:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) = \text{Const} - 1.0008 \frac{E_\alpha}{RT_\alpha} \quad (1)$$

where β_i is the heating rate, E_α activation energy and $T_{\alpha,i}$ the temperature in DTG or DSC curve at a certain conversion rate (α). Due to the large influence of experimental conditions on the data quality of the process “tails”, it is a common practice to consider only values of E_α obtained for the interval $\alpha = 0.3-0.7$ when calculating average value.

Based on the abovementioned average activation energy and preexponential factor, the rate constant at different temperature could be obtained by the following equation:

$$k(T) = A \exp\left(\frac{-E}{RT}\right) \quad (2)$$

where A is the pre-exponential factor and E is the activation energy. The corresponding kinetic parameters and the rate constant at the temperature of 170°C are obtained and summarized in Table 2.

Table 2. The calculated activation energies, critical temperatures, detonation velocities and heats of detonation of the explosives studied

Samples	$T_p/^\circ\text{C}$	log A	E_1	E_2	$T/^\circ\text{C}$	k	$T_b/^\circ\text{C}$	Q_{deton}	$S_p/^\circ\text{C}$
HMX-FORMEX	279.0	31.76	369.3	171.7	170.0	1.559E-12	224.7	5644	16.4
RDX-FORMEX	235.1	13.49	148.3	151.2	170.0	9.879E-05	201.4	5291	5.0
CL20-FORMEX	231.2	10.95	123.3	124.5	170.0	2.535E-04	207.8	5726	5.0
BCHMX-FORMEX	233.7	16.82	181.5	274.7	170.0	2.559E-05	231.4	5465	23.0

Notes: T_o , onset temperature of the peaks; A, preexponential factor, in s^{-1} ; T , attempted temperature for rate constant; k , rate constant (s^{-1}); T_b , critical temperature; E_1 and E_2 , Activation energy of PBXs (average value of $\alpha = 0.3 - 0.7$) and corresponding nitramines, in $\text{kJ}\cdot\text{mol}^{-1}$; T_p , peak temperatures; S_p , Peak shift on DSC curves at pressure of 0.1 MPa due to addition of Formex base (containing 25% styrene-butadiene rubber (SBR) plasticized by 75% oily material).

2.6. Calculation of critical temperature

The critical thermal decomposition temperature (T_b) is an important parameter required to insure the safe storage and process operations involving explosives, propellants and pyrotechnics. It is defined as the lowest temperature to which energetic materials may be heated without undergoing thermal decomposition. T_b may be calculated from the inflammation theory and appropriate thermokinetic parameters namely the pre-exponential factor by the following equations [19].

$$T_b = T_{eo} + \frac{1}{b} \quad (3)$$

First of all, one can easily obtain the onset temperature (T_{ei}) from the nonisothermal TG curves, the value of T_{eo} from the equation

$$T_{ei} = a_0 + a_1\beta_i + a_2\beta_i^2 + a_3\beta_i^3, i = 1-4 \quad (4)$$

the values of b from the equation

$$\ln \beta_i = \ln \left[\frac{A_0}{bG(\alpha)} \right] + bT_i \quad (5)$$

where b , a_0 , a_1 , a_2 and a_3 are coefficients, R is the gas constant; After the data (\hat{a}_i , T_i , $i=1, 2, \dots, L$) are fitted to Eq. (4) by the linear least-squares method on the computer, the value of b could be obtained from the slope ($\ln\beta_i$ versus T_i). Besides, the value of the onset temperature (T_{co}) corresponding to $\beta \rightarrow 0$ obtained by Eq. (4) is equal to a_0 . Thus, the critical temperatures of thermal explosion (T_b) calculated by Eq. (3) and summarized in Table 2.

3. RESULTS AND DISCUSSION

According to the sensitivity parameters obtained from the literature, as shown in Table (1), it is obvious that the drop energy needed to initiate the explosive crystals is much higher than that needed to initiate the Formex P1. The impact and spark sensitivity of the BCHMX is also higher than that of the other nitramines.

