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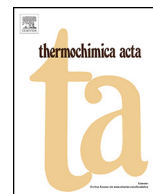


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Thermal behavior and decomposition kinetics of Viton A bonded explosives containing attractive cyclic nitramines

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ABSTRACT

The thermal behavior and decomposition kinetics of Viton A bonded PBXs containing some attractive cyclic nitramines were investigated by means of nonisothermal TG and DSC techniques. It has been shown that only a single decomposition process has been observed for RDX-VA, CL-20-VA and HMX-VA while an obvious two-step process for BCHMX-VA under $1.0^{\circ}\text{C min}^{-1}$. The exothermic onset temperatures of RDX-VA, BCHMX-VA, HMX-VA and CL-20-VA were found as 212.6, 241.3, 277.6 and 237.8°C with the peak maximum of 234.1, 242.6, 278.7 and 238.6°C , respectively. Their corresponding heat releases were determined as 1552, 1263, 1302 and 1597 J g^{-1} , which are much lower than that of the pure cyclic nitramines. It has been proved that Formex polymer is not good binder for BCHMX, while Viton A is better than C4 and Formex as the binder of cyclic nitramines for the sake of greater thermal stability. Viton A has a significant effect on the activation energy distribution of cyclic nitramines, and the initial autocatalysis effect for RDX and BCHMX was weakened or inhibited. The activation energies for thermolysis of RDX-VA, BCHMX-VA, HMX-VA and CL-20-VA were found almost independent on the extent of conversion at interval of 0.3–0.7 with the mean values of 174.4 ± 3.1 , 183.3 ± 1.3 , 285.8 ± 11.7 and $184.0 \pm 4.3\text{ kJ mol}^{-1}$, respectively.

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1. Introduction

Plastic bonded explosive or polymer-bonded explosive (PBX), an explosive powder bonded by typically 5–10% by weight of a synthetic polymer, has been widely used in many military and civilian applications due to its high safety, processing ease and superior strength properties [1,2]. The next generation of PBX materials will be improved in terms of insensitivity, high energetic density combined with an enhanced mechanical integrity [3]. Development of energetic fillers with improved detonation properties and low sensitivity is underway to meet aforementioned requirements. Such new energetic fillers 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], and they

have already been used and evaluated in several kinds of PBXs [7–10].

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 firstly in currently used polymer bases including fluoropolymers such as vinylidene-chlorotrifluorethene copolymer (Kel-F800), Viton A, Oxy 461, Cytop A and Hyflon AD60. Viton A is an elastomer with a fluorine content of 66% and a density of $1.78\text{--}1.82\text{ g cm}^{-3}$ [11], ideal for an explosive binder. Viton A has been used mostly in LX series compositions in United States. For instance, LX-07, LX-11, LX-10 and LX-04 are 90/10, 80/20, 95.5/4.5 and 85/15 weight percent composites of HMX/Viton A, and LX-04 was used as a substitution of PBX-9404 containing 94% of HMX, 3% of nitrocellulose (NC) and 3% of Tris(2-chloroethyl)phosphate (CEF) in B43 nuclear bomb, W62 and W70 cruise missile warheads [14]. The glass transition temperature of Viton A is around -18°C , and Viton A based formulations containing 90–95% of RDX, HMX and HNS have great mechanical properties with compression strength of more than 113 kg cm^{-2} [12]. Viton A could also be used as a binder in 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105) [13], BCHMX or CL-20 based PBXs [14,15]. The dynamical mechanical properties of Viton A bonded explosives has been investigated, which showed that mechanically robust pressed booster compositions with superior divergence

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characteristics could be formulated using the fluoropolymer binders [11,16]. Moreover, a new methodology has been developed to characterize and quantify the Viton based PBXs by Fourier transform infrared spectroscopy (FT-IR) [17].

Thermal degradation of polymer matrix plays an important role in thermal reactivity of corresponding solid propellants and high energy PBXs [18,19]. Felix et al. [20] studied the effect of Kel F800 and Viton A on the thermal degradation kinetics of corresponding PBXs containing keto-RDX. Comparing with their previous investigations, they pointed out that these binders played a significant role in facilitating the condensed phase reactions and reducing the contribution of competing gas phase processes during thermolysis of those PBXs. We also conducted some investigations on thermal decomposition kinetics of Formex P1 and C4 bonded PBXs containing abovementioned cyclic nitramines by DSC and TG techniques [21,22] and their low temperature thermal analysis behavior by STA-BIL method [23,24]. On this basis, the effect of C4 matrix on the thermal stability of CL-20 has also been studied [25,26]. Moreover, the mutual relationships between sensitivity parameters and detonation performance of Semtex, C4 and Viton A bonded PBXs containing such cyclic nitramines are systematically investigated [27]. However, as very important factors for performance prediction and safety evaluation, the effects of Viton A binder on the thermal behavior, stability and decomposition kinetics of BCHMX and CL-20 fillers are still not well known. Based on aforementioned experimental work, some interesting results have already been obtained, which will be discussed together with our current findings in this paper, concerning the effects of Viton A polymer on thermal behavior of BCHMX, HMX, RDX and CL-20 nitramines.

2. Experimental

2.1. Materials

BCHMX: cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (bicycle-HMX), which is a new polycyclic nitramine, was prepared by a two step continuous laboratory synthesis in our workgroup [6]. About 91% of BCHMX, β -HMX, RDX and ϵ -2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (ϵ -CL-20) by weight was bonded by 9% binder Viton A 200 prepared by modified water-solvent slurry method [28]. Viton A 200, produced by DuPont Performance Elastomers, is an elastomer with fluorine content of 66% and density of $1.78\text{--}1.82\text{ g cm}^{-3}$. This fluorine content implies a 60/40 weight ratio of vinylidene fluoride to hexafluoropropene monomers or approximately 77.83% mole of vinylidene fluoride [13]. The nitramine was mixed in water (aqueous phase) and Viton A was dissolved in an organic solvent with low boiling point, immiscible with water, which was added during the process. This process was carried out under vigorous stirring (500–600 rpm). The solvent was removed by distillation under continuous stirring, and the polymer precipitates on the surface of the nitramine crystals after the elimination of the solvents. For the sake of simplicity, PBX samples based on Viton A binder in this paper will be named as BCHMX-VA, HMX-VA, RDX-VA and CL-20-VA.

