



The Influence of the Semtex Matrix on the Thermal Behavior and Decomposition Kinetics of Cyclic Nitramines

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Abstract: The thermal behavior and decomposition kinetics of Semtex 10 polymeric matrix (Semtex) bonded PBXs containing RDX (1,3,5-trinitro 1,3,5-triazinane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane), BCHMX (cis-1,3,4,6-tetranitrooctahydroimidazo [4,5-d] imidazole), HNIW (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) have been investigated by means of non-isothermal TG and DSC techniques. It is shown that only a single decomposition process occurs for RDX-SE and HMX-SE whilst an obvious two-step process occurs for CL-20-SE and BCHMX-SE. The onset of the exotherms were observed at 210.6, 239.7, 279.2 and 229.4 °C with the peak maxima at 232.2, 249.4, 280.4 and 240.2 °C, and energy changes of 1808, 2140, 612 and 1757 J·g⁻¹ for RDX-SE, BCHMX-SE, HMX-SE and CL-20-SE, respectively. It has been found that the Semtex matrix has little influence on the activation energy distribution for RDX, BCHMX and ε-CL-20. The activation energies for BCHMX-SE and CL-20-SE decomposition are almost independent of the degree of conversion, with mean values of 159.6 ± 1.9 and 187.3 ± 1.8 kJ·mol⁻¹. It has been proved that Semtex and Viton A are better binders than C4 and Formex for ε-CL-20 and RDX based PBXs in terms of their greater thermal stability, and Formex is a poor binder for BCHMX.

Keywords: cyclic nitramines, thermal decomposition, activation energy, Semtex, PBX

Introduction

The next generation of polymer-bonded explosives (PBXs) need to be improved in terms of insensitivity and higher energetic density properties, combined with enhanced mechanical integrity [1]. The development of energetic materials with improved detonation properties and lower sensitivity is continuing to meet the superior performance requirements of PBXs, and there appear to be several future candidates to compete with the currently used high performance, high energy materials such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and β -1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (β -HMX). In fact, *cis*-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX, bicycle-HMX) and ϵ -2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (ϵ -CL-20) are energetic compounds of this kind [2-4]. The prominent energetic substitutes for RDX, namely BCHMX and CL-20 have been used and evaluated in several kinds of PBXs [5-8]. In order to study the compatibility, thermal reactivity and detonation performances of such new energetic fillers when introduced in PBXs, it is essential to study them initially in the currently used polymeric bases, including the polymer matrices of Semtex[®], which is a general-purpose, plastic explosive containing RDX and PETN. It is commercially available at Explosia Company in the Czech Republic [9] and has been used in commercial blasting and demolition, and in certain military applications. Semtex[®] became notoriously popular with terrorists because it was, until recently, extremely difficult to detect [10]. For its military use it was manufactured originally under the name B1. It has been manufactured since 1964 in Semtín, which is a suburb of Pardubice in the Czech Republic, and was therefore labelled firstly as Semtex 1A (a combination of 'SEMTín' and 'EXplosive'), since 1967 as Semtex H and since 1987 as Semtex 10. The Semtex[®] for military applications contains 14% of acrylonitrile-butadiene rubber, as the binder (black color), whilst that for civilian uses contains 16-17% styrene-butadiene, plasticized with mineral oil. Semtex is known for its excellent resistance to abrasion, water, and many kinds of oils and acids. Semtex[®] is very similar to the C4 plastic explosive, where polyisobutylene plasticized with dioctyl sebacate (see Scheme 1) is used as the binder. However, Semtex[®] is usable over a greater temperature range than the other plastic explosives, as it remains plastic between -40 and +60 °C [11].

The polymer matrix usually plays an important role in the thermal initiation of the corresponding solid propellants and also high energy PBXs [12, 13]. The influence of Kel F800 and Viton A on the thermal degradation kinetics of the corresponding plastic bonded explosives containing keto-RDX has been studied [14]. Combined with their previous investigations, these authors pointed

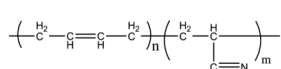
out that the binder plays a significant role in facilitating the condensed phase reactions and in reducing the contribution of the competing gas phase processes during thermolysis of these PBXs. We have already investigated the thermal decomposition kinetics of Formex P1 [15], C4 [16] and Viton A [17] bonded PBXs containing the above mentioned cyclic nitramines by DSC and TG techniques, and their low temperature thermolytic behavior by the STABIL method [18, 19]. At the same time, the influence of the C4 matrix on the thermal stability of ϵ -CL-20 has also been studied [20, 21]. Moreover, the mutual relationships between sensitivity parameters and detonation performance of Formex P1, C4 and Viton A bonded PBXs containing such cyclic nitramines are being systematically investigated by our group [22-25]. As a well-known binder, the Semtex matrix has been widely used in PETN and RDX based plastic explosives. However, although they are very important factors for performance prediction and safety evaluation, the influence of the Semtex matrix on the thermal behavior, stability and decomposition kinetics of HMX, BCHMX and ϵ -CL-20 fillers are still not well known. This paper will discuss therefore some new findings, together with previously published results concerning the influence of the Semtex matrix on the thermal behaviour of the BCHMX, β -HMX, RDX and ϵ -CL-20 nitramines.

Experimental

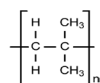
Materials

BCHMX was prepared by a two-step, continuous, laboratory synthesis in our group [4]. About 85 wt% of BCHMX, β -HMX, RDX or ϵ -CL-20 was bonded with 15% binder Semtex [26]. Semtex, produced by Explosia a. s., contains 25% of acrylonitrile-butadiene rubber (NBR) plasticized with a non-energetic plasticizer. The explosive was mixed with the binder matrix at a temperature of 70 °C for 70 min in vacuum using a computerized mixer, Plastograph BRABENDER. The samples prepared were extruded by means of a 40 mm screw extruder to obtain long charges of plastic explosive of 16 mm diameter. For the sake of simplicity, PBX samples based on the Semtex binder in this paper will be named as BCHMX-SE, HMX-SE, RDX-SE and CL-20-SE.