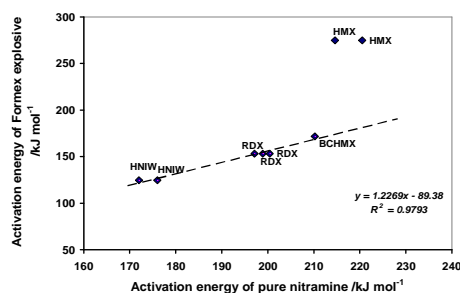


Fig. 1. Relation between the activation energies of thermal decomposition of the Formex bonded explosives and of their pure fillers

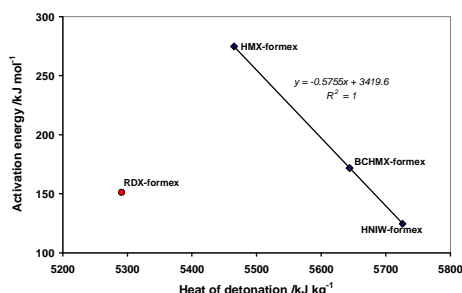


Fig. 2. Relationship between the activation energies of thermal decomposition and heats of detonation of the studied Formex bonded explosives

With regards to the calculated activation energies for pure nitramines and their Formex bonded explosives, except for HMX, a linear relationship represented by a straight line was found between them as shown in Fig. (1), which proves the effect of Formex polymer base on thermal decomposition of HMX is different from others. For HMX, the Formex base could increase the activation energy while the others are decreased by it. However, the relationship between the activation energy of these PBXs and their heat of detonation is a little bit different.

Except for RDX, the heat of detonation decreases with the increase of activation energy. It reveals that when the energy barrier increases, the heat of the detonation will decrease. RDX decomposes under liquid state, and its energy barrier affects the heat of the detonation in a different way.

It is reasonable that RDX-Formex may belong to some other nitramine group which decomposes in a liquid state such as TNAZ and TNT.

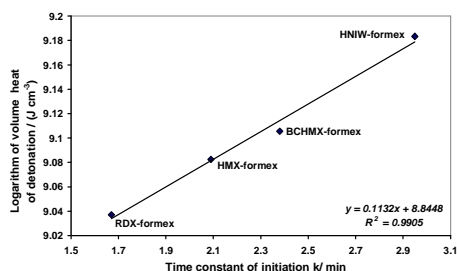


Fig. 3. The correlation of time constant of initiation with the volume heat of detonation for Formex bonded explosives

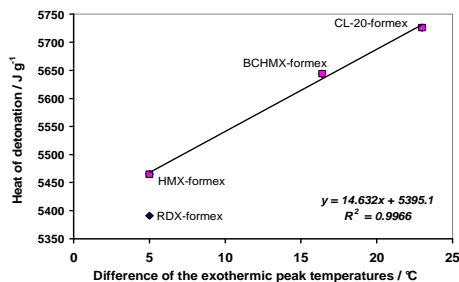


Fig. 4. The correlation of peak temperature shift with the heat of detonation for Formex bonded explosives

Interestingly, with regard to the thermal behavior, after comparing the time constant of initiation (k_i), obtained from the slope of linear regression of the onset temperature versus heating rate, with the volume heat of detonation ($Q_{\text{det}}\rho$) calculated by EXPLO 5, as shown in Fig. 3, a good linear correlation has been found. It was indicated that the logarithm of volume heat of detonation for formex based explosives is linearly dependent on the time constant of initiation for cyclic nitramine based PBXs. In fact, the low-temperature characteristics of PBXs (including the onset temperature or initiation temperature, kinetic parameters of low-temperature decomposition) could be correlated with detonating properties, because during detonation and initiation part of low-temperature decomposition, the effect of autocatalysis was excluded [21].

However, regarding the mutual comparisons of particular energetic materials, there are big differences between the exothermic peak temperatures of cyclic nitramines with their PBXs. There should be some relationship between the shifts of the peak temperatures (see Table 2) with the detonation properties. The correlation of the heat of detonation with the peak temperature shift is shown in Figure(4). It was found that, except for RDX-Formex, the shift of peak temperature is linearly dependent on the heat of detonation. Similar to the abovementioned energy barrier, this fact could be interpreted by their different decomposition states, only RDX-Formex decomposed in a complete liquid state, while the others decomposed in solid state (HMX-Formex and CL-20-Formex) or partially liquid state (BCHMX-Formex). The peak temperature of RDX-Formex is greatly affected by the heat absorption of its melting process, thus its peak shift may have a different correlation coefficient with the heat of detonation.

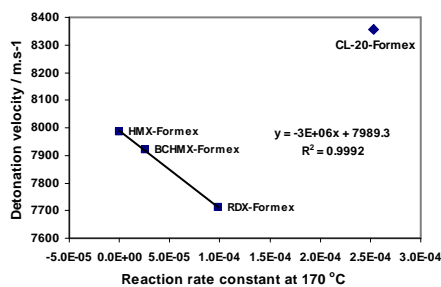


Fig. 5. Relationship between the detonation velocities and decomposition rate constant of the samples studied