2.2. Experimental techniques

The thermal decomposition kinetics of involved samples were studied by using Thermogravimetry technique (TG, Netzsch 209F3 instrument, Al_2O_3 crucible) under the heating rates of 1, 2, 3, 4, 5 (with data collecting rate of 40 points per Kelvin), 7 and $10^\circ\text{C min}^{-1}$ (with data collecting rate of 60 points per Kelvin). The test temperature range for TG was $30\text{--}300^\circ\text{C}$, with the sample mass of about $1.85\text{--}2.35\text{ mg}$ under 30 ml min^{-1} dynamic nitrogen

atmosphere. Their heat flow properties were recorded by the technique of differential scanning calorimetry (DSC, Netzsch 200F3 instrument, Aluminum pan with a pin hole cover in dynamic nitrogen atmosphere under pressure of 0.1 MPa). The sample mass for DSC was about 1.5 mg with a heating rate of 5°C min^{-1} (temperature range: $40\text{--}350^\circ\text{C}$).

3. Results and discussions

3.1. TG/DTG studies

TG/DTG curves of RDX-VA, BCHMX-VA, and HMX-VA under the heating rates of 1, 2, 3, 4, 5, 7 and $10^\circ\text{C min}^{-1}$ were recorded (see Fig. 1a–d.). It has been shown that only a single decomposition process has been observed for RDX-VA, HMX-VA and CL-20-VA, while an obvious two-step process appeared for the mixture of BCHMX-VA especially at lower heating rates (see shoulder peak in Fig. 1, for 1.0 and $2.0^\circ\text{C min}^{-1}$). It follows a similar two-step decomposition trend as the pure BCHMX [29]. In order to make a quantitative comparison, the characteristic parameters of these TG/DTG curves are summarized in Table 1.

According to Table 1, it has been shown that for Viton A bonded PBXs, their extremum of mass loss rates are comparable when the heating rate is less than 2°C min^{-1} . However, the peak temperature and mass loss rate of HMX-VA are very dependent on the heating rate. For BCHMX-VA, it is obvious from DTG curves that the initial step of the decomposition starts from around 202°C at the heating rate of 1.0 K min^{-1} with the mass loss of around 5.2%. However, at higher heating rate, only a one-step mass loss process was observed, which means that the aforementioned two steps could merge together at higher heating rate. With regard to the mass loss during the main decomposition step, HMX-VA decomposed more complete (over 90% reacted) than the other samples. The extent of CL-20-VA thermolysis is less than 75%, and it may be caused by unfinished decomposition of Viton A. It has been found that the mass loss of the main stage for Viton A bonded PBX containing 90% of RDX was around 87% at the heating rate of $10^\circ\text{C min}^{-1}$ [30], which is in good agreement with our result for RDX-VA. According to the results, there was another 9% mass loss at around $450\text{--}500^\circ\text{C}$ corresponding to the degradation of Viton A. In fact, a initial decomposition temperature of Viton A is above 460°C at the heating rate of $10^\circ\text{C min}^{-1}$ [20], which means that its thermal stability is greater than C4 and Formex polymer bases. Here the main research objective was placed on the influence of Viton A on thermal decomposition of cyclic nitramines and accordingly the applied temperature range was limited to the complete decomposition of corresponding nitramines.

The corresponding α -T curves are obtained (see Fig. 2) from integration of DTG peaks. It has been shown that all of the decomposition curves basically obey the sigmoidal trend. However, in case of the HMX-VA material, the shape of determined dependencies of α -T largely changes with the heating rate due to the fact that kinetically controlled decomposition at lower heating rates, fast deflagration reaction at higher heating rates. As a matter of fact, fast deflagration reaction was also found for Formex and C4 bonded PBXs containing BCHMX, ϵ -CL-20 and β -HMX when the heating rate is greater than 5°C min^{-1} [21,22]. It has also been found that with regard to CL-20-Formex [21], very sharp DTG peaks were observed indicating “burning or deflagration kinetics” controlled the reaction mechanism, while relatively slow kinetically controlled decomposing reaction was obtained for CL-20-VA under the same heating rates. It reveals that Viton A and Formex matrix affect the thermal behavior of cyclic nitramines in a different way. The α -T curves are very important for kinetic calculation.

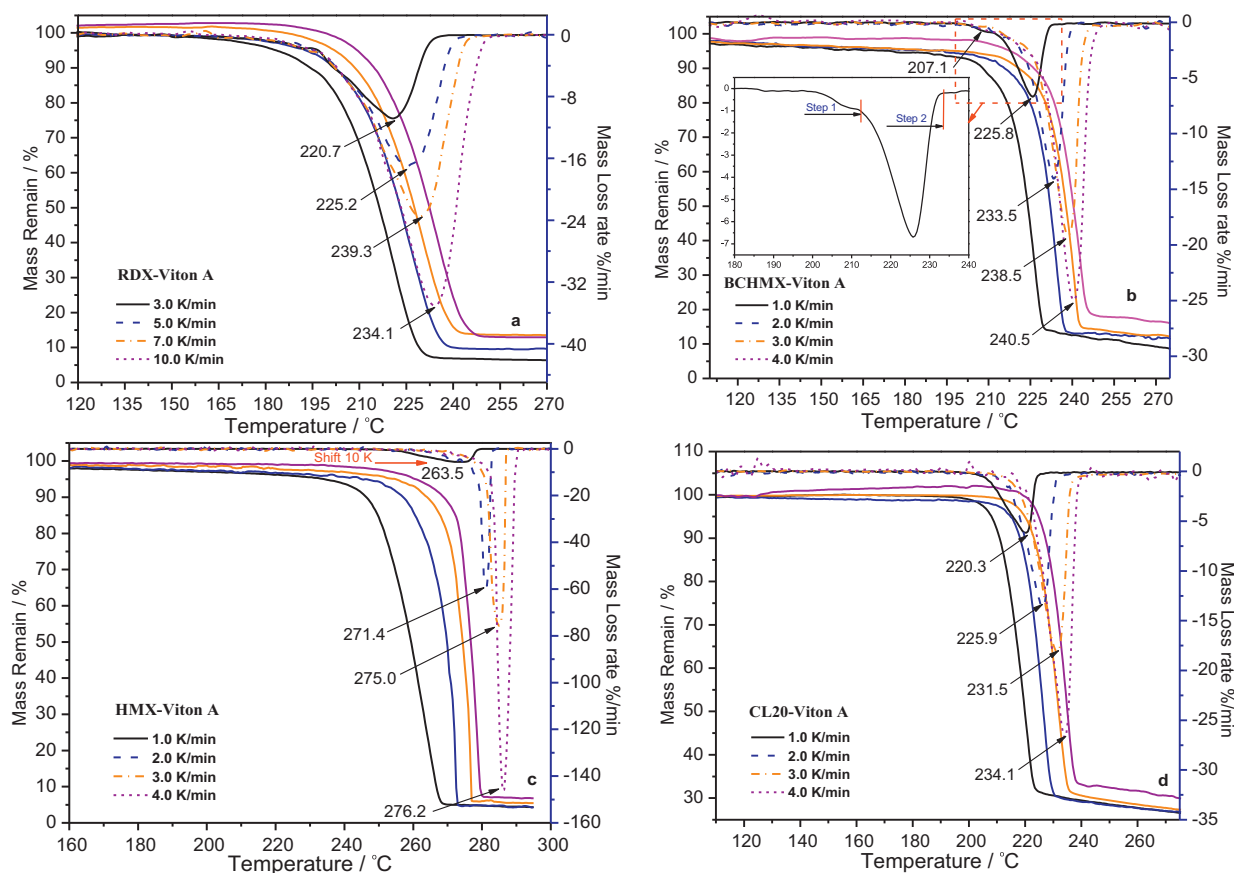


Fig. 1. TG/DTG curves of RDX-VA, BCHMX-VA, HMX-VA and CL-20-VA under heating rates of 1.0, 2.0, 3.0, 4.0, 5.0, 7.0 and 10.0 °C min⁻¹.