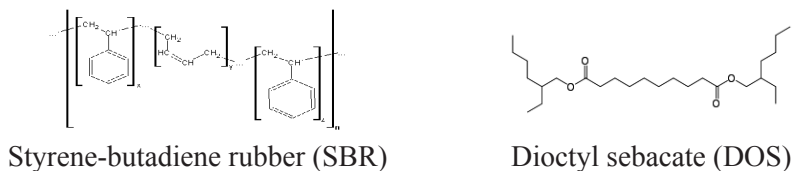
The molecular structures of the main components of the Semtex, C4 and Formex P1 matrices are shown in Scheme 1.



Nitrile rubber (NBR)



Polyisobutylene (PIB)



Scheme 1. The molecular structures of the main components of the Semtex, C4 and Formex P1 matrices.

Experimental techniques

The samples were studied with regard to their thermal decomposition kinetics using different heating rate Thermogravimetry (TG, Netzsch 209F3 instrument, Al_2O_3 crucible) using the heating rates of 1, 2, 3, 4, 5 (with a data collecting rate of 40 points per Kelvin), 7 and $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ (with a data collecting rate of 60 points per Kelvin). The test temperature range for TG was $30\text{--}300\text{ }^\circ\text{C}$, with a sample mass of 1.85–2.35 mg under a $30\text{ mL}\cdot\text{min}^{-1}$ dynamic nitrogen atmosphere. Their heat flow properties was also recorded by the technique of Differential Scanning Calorimetry (DSC, Netzsch 200F3 instrument, aluminum pan with a pin hole cover), which was performed under a dynamic nitrogen atmosphere at a pressure of 0.1 MPa. The sample mass for DSC was about 1.5 mg (heating rate, $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$; temperature range $40\text{--}350\text{ }^\circ\text{C}$).

Results and Discussion

TG/DTG studies

The TG/DTG curves of RDX-SE, BGHMX-SE, and HMX-SE at the heating rates of 1, 2, 3, 4, 5, 7 and $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ were recorded (see Figure 1, a-d). It was observed that a single decomposition process occurs for RDX-SE and HMX-SE, whilst an obvious two-step process occurs for the mixtures of BCHMX-SE and CL-20-SE, especially at lower heating rates (see shoulder of peak in Figure 1, b-d). A similar two-step decomposition trend was also found for pure BCHMX [8], but only a one-step process for the BCHMX-Formex mixture [15]. In order to make a quantitative comparison, the characteristic parameters of these TG/DTG curves are summarized in Table 1.

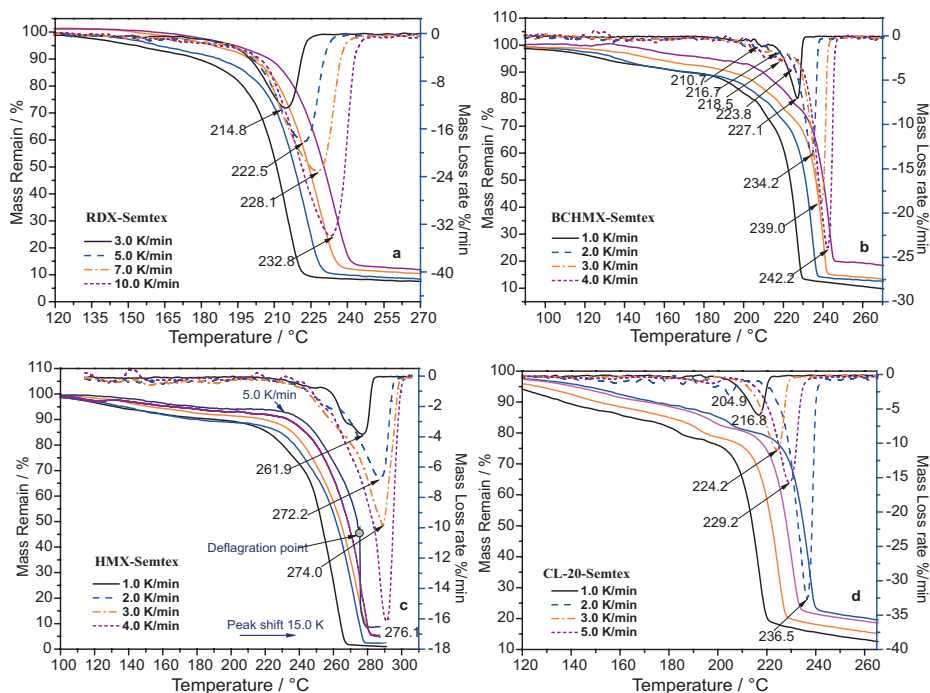


Figure 1. TG/DTG curves of Semtex bonded PBXs at heating rates of 1.0, 2.0, 3.0, 4.0, 5.0, 7.0 and 10.0 °C·min⁻¹.

From Table 1, it was found that for Semtex bonded PBXs, their limits of rates of mass loss are very different, whilst they are comparable when Viton A is used as the binder [17]. Moreover, their peak temperatures and rates of mass loss are very dependent on the heating rate, except in the case of RDX-SE. For BCHMX-SE and CL-20-SE, it is obvious from the DTG curves that at the heating rate of 1.0 K·min⁻¹, the initial step of the decomposition starts at around 218 and 210 °C, respectively, with a slow mass loss of about 24%, followed by a rapid mass loss of about 62% and 67%. For RDX-SE and HMX-SE, only a one-step process with a mass loss of 85-88% was observed at higher heating rates (>3 °C·min⁻¹). For HMX based PBXs, their decomposition mechanism is very dependent upon the heating rate [15-17]. The decomposition peaks may overlap with each other at higher heating rates but be well separated at lower heating rates. It can be seen from Figure 1c that there are shoulder peaks on the DTG curves at the heating rates of 1 and 2 °C·min⁻¹. Even though their decomposition processes are very different, their total mass losses are very close to each other for all these materials, which is between 82-90% at all heating rates studied.