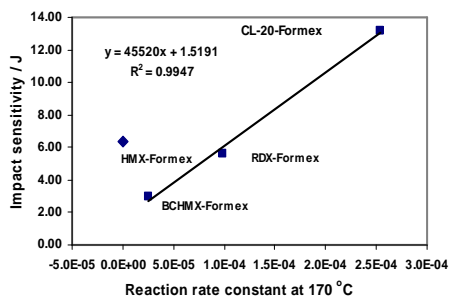


Fig. 6. Relationship between the impact sensitivity and decomposition rate constant of the samples studied

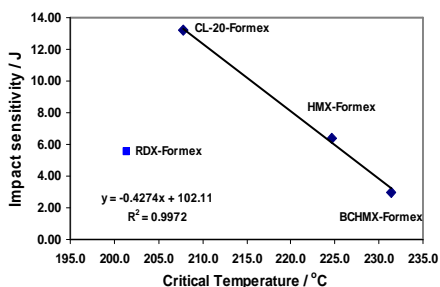


Fig. 7. Relationship between the impact energy and critical temperature for initiation of the samples studied

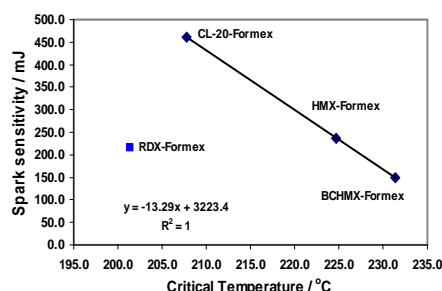


Fig. 8. Relationship between the spark energy and critical temperature for initiation of the samples studied

In addition to the detonation parameters, the sensitivity of the nitramine fillers also has some correlations with the thermal properties. In fact, except for hot spot theory, various methods based on bond dissociation concerning energy, electronic structure properties and energetic transfer rates have been proposed to evaluate and interpret the impact and spark sensitivity of energetic compounds. Though the sensitivities were correlated with direct and indirect molecular properties such as oxygen balance, electronegativity, vibrational states, partial atomic charge, etc., they only show a kind of rough correspondence to external stimuli.

As a matter of fact, impact and spark sensitivity are a function of molecular structure [20, 21] and decomposition pathways together. As this paper indicates (Figs. 1, 6, 7 and 8) the molecular structure (see scheme 1) has a dominating influence also in the initiation of the nitramine mixtures with polymeric binders. The polymeric binder components are projected into this influence predominantly through their affecting on physical state of the given nitramine (mainly through its solubility in plasticizers) [22].

An exact standard for sensitivity, therefore, should be experimentally established for all of the energetic compounds and their mixtures, which was once proposed by Shackelford [23] and Zhang [24] but not successfully achieved. The relationships among the sensitivity, the critical temperature and rate constants are established herein, as shown in Figures (6), (7) and (8).

The rate constant is a parameter that determines the decomposition reaction rate at a certain temperature (170°C was selected herein), which should be in the range of namely decomposition process (initial to end temperature of thermolysis). It is interesting that except for HMX, the rate constant of PBXs is linearly dependant on the impact sensitivity of their pure nitramine fillers. The higher impact energy (more difficult to initiate by impact stimuli), a larger rate constant could be obtained. In addition, with regard to the critical temperature, except for RDX, the spark energy and impact energy of cyclic nitramine fillers decreases with the increase in the critical temperature of their PBXs. It was revealed that formex bases could make the most sensitive nitramine stable. Therefore, in fact, the typical sensitivity data could be equivalent to the absorption of thermal energy including inner energy. For RDX, the melting process is not included in the evaluation of the critical temperature, thus its PBX is not in the same group. Though so many correlations have been found for the thermal properties with the detonation performances and sensitivities of nitramine based PBXs, there is still much work that needs to be done, providing the same data on some other polymer bonded explosives containing these nitramines, which will make these kind of correlations more reliable and persuasive.

4. CONCLUSIONS

The thermal decomposition processes of formex bonded explosives containing BCHMX, HMX, RDX and CL-20 are recorded using DSC and TG techniques. The kinetic parameters were calculated by a modified isoconversion KAS method and some relationships were found amongst their thermal properties, sensitivities and detonation performances. The following conclusions could be made:

1) The effect of a formex polymer base on the thermal decomposition of HMX is different from other cyclic nitramines, where the formex base could increase the activation energy of HMX, it also decreases that of others.

2) The logarithm of volume heat of detonation for formex based explosives is linearly dependent on the time constant of initiation.

3) Except for RDX, the heat of detonation decreases with the increase of activation energy, and the spark energy and impact energy of cyclic nitramine fillers decreases with the increase of critical temperature of their PBXs.

4) Except for HMX, the rate constant of PBXs is linearly dependent on the impact sensitivity of their pure nitramine fillers.

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