Usually, in order for reliable kinetic evaluation, it is necessary to apply the multiple heating rates with a wider dynamic range [18]. However, for most PBXs, especially for those containing high energy density fillers including BCHMX, ϵ -CL-20 and β -HMX, the situations will be complicated. On the one hand, decomposition processes of such PBXs depend largely on the heating rate (e.g. HMX-Formex, HMX-C4 and HMX-VA). On the other hand, the kinetically controlled thermal decomposition could not be

realized at slightly higher heating rates (e.g. 5.0 °C min⁻¹ for CL-20-Formex, BCHMX-C4, BCHMX-VA and HMX-C4 etc.). Hence the kinetic evaluation for such energetic materials would be limited to a very small heating rate scope (e.g. 1.0–4.0 °C min⁻¹). In particular, with regard to HMX-VA, according to Fig. 2, only data from the curves of 2.0, 3.0 and 4.0 °C min⁻¹ could be used in isoconversional kinetic calculation in order for acceptable correlation coefficients.

Table 1

The kinetic parameters from non-isothermal TG data of Viton A bonded PBXs containing different cyclic nitramines.

PBXs gradients	β (°C min ⁻¹)	TG curves			DTG peaks		
		T_{ot} (°C)	T_i (°C)	Mass loss (%)	L_{max} (% min ⁻¹)	T_p (°C)	T_{oe} (°C)
RDX-VA	3.0	202.5	172.5	93.23	−10.84	220.7	235.2
	5.0	208.7	173.9	89.79	−17.14	225.2	242.6
	7.0	211.6	175.6	87.88	−23.49	229.3	246.7
	10.0	216.5	176.8	89.41	−35.09	234.1	252.4
BCHMX-VA	1.0	217.8	202.5	86.14	−6.70	225.8	232.5
	2.0	226.5	203.1	91.35	−14.13	233.5	241.6
	3.0	231.4	204.6	84.73	−19.16	238.5	247.5
	4.0	232.6	205.8	87.93	−24.99	240.5	252.2
HMX-VA	1.0	251.1	241.0	94.06	−5.59	263.5	270.3
	2.0	265.5	249.9	96.22	−58.75	271.4	274.6
	3.0	270.0	253.1	91.27	−75.79	275.0	277.6
	5.0	272.2	256.3	92.50	−147.48	276.2	280.9
CL-20-VA	1.0	211.4	198.0	70.62	−6.16	220.3	227.6
	2.0	219.5	207.4	73.93	−13.71	225.9	234.2
	3.0	223.9	209.4	70.55	−18.23	231.5	239.6
	4.0	227.3	211.6	71.41	−26.80	234.1	243.8
Viton A [20]	10.0	–	462.0	97.8	–	477.0	485.0

Note: T_{ot} : onset temperature of decomposition; T_{oe} : onset temperature of the end 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 DTG peak; L_{max} : the maximum mass loss rate.

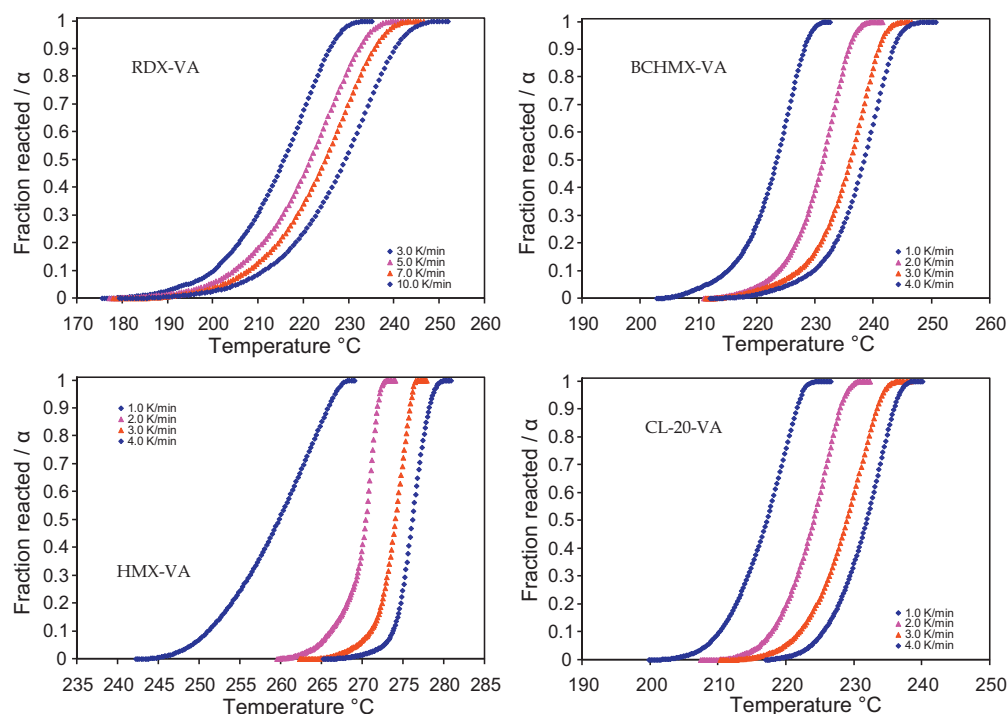


Fig. 2. The α - T curves of Viton A bonded PBXs containing different cyclic nitramines under the heating rates of 1.0, 2.0, 3.0, 4.0, 5.0, 7.0 and 10.0 °C min⁻¹.

3.2. DSC studies

TG/DTG results could be further supplemented by DSC studies. The samples were encapsulated in an aluminum pan with a pin hole and measurements were performed under identical conditions for both, pure energetic materials and their Viton A bonded mixtures. The obtained curves are shown in Fig. 3 and the characteristic parameters are summarized in Table 2.