Table 1. The kinetic parameters from the non-isothermal TG data of Semtex bonded PBXs containing different cyclic nitramines

PBXs Gradients	$\beta /$ $^{\circ}\text{C} \cdot \text{min}^{-1}$	TG curves				DTG peaks			
		$T_{\text{ot}}/^{\circ}\text{C}$	$T_{\text{i}}/^{\circ}\text{C}$	Mass loss / %		L_{max} $\% \cdot \text{min}^{-1}$	$T_{\text{p}}/^{\circ}\text{C}$		$T_{\text{oe}}/^{\circ}\text{C}$
				Stage 1	Stage 2				
RDX-SE	3.0	200.2	174.3	-84.27	-	-12.51	214.8		228.5
	5.0	205.8	174.6	-82.56	-	-18.12	222.5		236.9
	7.0	209.0	175.2	-85.45	-	-23.02	228.1		244.3
	10.0	215.3	175.8	-84.73	-	-33.98	232.8		249.4
BCHMX-SE	1.0	218.9	200.8	-24.66	-62.33	-7.06	210.7	227.1	232.0
	2.0	226.4	201.2	-25.09	-65.10	-13.58	216.7	234.2	239.9
	3.0	232.2	202.0	-25.39	-62.27	-18.86	218.5	239.0	245.6
	4.0	230.0	202.9	-21.43	-58.84	-23.97	223.8	242.2	249.0
HMX-SE	1.0	244.4	211.8	-86.17	-	-3.83	261.9		270.9
	2.0	252.3	212.9	-90.26	-	-6.74	272.2		282.1
	3.0	251.8	213.5	-88.01	-	-9.86	274.0		285.5
	4.0	259.4	214.7	-85.78	-	-16.17	276.1		288.2
CL-20-SE	1.0	210.1	179.4	-24.26	-67.13	-5.88	184.1	216.8	223.2
	2.0	217.9	183.3	-20.83	-66.56	-10.94	191.9	224.2	231.0
	3.0	223.2	187.3	-18.48	-63.03	-15.74	197.2	229.2	237.9
	5.0	230.9	190.7	-17.47	-65.70	-32.69	204.9	236.5	244.8

Note: T_{ot} – onset temperature of decomposition; T_{oe} – onset temperature of the end of decomposition; T_{i} – the initial temperature for thermal decomposition; T_{p} – the peak temperature of mass loss rate; Mass loss – from initial temperature to the end temperature of the DTG peak; L_{max} – the maximum rate of mass loss.

The corresponding α - T curves are obtained (see Figure 2) by integration of the DTG peaks. It was found that all of the decomposition curves basically obey the sigmoidal trend. However, in the case of the HMX-SE material, the shape of the determined dependencies of α - T largely changes with the heating rate, due to the fact that kinetically controlled decomposition occurs at lower heating rates, and a rapid deflagration reaction occurs at higher heating rates (e.g. $5^{\circ}\text{C} \cdot \text{min}^{-1}$, see Figure 1c). As a matter of fact, a rapid deflagration reaction was also found for Formex P1, C4 and Viton A bonded PBXs containing BCHMX, ϵ -CL-20 and β -HMX when the heating rate was greater than $5^{\circ}\text{C} \cdot \text{min}^{-1}$ [15-17]. It has also been found that with regard to CL-20-Formex [15], very sharp DTG peaks are observed, indicating ‘burning or deflagration kinetics’ controlled the reaction mechanism at $5^{\circ}\text{C} \cdot \text{min}^{-1}$, whilst a relatively slow kinetically controlled, decomposition reaction was observed for CL-20-SE at the same heating rate. This reveals that the Semtex and Formex matrices affect the thermal behavior of cyclic nitramines differently from the other matrices. α - T curves are very important for the evaluation of kinetic parameters at different degrees of conversion. Usually, for reliable kinetic evaluation, it is necessary to apply multiple heating rates with a wide dynamic range [27]. However, for most PBXs, especially for those containing high energy density fillers including BCHMX, ϵ -CL-20 and β -HMX, the situation will be complicated. On the one hand, the decomposition

processes of such PBXs depend largely on the heating rate (*e.g.* HMX-Formex [15], HMX-C4 [16], HMX-Viton A [17] and HMX-Semtex). On the other hand, kinetically controlled thermal decomposition could not be realized at slightly higher heating rates (*e.g.* $5.0\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$). Hence the kinetic evaluation for such energetic materials would be limited to a very narrow range of heating rates (*e.g.* $1.0\text{--}4.0\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$). For HMX-SE in particular, only data from the curves at 2.0 , 3.0 and $4.0\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ could be used in isoconversional kinetic calculations in order to obtain acceptable correlation coefficients.

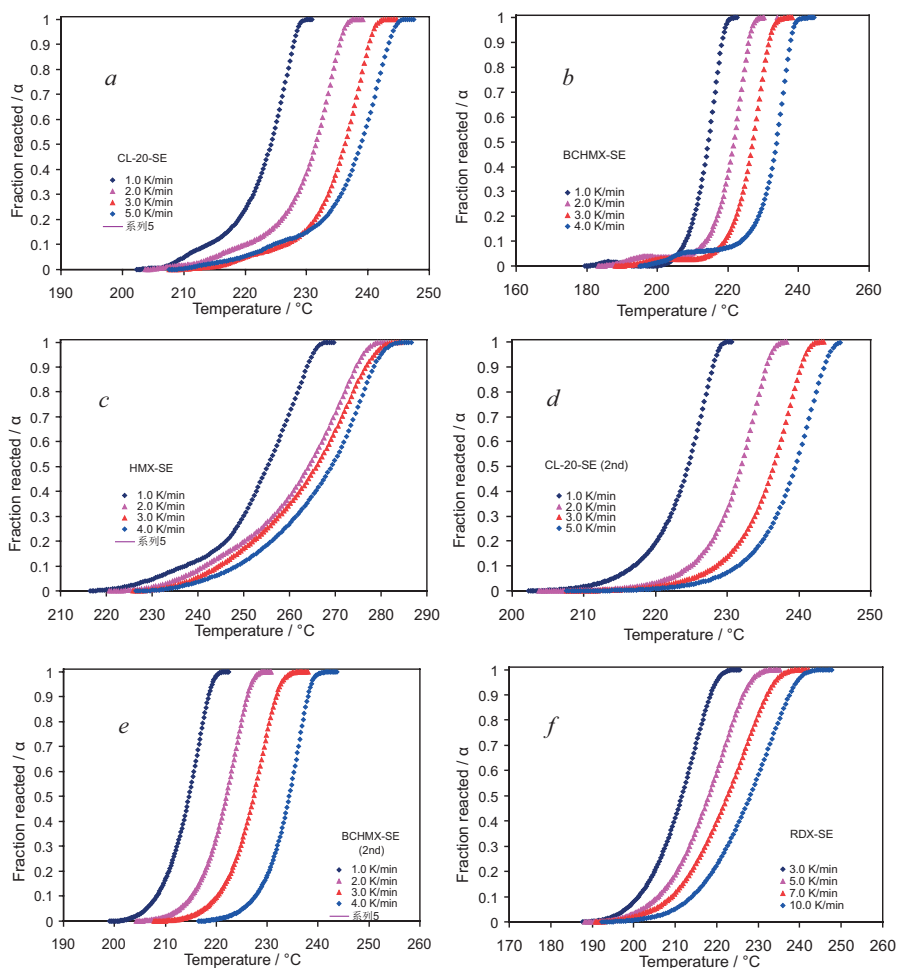


Figure 2. The α - T curves of Semtex bonded PBXs containing different cyclic nitramines at the heating rates of 1.0 , 2.0 , 3.0 , 4.0 , 5.0 , 7.0 and $10.0\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

It is shown from Figures 2a and b that, with regard to CL-20-SE and BCHMX-SE, there are some mutual interactions between the different decomposition steps, especially at higher heating rates, where peaks are partially overlapped. This will cause huge errors during kinetic evaluation by the model-free method if such interactions are not taken into account [27]. It is true that the model-free method does provide correct predictions for temperature conditions where no overlapping occurs or for well-separated peaks [28]. In order to eliminate such sources of error, the overlapped peaks should be separated [21]. One of the effective ways of peak separation is by curve fitting. PeakFit (Version 4.12) software is appropriate and recommended for this purpose. During curve fitting, one important step is the selection of a proper fitting function. It has been suggested that the Fraser-Suzuki function (Eq. 1) allows fitting of asymmetric peak curves for most of the complex, multi-step, solid state reactions [29], such as the thermal decomposition of PBXs [13].

$$y = a_0 \exp \left[- \ln 2 \left(\ln \left(1 + 2a_3 \frac{x - a_1}{a_2} \right) / a_3 \right)^2 \right] \quad (1)$$

where: a_0 , a_1 , a_2 , and a_3 are amplitude, position, half-width and asymmetry of the curve, respectively. In this way, the experimental curves of CL-20-SE and BCHMX-SE were successfully fitted and separated. Here only the second peaks are shown as Figures 2d and e, because only the influence of the Semtex matrix on the distribution of activation energies for the major step in the decomposition of the nitramines will be considered in this paper.

DSC studies

The mass loss processes can be compared with the enthalpy changes in the DSC curves. The samples were encapsulated in an aluminum pan with a pin hole and measurements were performed under identical conditions for both the pure energetic materials and their Semtex bonded mixtures. The curves obtained are shown in Figure 3 and the characteristic parameters are summarized in Table 2.

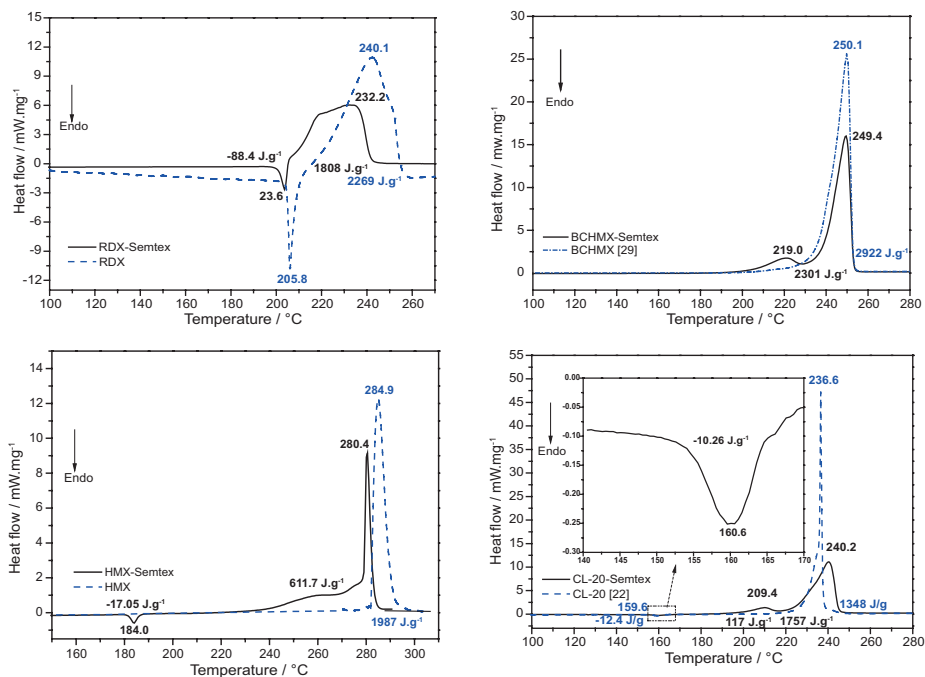


Figure 3. The DSC curves of the Semtex bonded PBXs containing cyclic nitramines at a heating rate of $5.0\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ (pressure 0.1 MPa).