According to Fig. 3, we can firstly pay attention to the pure energetic materials, it can be seen that their exothermic peaks are well formed except ϵ -CL-20, showing signs of kinetically controlled decomposition processes. However, if we look at the Viton A based mixtures of these compounds, only the RDX-VA (maybe also for initial stage of CL-20-VA) exhibits similar characteristics at this heating rate, and the other Viton A mixtures then show very sharp peaks corresponding to rapid heat evolution associated either with extremely fast decomposition kinetics or deflagration as mentioned in Section 3.1. In addition, it can be seen that for all studied materials the peak temperatures for Viton A mixtures are shifted to lower level except CL-20-VA. If considering the peak difference, it is around 8.5 °C for BCHMX-VA and BCHMX, which is higher than that of the others (around 2–6 °C). Based on the standard criterion for compatibility of energetic materials [31], it seems that BCHMX and Viton A is less chemically compatible than the other cyclic nitramines resulting in relatively lower thermal stability and heat release (less than 50% of the pure BCHMX). According to Table 2, if we compare the decomposition enthalpies, those for four mixtures are significantly lower than those for the pure energetic fillers – and not only due to the 9% of the inert material (Viton A 200). This may be probably explained by the involved deflagration, where the heat release is so rapid that it cannot be properly recorded by the DSC sensor.

Another effect that can be observed in the obtained curves is the small endothermic peak at 167.3 and 187.6 °C which

corresponds to the crystal transformation of ϵ -CL-20 and β -HMX, respectively. Such endothermic peak temperature differs considerably due to different crystal lattice structure for ϵ -CL-20 and β -HMX, but enthalpies of transformation associated with this effect is comparable. It is clear that there is no similar endothermic peak for RDX-VA and BCHMX-VA because RDX and BCHMX are not polymorphic. It has been found that two major conversions occur for thermal decomposition of pure ϵ -CL-20: a solid–solid phase transition from ϵ - to γ -polymorphs at 160–170 °C, followed by the thermal decomposition of the γ -polymorph [32]. With the effect of Viton A, the ϵ - to γ -phase transition point shifted from 159.6 °C to 167.3 °C, which is very close to that of pure Rs- ϵ -CL-20 (167.1 °C) [25] and those of coated by C4 or Formex polymer bases (at around 167.6 °C with an enthalpy of -18.6 J g^{-1}) [21,22]. It is interesting that the exothermic peak temperature of CL-20-VA is also very close to that of the pure Rs- ϵ -CL-20 (238.4 °C) [25], indicating that the thermostable inert polymer Viton A has the equivalent effect as reducing sensitivity by recrystallization. HMX exists in 4 polymorphic forms (α -HMX, β -HMX, δ -HMX, γ -HMX) and the most stable modification at room temperature is β -HMX as used herein. It has been found that for coarse HMX, a phase transition from β - to δ - can be clearly observed at about 160–170 °C while it occurred at 170–190 °C for the fine β -HMX [33]. It is, therefore, reasonable that this conversion was found to occur at around 180 °C in this paper because the pure fine β -HMX was used herein. However, it is confusing and interesting that there are several small shoulder endothermic peaks for this transformation under the effect of Viton A, which still needs more detailed investigations to illustrate. In fact, when β -HMX was coated by Formex and C4 polymer bases, the same effect could be observed but with only one endothermic peak [21,22]. Besides, in case of RDX-VA mixture, a endothermic effect can be observed at 205.1 °C, which should correspond to the melting of RDX (similar effect can also be found at almost the same temperature 205.8 °C for the pure RDX, which confirms that both RDX and RDX-VA decompose at a liquid state).

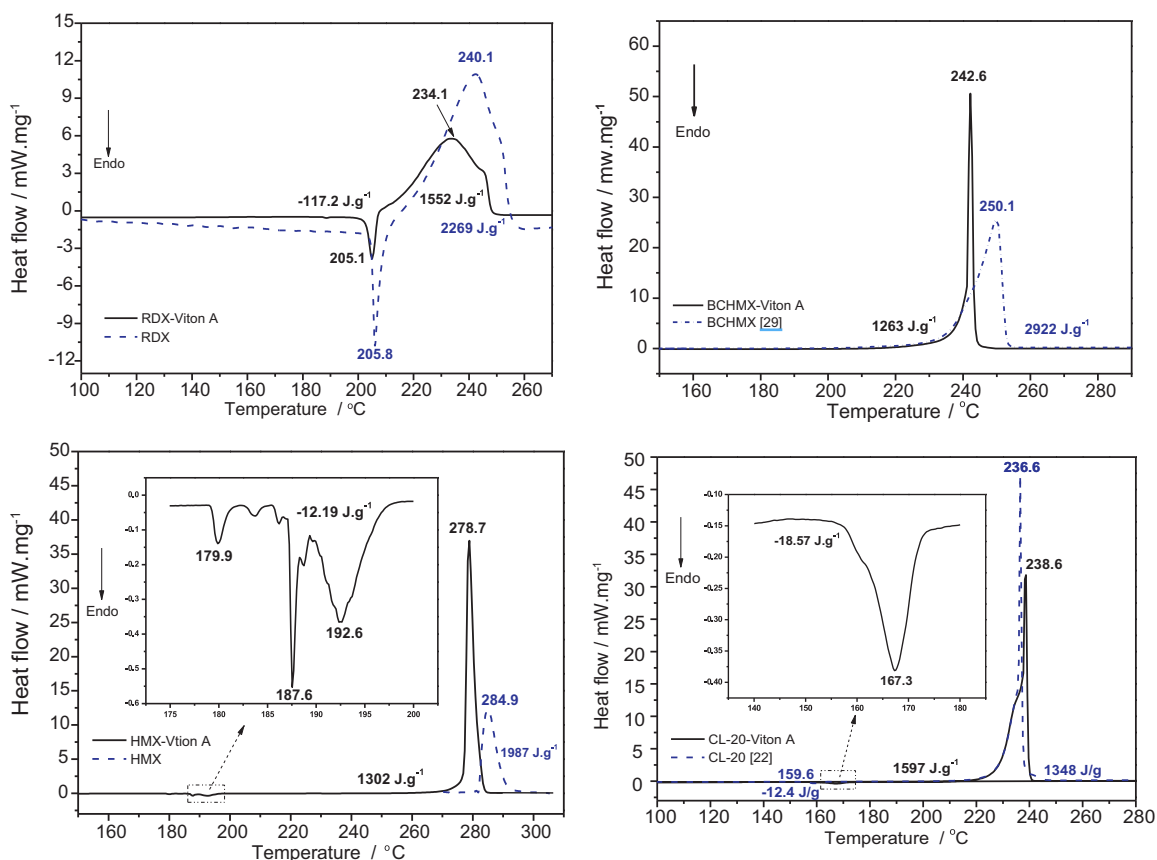


Fig. 3. The DSC curves of Viton A bonded PBXs containing cyclic nitramines at a heating rate of $5.0^{\circ}\text{C min}^{-1}$ (pressure, 0.1 MPa).