According to Figure 3, initially paying attention to the pure energetic materials, it can be seen that their exothermic peaks are well formed except for ϵ -CL-20, showing signs of kinetically controlled decomposition processes. If we then look at the Semtex based mixtures of these compounds, the second stages of HMX-SE and BCHMX-SE decomposition exhibit very similar peaks to the corresponding pure fillers, due to rapid heat evolution associated with extremely fast decomposition kinetics. However, the presence of Semtex mitigated the fast decomposition process of ϵ -CL-20. In addition, it can be seen that for all of the materials studied except CL-20-SE, the peak temperatures for the Semtex mixtures are shifted to lower values. For CL-20-SE the behaviour is the same as with a Viton A binder [17]. We have also found that BCHMX is less chemically compatible with Viton A than the other nitramine fillers, resulting in much lower thermal stability and heat release [17]. Here the results are different; the Semtex matrix is very compatible with BCHMX and less compatible with RDX according to the evaluation criteria by the DSC method (here with a peak shift of around $8\text{ }^{\circ}\text{C}$) [30]. According to Table 2, if we compare the decomposition enthalpies, those for the Semtex mixtures are lower than those for the pure energetic fillers except for

CL-20-SE, which is slightly higher. For HMX-SE, the enthalpy is significantly lower than for the pure filler, due not only to the presence of 9.0% inert material (Semtex 200). Both of these observations could probably be explained by the involvement of deflagration for pure CL-20 and HMX-SE, where the heat release is so rapid that it cannot be properly recorded by the DSC sensor.

Table 2. DSC Parameters of Semtex bonded PBXs containing cyclic nitramines at a heating rate of $5.0\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$

Samples	Endothermic peaks				Exothermic peaks			
	$T_o/ ^{\circ}\text{C}$	$T_p/ ^{\circ}\text{C}$	$T_e/ ^{\circ}\text{C}$	$\Delta H_1/\text{J}\cdot\text{g}^{-1}$	$T_o/ ^{\circ}\text{C}$	$T_p/ ^{\circ}\text{C}$	$T_e/ ^{\circ}\text{C}$	$\Delta H_2/\text{J}\cdot\text{g}^{-1}$
RDX	204.1	205.8	210.2	-286.2	217.2	240.1	260.1	2269
RDX-SE	201.2	203.6	205.1	-88.4	210.6	232.2	241.5	1808
BCHMX	-	-	-	-	239.5	250.1	253.2	2922
BCHMX-SE	-	-	-	-	206.6	219.0	227.2	162
					239.7	249.4	253.0	2140
HMX	179.2	181.5	186.3	-41.3	281.6	284.9	297.1	1987
HMX-SE	181.8	184.0	185.9	-17.5	279.2	280.4	282.9	612
ϵ -CL-20	155.4	159.6	163.8	-12.4	235.7	236.6	237.3	1348
ϵ -CL-20-SE	155.8	160.6	164.3	-10.3	199.9	209.4	214.9	117
					229.4	240.2	244.8	1757

Note: T_o , onset temperature of the peak; T_p , peak temperature of thermal event; T_e , end temperature for heat change; ΔH_1 , heat absorption; ΔH_2 , heat release.

Another effect that can be observed in the DSC curves of CL-20-SE and HMX-SE is the small endothermic peak, at 159.6 and 181.5 $^{\circ}\text{C}$ respectively, corresponding to crystal transformations of ϵ -CL-20 (ϵ to γ) and β -HMX (β to δ). With regard to RDX-SE and BCHMX-SE, there are no corresponding endothermic peaks because RDX and BCHMX are not polymorphic. It is well-known that two major conversions occur during the linear heating of pure ϵ -CL-20: a solid-solid phase transition from ϵ - to γ -polymorph at 160-170 $^{\circ}\text{C}$, followed by thermal decomposition of the γ - polymorph [31]. On the one hand, the peak temperature and enthalpy of CL-20-SE for this transition is almost the same as with that of pure ϵ -CL-20, indicating that the Semtex polymer matrix has little influence on the polymorphic transitions. However, the corresponding endothermic peaks for ϵ -CL-20 bonded by Formex [15], C4 [16], and Viton A [17] polymer matrices were found to be almost identical, but shifted to around 168 $^{\circ}\text{C}$. This reveals that the stability of the ϵ -polymorph of CL-20 can be improved by mixing with these polymer matrices. On the other hand, the Semtex matrix can increase the peak temperature and decrease the enthalpy of the polymorphic transition of β -HMX. Under the influence of Semtex, the transition temperature shifted from 181.5 to 184.0 $^{\circ}\text{C}$. It has been found that for coarse HMX, a phase transition from β to δ can be clearly observed at about 160-170 $^{\circ}\text{C}$, whilst it occurred at 170-190 $^{\circ}\text{C}$ for fine β -HMX [32]. It is, therefore, reasonable that this conversion was found

to occur at around 184 °C in this paper because fine β -HMX was used. It is interesting that the exothermic peak temperature of ϵ -CL-20-SE is higher than that of the pure reduced sensitivity (RS)- ϵ -CL-20 (238.4 °C) [20], indicating that the inert Semtex polymer matrix has a positive influence on its thermal stability. In the case of RDX-SE, an endothermic peak is observed at 203.6 °C, which should correspond to the melting of RDX (a similar peak is also be found for pure RDX at the slightly higher temperature of 205.8 °C, which confirms that both RDX and the RDX-based PBX decompose in the liquid state).

Thermal decomposition kinetics

Kinetic parameters obtained by the Kissinger method

The kinetics of the thermal decomposition of Semtex bonded PBXs at different temperatures ranges were studied by non-isothermal TG (the mass loss was recorded with respect to temperature). The kinetic parameters were initially calculated according to the traditional Kissinger method based on the shift of the peak temperatures presented in Table 1. The corresponding calculation results, together with data from the literature, are summarized in Table 3.

According to Table 3, it is found that the errors for the thermolysis kinetic parameters of β -HMX based PBXs are much higher those of the others. Such large errors (over 10%) are caused by the huge variation in decomposition mechanisms under different heating rates. Because these errors were caused by the poor correlation between the peak temperatures and the heating rates, they could reflect the dependence of the reaction mechanism on the temperature gradient of the samples. As mentioned above, for β -HMX, BCHMX and some types of ϵ -CL-20 based PBXs, the kinetically controlled decomposition processes occurring at lower temperature gradients could change to rapid mass loss associated with burning or deflagration kinetics at higher temperature gradients. If burning or deflagration happened within the range of heating rates used, the kinetic results for this material could not be considered physically meaningful (*e.g.* HMX-Semtex, HMX-Formex [15] and HMX-C4 [16] at more than 5 °C·min⁻¹). With regard to pure ϵ -CL-20 and its C4 and Semtex PBXs, the activation energies of the initial step are much lower than those of the second step. Under the influence of Formex and Viton A, the two-step decomposition process of BCHMX changes to a single step mechanism, whilst the one-step mechanism for ϵ -CL-20 changes to a two-step decomposition process under the influence of C4 and Semtex binders [21, 28]. The activation energy of RDX bonded by Semtex is much lower than when bonded by the other binders, and the activation energy of CL-20 bonded by the Formex binder is the lowest.

Table 3. Comparison of the kinetic parameters obtained by the Kissinger method for Semtex and other PBXs containing cyclic nitramines

Sample	Temperature range		Arrhenius parameters			
	$T_i / ^\circ\text{C}$	$T_e / ^\circ\text{C}$	$E_a / \text{kJ}\cdot\text{mol}^{-1}$	$\log A / \text{s}^{-1}$	r	k at 230 $^\circ\text{C}$
RDX [34] ^a	220	240	157.0	14.76	0.9901	2.85E-02
RDX-Estane (RXE9505) [34] ^a	215	235	189.0	18.06	0.9929	2.71E-02
RDX-VA (RXV9505) [34] ^a	215	230	201.0	19.76	0.9906	7.69E-02
RDX-VA [17]	220	235	177.2±12.8	16.41±2.74	0.9948	1.02E-02
RDX-SE	214	233	127.2±4.3	11.13±1.38	0.9988	0.83E-02
RDX-C4 [16]	218	236	197.7±19.1	18.65±3.58	0.9907	1.31E-02
RDX-Formex [15]	216	232	179.8	16.74	0.9950	1.17E-02
β-HMX [35]	265	274	227.1	19.70	-	13.0E-05
β-HMX-VA [17]	263	277	244.9±27.8	21.06±4.41	0.9873	4.24E-05
β-HMX-C4 [16]	260	277	1023±107.9	98.36±12.61	0.9891	1.32E-08
β-HMX-Formex [15]	268	274	643.1±41.8	60.10±5.93	0.9968	2.06E-07
β-HMX-SE	260	277	430.6±62.1	39.04±8.01	0.9898	0.21E-05
BCHMX (1st peak) [8]	205	217	241.9±16.8	24.09±3.29	0.9942	9.30E-02
BCHMX (2nd peak) [8]	234	249	191.5±10.4	17.19±2.38	0.9990	2.01E-03
BCHMX-VA [17]	225	241	186.4±10.4	16.69±2.39	0.9969	2.15E-03
BCHMX-C4 (1st peak) [16]	210	225	190.2±3.6	17.78±1.24	0.9996	1.07E-02
BCHMX-C4(2nd peak) [16]	228	242	204.8±10.8	18.60±4.71	0.9809	2.14E-03
BCHMX-Formex [15]	229	242	183.4	16.66	0.9924	4.11E-03
BCHMX-SE (1st peak)	210	224	209.2±32.7	19.88±5.30	0.9764	1.43E-02
BCHMX-SE (2nd peak)	227	243	187.6±3.6	16.77±1.23	0.9996	1.94E-03
ε-CL-20 [20]	216	234	168.6	15.62	0.9988	12.9E-03
ε-CL20-VA [17]	220	235	194.0±15.57	17.77±3.11	0.9936	4.20E-03
ε-CL-20-C4 (1st peak) [20]	221	240	135.3±3.6	12.20±0.94	0.9967	14.1E-03
ε-CL-20-C4 (2nd peak) [20]	221	238	174.3±3.8	15.96±0.98	0.9986	7.22E-03
Rs-ε-CL-20-C4 (1st peak) [21]	222	234	130.4±2.1	12.78±0.92	0.9980	173.E-03
Rs-ε-CL-20-C4 (2nd peak) [21]	222	232	161.0±3.4	15.62±1.13	0.9987	79.4E-03
ε-CL-20-Formex [15]	211	232	122.9	10.68	0.9988	8.26E-03
ε-CL-20-SE (1st peak)	184	205	132.8±6.0	12.30±1.75	0.9979	32.3E-03
ε-CL-20-SE (2nd peak)	216	237	161.4±7.4	14.35±1.95	0.9979	3.88E-03

Notes: T_i and T_e , initial and end temperatures for evaluation; Rs-ε-CL20, ε-CL-20 with reduced sensitivity by recrystallization; a, kinetic parameters obtained in this Ref. was calculated from isothermal TG data by the model fitting method; Estane, Estane 5703P (poly[ester urethane] block copolymer); C4, containing 25 wt% of polyisobutylene (PIB), 59 wt% of dioctyl sebacate (DOS) and 16 wt% of oil HM46; Formex, containing 25 wt% styrene-butadiene rubber (SBR) plasticized by 75 wt% oily material; VA, Viton A 200, which is an elastomer with a fluorine content of 66% and density of 1.78-1.82 g·cm⁻³; k , rate constant.

As in our previous studies listed in Table 3, the heating rates applied in this investigation were limited to a narrow range, and hence the kinetic parameters E_a and $\log A$ may involve large errors. However, the rate constants could be defined more accurately even in a narrow heating rate range [33]. Therefore, when comparing the thermal stability of substances, it is more reliable to compare the rate constants rather than the activation energies. The rate constants at 230 $^\circ\text{C}$ (between the intervals studied) have been obtained and included in Table 3. It can be seen that the rate constants obtained for different nitramine based

PBXs are comparable, except for the case of HMX. This is due to a huge error when the kinetic parameters are calculated by the model-free method, caused by a change in mechanism with heating rate for the decomposition of HMX based PBXs. According to Figure 4, Semtex is a very good binder for RDX, even better than Viton A. This is why PETN in the original Semtex PBXs has been replaced by RDX for military use [9]. For ϵ -CL-20 and BCHMX, Semtex seems to be as good a binder as Viton A. In fact, except for Formex, the other binders are suitable for BCHMX. In contrast to the Semtex, Viton A and C4 polymer matrices, the influence of Formex on the thermal decomposition of BCHMX and ϵ -CL-20 is negative, resulting in lower activation energies and higher rate constants.