3.3. Thermal decomposition kinetics

3.3.1. Kinetic parameters and rate constant obtained by Kissinger method

The activation energy (E_a) obtained by the traditional Kissinger method, which depends on the reaction pathway and the specific intermediate(s) involved, is usually comparable to the activation energy at half conversion obtained by isoconversional method [18]. The kinetics of the thermal decomposition of Viton A bonded PBXs at different temperatures ranges were studied by non-isothermal TG (the mass loss was recorded with respect to temperature). Similar to our previous study [29], the kinetic parameters were calculated according to the traditional Kissinger method based on the shifts of the peak temperature presented in Table 1. The

temperature scope and corresponding calculation results are summarized in Table 3. Because the heating rate (or peak temperature) range of this investigation was limited to a small scope (as mentioned in Section 3.1), the kinetic parameters E_a and $\log A$ may be determined with a large error. However, the rate constants could be defined more accurately even in a narrow heating rate range [30]. Therefore, when comparing the thermal stability of substances, it is more correct to compare rate constants rather than activation energies. Hence the rate constants at 230°C (between studied interval) have been obtained and included in Table 3.

According to Table 3, it could be found that the errors for thermolysis kinetic parameters of β -HMX based PBXs are much higher than pure β -HMX. Such large errors (over 10%) are caused by their huge variation of decomposition mechanism under different

Table 2

DSC Parameters of Viton A bonded PBXs containing cyclic nitramines under the heating rate of $5.0^{\circ}\text{C min}^{-1}$.

Samples	Endothermic peaks				Exothermic peaks			
	T_0 ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	T_e ($^{\circ}\text{C}$)	ΔH_1 (J g^{-1})	T_0 ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	T_e ($^{\circ}\text{C}$)	ΔH_2 (J g^{-1})
RDX	204.1	205.8	210.2	−286.2	217.2	240.1	260.1	2269
RDX-VA	203.2	205.1	206.9	−117.2	212.6	234.1	247.7	1552
RDX-VA (RXV9010) [31] ^a	—	—	—	—	224.0	240.0	255.0	1500
BCHMX	—	—	—	—	207.8	239.5	250.1	2922
BCHMX-VA	—	—	—	—	241.3	242.6	243.1	1263
HMX	179.2	181.5	186.3	41.3	281.6	284.9	297.1	1987
HMX-VA	189.8 (Sp: 187.3)	192.6 (Sp: 187.6)	194.9 (Sp: 187.9)	−12.2 (Sp: −4.9)	277.6	278.7	281.4	1302
ϵ -CL-20	163.4	159.6	162.8	−12.4	235.7	236.6	237.3	1348
ϵ -CL-20-VA	163.7	167.3	171.7	−18.6	237.8	238.6	239.4	1597

Note: T_0 : onset temperature of the peaks; T_p : peak temperature of thermal events; T_e : the end temperature for heat change; ΔH_1 : heat absorption; ΔH_2 : heat release; Sp, for shoulder peak.

^a The heating rate in this Ref. is $10.0^{\circ}\text{C min}^{-1}$.

Table 3

Comparison of the kinetic parameters obtained by Kissinger method for Viton A and other polymer bonded PBXs containing cyclic nitramines.

Sample names	Temperature range		Arrhenius parameters			
	T_i (°C)	T_e (°C)	E_a (kJ mol ⁻¹)	log A (s ⁻¹)	r	k at 230 °C
Viton A [35] ^a	462	485	216.8	–	–	–
RDX [31] ^a	220	240	157.0	14.76	0.9901	2.85E-02
RDX-Estane (RXE9505) [31] ^a	215	235	189.0	18.06	0.9929	2.71E-02
RDX-VA (RXV9505) [31] ^a	215	230	201.0	19.76	0.9906	7.69E-02
RDX-VA	220	235	177.2 ± 12.8	16.41 ± 2.74	0.9948	1.02E-02
RDX-C4 [22]	218	236	197.7 ± 19.1	18.65 ± 3.58	0.9907	1.31E-02
RDX-Formex [21]	216	232	179.8	16.74	0.9950	1.17E-02
β-HMX [35]	171	314	227.1	19.70	–	13.0E-05
β-HMX-VA	263	277	244.9 ± 27.8	21.06 ± 4.41	0.9873	4.24E-05
β-HMX-C4 [22]	260	277	1023 ± 107.9	98.36 ± 12.61	0.9891	1.32E-08
β-HMX-Formex [21]	268	274	643.1 ± 41.8	60.10 ± 5.93	0.9968	2.06E-07
BCHMX (1st peak) [29]	205	217	241.9 ± 16.8	24.09 ± 3.29	0.9942	9.30E-02
BCHMX (2nd peak) [29]	234	249	191.5 ± 10.4	17.19 ± 2.38	0.9990	2.01E-03
BCHMX-VA	225	241	186.4 ± 10.4	16.69 ± 2.39	0.9969	2.15E-03
BCHMX-C4 (1st peak) [22]	210	225	190.2 ± 3.6	17.78 ± 1.24	0.9996	1.07E-02
BCHMX-C4 (2nd peak) [22]	228	242	204.8 ± 10.8	18.60 ± 4.71	0.9809	2.14E-03
BCHMX-Formex [21]	229	242	183.4	16.66	0.9924	4.11E-03
ε-CL-20 [23]	216	234	168.6	15.62	0.9988	12.9E-03
ε-CL20-VA	220	235	194.0 ± 15.57	17.77 ± 3.11	0.9936	4.20E-03
ε-CL-20-C4 (1st peak) [25]	221	240	135.3 ± 3.6	12.20 ± 0.94	0.9967	14.1E-03
ε-CL-20-C4 (2nd peak) [25]	221	238	174.3 ± 3.8	15.96 ± 0.98	0.9986	7.22E-03
Rs-ε-CL-20-C4 (1st peak) [25]	222	234	130.4 ± 2.1	12.78 ± 0.92	0.9980	173.E-03
Rs-ε-CL-20-C4 (2nd peak) [25]	222	232	161.0 ± 3.4	15.62 ± 1.13	0.9987	79.4E-03
ε-CL-20-Formex [21]	211	232	122.9	10.68	0.9988	8.26E-03

Note: T_i and T_e : the initial and the end temperature for evaluation; Rs-ε-CL20, ε-CL-20 with reduced sensitivity by recrystallization; Estane: Estane 5703P (poly[ester urethane] block copolymer); C4: containing wt. 25% of polyisobutylene (PIB), wt. 59% of dioctyl sebacate (DOS) and wt. 16% of oil HM46; Formex: containing wt. 25% styrene-butadiene rubber (SBR) plasticized by wt. 75% oily material; k : rate constant.