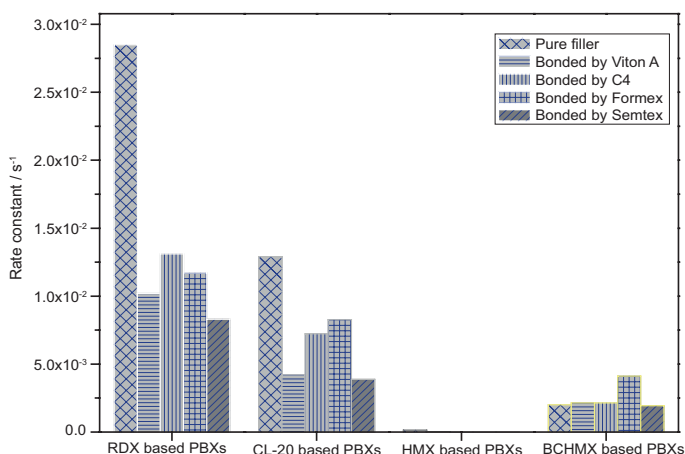


Figure 4. The rate constants for different polymer based PBXs containing cyclic nitramines at 230 °C as determined by the Kissinger method.

Dependence of kinetic parameters on the degree of conversion

As described in our previously published paper [8], based on the corresponding α - T curves shown in Figure 2, the dependence of the activation energy on the degree of conversion can be obtained by a modified Kissinger-Akahira-Sunose (KAS) isoconversional method. In the present paper, the activation energies at 5-90% degrees of conversion were determined for the materials studied, however, the mean values were calculated only for the $\alpha = 0.3$ - 0.7 interval as is commonly suggested, due to the increased inaccuracy in the case of the DTG peak tails. The corresponding calculation results ($\alpha = 0.1, 0.2, 0.3 \dots 0.9$) are summarized in Table 4.

Table 4. Kinetic data for Semtex bonded PBXs containing different cyclic nitramines by the modified KAS method

α reacted	RDX-SE			BCHMX-SE (2nd)			HMX-SE			CL-20-SE (2nd)		
	E_a	Log(A)	r	E_a	Log(A)	r	E_a	Log(A)	r	E_a	Log(A)	r
0.10	174.58	17.14	0.9964	157.41	14.47	0.9970	220.57	20.15	0.9851	189.44	17.62	0.9980
0.20	159.37	15.27	0.9977	155.65	14.18	0.9963	260.93	23.87	0.9747	187.35	17.26	0.9989
0.30	152.58	14.42	0.9983	157.81	14.38	0.9968	200.82	17.53	0.9302	186.05	17.08	0.9995
0.40	146.03	13.62	0.9985	159.71	14.54	0.9981	227.10	19.98	0.9395	189.72	16.97	0.9994
0.50	141.19	13.01	0.9997	159.23	14.46	0.9978	258.50	22.94	0.9497	187.58	17.15	0.9998
0.60	138.98	12.73	0.9997	158.46	14.34	0.9983	278.71	24.85	0.9441	188.24	17.18	0.9999
0.70	132.73	11.99	1.0000	162.69	14.76	0.9987	288.68	25.70	0.9685	185.10	16.81	0.9999
0.80	129.49	11.58	0.9998	160.99	14.56	0.9986	331.79	29.70	0.9759	185.28	16.81	0.9999
0.90	127.97	11.38	0.9999	161.39	14.57	0.9991	388.84	35.05	0.9691	188.88	17.15	0.9998
Mean	142.3 ± 7.4	13.15 ± 0.92		159.6 ± 1.9	14.50 ± 0.17		250.8 ± 36.5	22.20 ± 3.41		187.3 ± 1.8	17.04 ± 0.15	

Notes: E_a , calculated from non-iso-TG data, in $\text{kJ}\cdot\text{mol}^{-1}$ and Log A, in s^{-1} ; mean value, obtained in the interval of $\alpha = 0.3\text{-}0.7$.

As presented in Table 4, the mean activation energies of BCHMX-SE and CL-20-SE obtained by the modified KAS method agree well with those obtained by the Kissinger method (Table 3). In order to make a comprehensive comparison between the activation energies of pure nitramines and their PBXs, the dependence of the activation energies for these materials on the degree of conversion are plotted in Figure 5. The isoconversional activation energies for pure BCHMX [8], RDX [34], β -HMX [35, 36] and ϵ -CL-20 [20, 21] are obtained from our previously published papers and the literature. According to the investigations on the thermal decomposition kinetics of the nitramine based PBXs [15-19, 34-36], the activation energies of PBXs with non-energetic matrices is normally lower than those of the pure fillers including RDX, HMX and ϵ -CL-20.

According to Figure 5, it has been shown that, as with their pure nitramine fillers, the activation energies of ϵ -CL-20-SE and the main step of BCHMX-SE thermolysis are almost independent of the degree of conversion. For RDX-SE, as with pure RDX, the activation energy decreases with the degree of conversion, and the mean value is much lower than that obtained by the Kissinger method. This means that the Semtex matrix has little influence on the decomposition mechanism of RDX, which was proved to be autocatalytic. However, different results have been found for C4 and Viton A bonded PBXs containing RDX, where the autocatalytic effect occurring in the liquid-state decomposition of RDX (and BCHMX) could be weakened or inhibited by packing of the Viton A and C4 matrices [16, 17]. Interestingly, the activation energies of CL-20-SE are higher than those of the pure nitramine filler throughout almost the whole decomposition process. This means that Semtex could increase the thermal

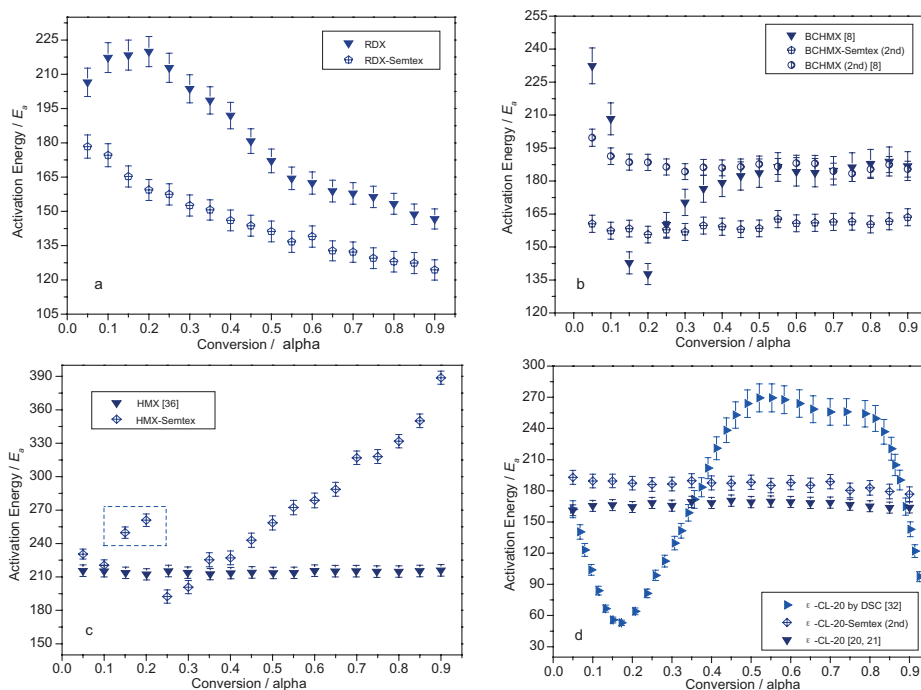


Figure 5. Dependence of the apparent activation energy of Semtex bonded PBXs containing RDX, HMX, BCHMX and CL-20 on the degree of conversion determined using the KAS method (open circles: $\beta = 1, 2, 3, 4, 5, 7$ and $10 \text{ } ^\circ\text{C}\cdot\text{min}^{-1}$).

stability of ϵ -CL-20, in good agreement with the DSC observations that its decomposition peak temperature is increased under the influence of Semtex. In the case of HMX-SE, there is a huge difference in the results obtained by the two methods, and the kinetic data obtained by the KAS method is less reliable, especially for the points at $\alpha = 0.2$ - 0.4 with correlation coefficients less than 0.94 (Figure 5c). This is caused by a dependence of the β -HMX decomposition mechanism on the heating rate under the influence of the polymer matrices. HMX usually does not melt during its decomposition because it could gradually dissolve in its thermolysis products [37, 38]. This is also a reason for the discrepancy between the kinetics parameters of β -HMX thermolysis in its alleged liquid and solid states [39, 40]. When packed with inert polymers (*e.g.* Semtex), this effect could be enhanced resulting in a much higher activation energy and greater sensitivity to the temperature gradient (the decomposition mechanism changes with the heating rate). For example, rupture of the intermolecular forces

rather than cleavage of covalent bonds within the molecule largely controls the rate of thermal decomposition of β -HMX [41] and this might also be the case for BCHMX. The difference between β -HMX and BCHMX molecules is the presence of crowding in BCHMX resulting in more rigid molecules and greater difficulty in cracking its crystal lattice [8]. The stabilizing effect from their crystal lattices will result in relatively lower rate constants of thermal decomposition (see Figure 4).

In addition, with regard to ϵ -CL-20, the distribution of its activation energy obtained by using the DSC method [35] is totally different from our previously published results [20] due to a different sample structure and evaluation method. In fact, when using non-isothermal TG data, these authors obtained very different results: the first stage ($0.0 < \alpha < 0.4$) showed a constant activation energy ($192 \pm 7 \text{ kJ} \cdot \text{mol}^{-1}$). This means that, as with our results, the rate-limiting step is unchanged over most of the period of initial decomposition. It has been found that the activation energy of CL-20 bonded by Viton A [17] and Semtex is higher than that of pure ϵ -CL-20 under the same experimental conditions. This indicates that after being coated with the inert and thermostable polymer, ϵ -CL-20 becomes safer to handle (less sensitive to mechanical initiation). It has been widely accepted that organic additives, mainly plasticizers and polymeric binders, could affect the initiation reactivity (sensitivity) of energetic fillers (mostly for polynitro compounds) through interactions with the molecules on the crystal surface, especially when defects are present [42]. It must be noted that the desensitizing influence of such inert additives results not only from the change in physical and mechanical properties of the corresponding energetic materials, but also from the inhibition of their decomposition by the trapping of reactive thermolysis products [43]. Here the Semtex binder could contribute to the desensitization of the corresponding cyclic nitramines by lowering their capability to generate radicals by the action of impact or friction and at the same time by increasing their heat capacity.

Conclusions

The thermal behavior and decomposition kinetics of Semtex bonded PBXs containing some attractive cyclic nitramines have been investigated by non-isothermal TG and DSC techniques. The following conclusions can be made:

(1) It has been shown that only a single decomposition process occurs for RDX-SE and HMX-SE, whilst an obvious two-step process occurs for CL-20-SE and BCHMX-SE.

(2) The onset of the exotherms were at 210.6, 239.7, 279.2 and 229.4 °C, with the peak maxima at 232.2, 249.4, 280.4 and 240.2 °C, for RDX-SE, BCHMX-SE, HMX-SE and CL-20-SE, respectively. The corresponding exothermic releases involved energy changes of 1808, 2140, 612 and 1757 J·g⁻¹, which are much lower than those of the pure cyclic nitramines.

(3) The Semtex matrix has little influence on the activation energy distribution of RDX, BCHMX and ϵ -CL-20. The activation energies of BCHMX-SE and CL-20-SE decomposition were found to be almost independent of the degree of conversion, with mean values of 159.6 \pm 1.9 and 187.3 \pm 1.8 kJ·mol⁻¹. The mean values for RDX-SE and HMX-SE are 142.3 \pm 7.4 and 250.8 \pm 36.5 kJ·mol⁻¹, respectively.

(4) Polymer bonded, high energetic materials, including β -HMX, ϵ -CL-20 and BCHMX, are very sensitive to the temperature gradient, and hence the applied heating rate for a kinetic study will be limited to a small range. For greater thermal stability, Semtex and Viton A are better binders than C4 and Formex for ϵ -CL-20 and RDX, whilst Formex is a poor binder for BCHMX.

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