^a The kinetic parameters obtained in this Ref. was calculated from isothermal TG data by model fitting method.

heating rate. Therefore, in following section, the calculation of the distribution of activation energy of HMX-VA will be based only on three heating rates with similar decomposition mechanism, therefore resulting in relatively lower errors ($r > 0.995$). Because these errors were caused by the poor correlations between the peak temperatures and the heating rates, they could reflect the dependence of reaction mechanism on the temperature gradient of the samples. In addition, the polymer bases could affect the decomposition mechanisms of cyclic nitramines resulting in different activation energy. As abovementioned, for β-HMX, BCHMX and some kinds of ε-CL-20 based PBXs, the kinetically controlled decomposition processes occurring at lower temperature gradient could change to a rapid mass loss associated with burning or deflagration kinetics at higher temperature gradient. If burning or deflagration happened within the applied interval of heating rates, the kinetic results for this material cannot be considered physically meaningful (e.g. HMX-Formex and HMX-C4). With regard to pure ε-CL-20 and its C4 bonded PBX, the activation energies of the initial step are much lower than those of the second step. Under the effect of Formex and Viton A, the two-step decomposition process of BCHMX changes to single step mechanism, while one step mechanism for ε-CL-20 changes to two-step decomposition process under the effect of C4 binder [21,25]. In fact, as aforementioned, thermostable polymer Viton A usually decomposes at much higher temperature than cyclic nitramine fillers, so it may greatly promote the activation energies (energy barrier) for thermal decomposition of corresponding PBXs. For RDX based PBXs, the effect of binder C4 on its thermal decomposition [22] is greater than that of Viton A and Formex, resulting in much higher activation energy and lower rate constant. Unlike Viton A and C4 polymer base, the effect of Formex on thermal decomposition of BCHMX and ε-CL-20 is negative, resulting in lower activation energy and higher rate constant.

In order to make a clear comparison for the thermal kinetic stability of involved materials, their rate constants at 230 °C were plotted as Fig. 4. It has been shown that the rate constants for pure HMX and its PBXs are much lower than the other pure nitramines

and relevant PBXs. It might be caused by the stabilizing effect of the crystal lattice (crack during heating). As a whole, the C4, Viton A and Formex polymer bases could decrease the rate constant for RDX, HMX and CL-20, while very slightly increase that of BCHMX. It reveals that the involved polymers could increase the thermal stability of cyclic nitramines except BCHMX. With regard to RDX and CL-20 based explosives, the order of their thermal stability should be ranked as: RDX-VA > RDX-Formex > RDX-C4 > RDX and CL20-VA > CL20-C4 > CL20-Formex > CL-20. It reveals that Formex is not good binder for BCHMX, while Viton A is better than C4 and Formex as the binder of cyclic nitramines for the sake of greater thermal stability. This might be the reason that Viton A has been widely used in the charges of nuclear bombs and cruise missiles in the United States.

3.3.2. Dependence of kinetic parameters on extent of conversion

As described in our previously published paper [31], based on the corresponding α - T curves shown in Fig. 2, the dependence of activation energy on the degree of conversion could be obtained by modified Kissinger–Akahira–Sunose (KAS) isoconversional method. In this paper, the activation energies at the conversion rates of 5–90% were determined. However, the mean values were calculated only for the interval of 0.3–0.7 as commonly suggested due to the increased inaccuracy in case of DTG peak tails. The corresponding calculation results ($\alpha = 0.1, 0.2, 0.3, \dots, 0.9$) are summarized in Table 4.

If we compare the results for the original Kissinger method (Table 3) and those obtained by the modified KAS equation (Table 4), it can be seen that a great agreement was basically obtained for the BCHMX-VA and RDX-VA materials. For the CL-20-VA material, a slightly lower activation energy was obtained from the Kissinger method. In case of HMX-VA, there is certainly a huge difference for the results obtained by these two employed methods. However, the activation energies obtained by KAS method for HMX-VA might be more physically meaningful because the obvious change of reaction mechanism was excluded (without using the

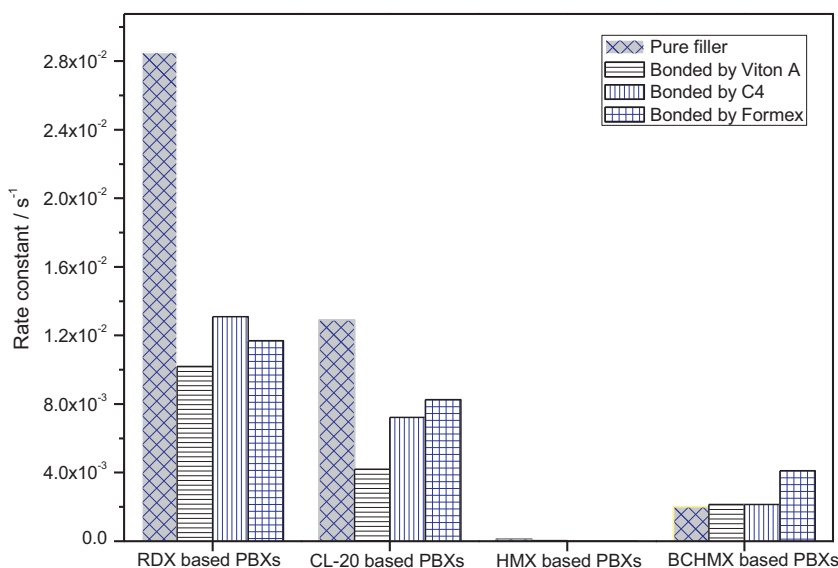


Fig. 4. The rate constants of different polymer based PBXs containing cyclic nitramines at 230 °C determined by Kissinger method.

data from $1.0\text{ }^{\circ}\text{C min}^{-1}$). In order to make a comprehensive comparison between the activation energies of pure nitramines with their PBXs, the dependence of activation energies for these materials on the degree of conversion are plotted in Fig. 5.

The isoconversional activation energies for pure BCHMX [29], RDX [31], β -HMX [37,38] and ϵ -CL-20 [23,24,39] are obtained from our previous paper and the literature. According to the investigations on thermal decomposition kinetics of RDX and β -HMX based PBXs [22–29,31–37], the activation energy of PBXs with non-energetic matrices is normally lower than that of the pure fillers including RDX, HMX and ϵ -CL-20. According to Fig. 5, unlike their pure nitramine fillers, the activation energies of RDX-VA and BCHMX-VA are almost overall independent on the extent of conversion. The activation energies of both ϵ -CL-20 and its Viton A based PBX are comparable and nearly remain constant throughout the decomposition process. The activation energy for the initial decomposition step of RDX ($\alpha < 0.5$) is higher than that of its Viton A based PBX while lower at the post step ($\alpha > 0.5$). Viton A matrix could greatly affect the initial activation energies of RDX and BCHMX, making them less dependent on the conversion rate. It might reveal that the autocatalytic effect occurring at liquid-state decomposition of RDX and BCHMX could be weakened or inhibited by packing of Viton A. Similar results could also be found for C4 polymer base [22]. However, the activation energies of HMX-VA and CL-20-VA PBXs are higher than that of their pure nitramine fillers nearly throughout the whole decomposition process. The pure β -HMX will probably not melt during its heating process because this

nitramine could gradually dissolve in the products of its thermal decomposition [36,40], which is also a reason for the discrepancy between kinetics parameters of the β -HMX thermolysis in its alleged liquid and solid states [41,42]. Under the package of thermal stable polymer (e.g. Viton A), this effect could be enhanced resulting in much higher activation energy and greater sensitivity to temperature gradient (decomposition mechanism changes with the heating rate). For example, rupture of the intermolecular forces rather than cleavages of covalent bonds within the molecule largely control the rate of thermal decomposition of β -HMX [43] and this might be also the case for BCHMX. Difference between the β -HMX and BCHMX molecules is in presence of crowding in BCHMX resulting in more rigid molecule [8]. In fact, melting-dissolution of BCHMX crystals leads to relatively quick and more deep decomposition (see mass loss values during the main exothermic process in Table 1).

In addition, with regard to ϵ -CL-20, the distribution of its activation energy obtained by using DSC method [32] is totally different from our previously published results [23] due to different sample structure and evaluation method. In fact, when using non-isothermal TG data, they obtained very different results: the first stage ($0.0 < \alpha < 0.4$) showed constant activation energy ($192 \pm 7\text{ kJ mol}^{-1}$). It means that, similar to our results, the rate-limiting step is unchanged over the most period of initial decomposition. The activation energy of CL-20-VA is higher than that of the pure ϵ -CL-20 especially after a conversion of 60% even the sample structure of ϵ -CL-20 and experimental

Table 4
Kinetic data of Viton A bonded PBXs containing different cyclic nitramines by modified KAS method.

α reacted	RDX-VA			BCHMX-VA			HMX-VA			CL-20-VA		
	E_a	log A	r	E_a	log A	r	E_a	log A	r	E_a	log A	r
0.10	193.8	19.34	0.9997	183.2	17.01	0.9942	215.7	18.60	0.9991	176.2	16.45	0.9999
0.20	176.0	17.09	0.9997	181.9	16.72	0.9974	255.0	22.39	0.9971	178.1	16.55	0.9999
0.30	177.0	17.03	0.9997	183.5	16.81	0.9978	269.5	23.76	0.9965	178.0	16.48	0.9999
0.40	175.5	16.73	0.9995	184.9	16.90	0.9971	279.2	24.68	0.9972	181.5	16.80	0.9998
0.50	174.3	16.49	0.9993	181.6	16.50	0.9980	289.3	25.64	0.9979	183.9	17.01	0.9995
0.60	179.1	16.96	0.9993	182.0	16.52	0.9980	299.8	26.65	0.9985	184.9	17.10	0.9992
0.70	170.7	15.89	0.9989	183.2	16.57	0.9981	277.3	24.42	0.9996	189.7	17.52	0.9986
0.80	172.3	15.99	0.9989	183.8	16.60	0.9981	271.7	23.87	0.9965	191.5	17.70	0.9976
0.90	170.8	15.71	0.9984	183.2	16.49	0.9987	269.4	23.62	0.9992	191.7	17.67	0.9965
Mean	174.4 \pm 3.1	16.57 \pm 0.46		183.3 \pm 1.3	16.68 \pm 0.18		285.8 \pm 11.7	25.30 \pm 1.13		184.0 \pm 4.3	16.97 \pm 0.38	

Note: E_a : calculated from noniso-TG data in kJ mol^{-1} and log A: in s^{-1} ; mean value, obtained in the range of $\alpha = 0.3\text{--}0.7$.

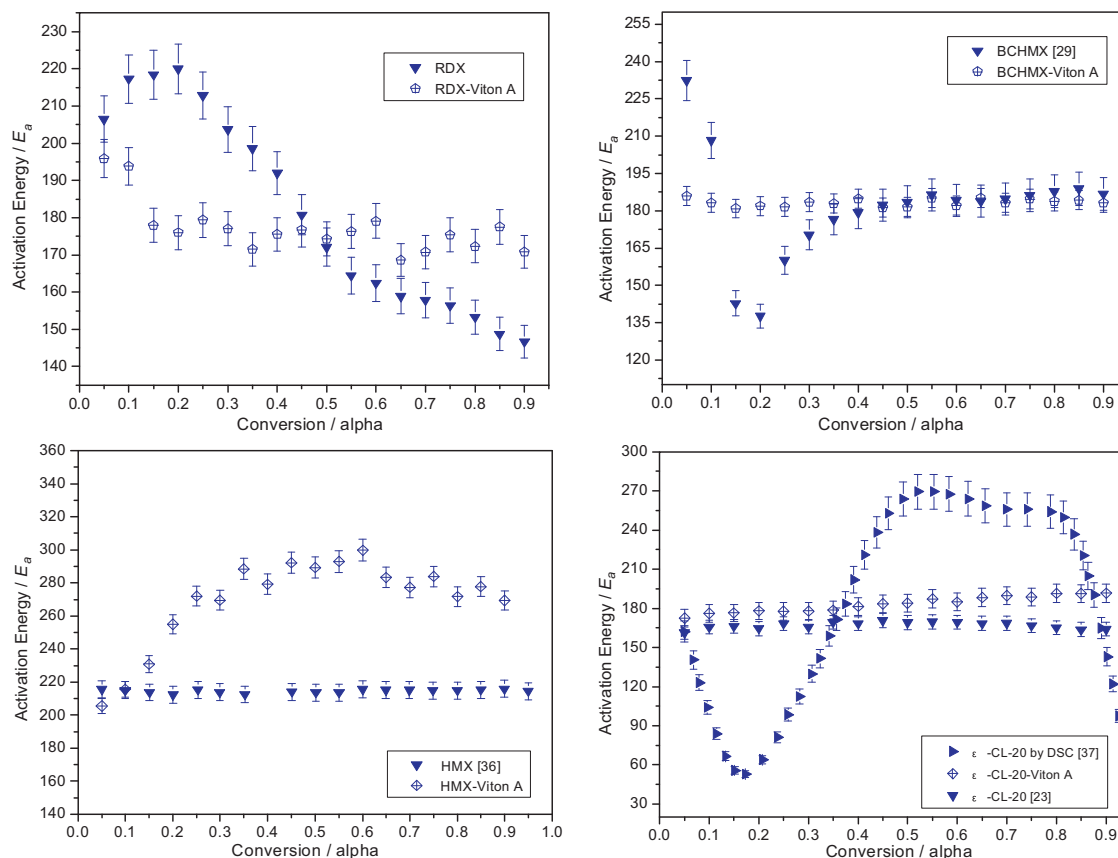


Fig. 5. Dependence of the apparent activation energy of Viton A bonded PBXs containing RDX, HMX, BCHMX and CL-20 on the degree of conversion determined by using KAS method (open circles: $\beta = 1, 2, 3, 4, 5, 7$ and $10^\circ\text{C min}^{-1}$).

conditions are the same. It indicates that after coated by the inert and thermostable polymer (e.g. Viton A), ϵ -CL-20 becomes more safe to handle (less mechanical sensitive). However, at the same time, the detonation velocities of these cyclic nitramines were decreased accordingly (e.g. detonation velocity for BCHMX only decreases 230 ms^{-1} due to increase of loading density and for the others decrease more than 500 ms^{-1}) [27,44]. It has been widely accepted that the organic additives mainly plasticizers and polymeric binders could affect the initiation reactivity (sensitivity) of involved energetic fillers (mostly for polynitro compounds) through their interactions with the molecules on the crystal surface especially when defects are included [45]. It must be noted that the desensitizing effect of such inert additives is resulted not only from the change of physical and mechanical properties of corresponding energetic materials, but also from the inhibition of their decomposition by trapping the active thermolysis products [46]. Here Viton A binder could contribute to desensitizing the corresponding cyclic nitramines by lowering their capability of generating radicals by action of impact or friction.

4. Conclusions

The thermal behavior and decomposition kinetics of Viton A bonded PBXs containing some cyclic nitramines were investigated by nonisothermal TG and DSC techniques. The following conclusions could be made:

- (1) It has been shown that only a single decomposition process has been observed for RDX-VA, CL-20-VA and HMX-VA while an probably two-step process for BCHMX-VA under $1.0^\circ\text{C min}^{-1}$;

- (2) The onset of the exotherms were noticed at $212.6, 241.3, 277.6$ and 237.8°C with the peak maximum at $234.1, 242.6, 278.7$ and 238.6°C for RDX-VA, BCHMX-VA, HMX-VA and CL-20-VA, respectively. Their corresponding exothermic releases were covered by energy changes of $1552, 1263, 1302$ and 1597 J g^{-1} , which are much lower than that of the pure cyclic nitramines;
- (3) The polymer bonded high energetic materials including β -HMX, ϵ -CL-20 and BCHMX are very sensitive to temperature gradient, and hence the applied heating rate for kinetic study will be limited to a small range; For the sake of greater thermal stability, Formex is not good binder for BCHMX while Viton A is better than C4 and Formex as a binder of cyclic nitramines;
- (4) The thermostable polymer Viton A has significant effect on the activation energy distribution of cyclic nitramines, and the initial autocatalysis effect for RDX and BCHMX was weakened or inhibited. The activation energies for thermolysis of RDX-VA, BCHMX-VA, HMX-VA and CL-20-VA are found almost independent on the conversion rate ($0.3 < \alpha < 0.7$) with the mean values of $174.4 \pm 3.1, 183.3 \pm 1.3, 285.8 \pm 11.7$ and $184.0 \pm 4.3\text{ kJ mol}^{-1}$, respectively.

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References

- [1] B.E. Clements, E.M. Mas, A theory for plastic-bonded materials with a bimodal size distribution of filler particles, *Modell. Simul. Mater. Sci. Eng.* 12 (3) (2004) 407–421.
- [2] B. Nouguez, B. Mahé, P.O. Vignaud, Cast PBX related technologies for IM shells and warheads, *Sci. Technol. Energ. Mater.* 70 (5–6) (2009) 135–139.
- [3] R.D. Chapman, W.S. Wilson, J.W. Fronabarger, L.H. Merwin, G.S. Ostrom, Prospects of fused polycyclic nitroazines as thermally insensitive energetic materials, *Thermochim. Acta* 384 (1–2) (2002) 229–243.
- [4] A. Elbeih, J. Pachman, S. Zeman, Z. Akštein, Replacement of PETN by Bicyclo-HMX in Semtex 10, in: 8th International Armament Conference on Scientific Aspects of Armament and Safety Technology, vol. 2(2), Pułtusk, Poland, 2010, pp. 7–16.
- [5] A. Elbeih, J. Pachman, S. Zeman, W.A. Trzcinski, Z. Akštein, Advanced plastic explosive based on BCHMX compared with Composition C4 and Semtex 10, in: *New Trends in Research of Energetic Materials*, Czech Republic, 2011, pp. 119–126.
- [6] D. Klasovity, S. Zeman, Method of preparing cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (bicyclo-HMX, BCHMX), Czech Pat. 302068, Int. Cl.: C07D 487/04, University of Pardubice, July 28th, 2009.
- [7] R.F. Gilardi, J.L. Anderson, R. Evans, Cis-2,4,6,8-tetranitro-1H,5H-2,4,6,8-tetraazabicyclo [3.3.0] octane, the energetic compound (bicyclo-HMX), *Acta Crystallogr. Sect. E: Struct. Rep. Online* 58 (2002) o972–o974.
- [8] D. Klasovity, S. Zeman, A. Ruzicka, M. Jungova, M. Rohac, Cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX), its properties and initiation reactivity, *J. Hazard. Mater.* 164 (2–3) (2009) 954–961.
- [9] A. Elbeih, J. Pachman, W.A. Trzcinski, S. Zeman, Z. Akštein, J. Selesovsky, Study of plastic explosives based on attractive cyclic nitramines. Part I: detonation characteristics of explosives with PIB binder, *Propell. Explos. Pyrotech.* 36 (5) (2011) 433–438.
- [10] Q.-L. Yan, S. Zeman, A. Elbeih, R. Svoboda, Thermodynamic properties, decomposition kinetics and reaction models of BCHMX and its Formex bonded explosive, *Thermochim. Acta* 547 (2012) 150–160.
- [11] A. Taguet, B. Ameduri, B. Boutevin, Crosslinking of vinylindene containing fluoropolymers, *Adv. Polym. Sci.* 184 (2005) 127–211.
- [12] Q.-L. Yan, S. Zeman, A. Elbeih, Recent advances in thermal analysis and stability evaluation of insensitive plastic bonded explosives (PBXs), *Thermochim. Acta* 537 (2012) 1–12.
- [13] D.M. Hoffman, K.T. Lorenz, B. Cunningham, F. Gagliardi, Formulation and mechanical properties of LLM-105 PBXs, in: 39th International Annual Conference of ICT, 24 June, Karlsruhe, Germany, 2008.
- [14] S. Zeman, A. Elbeih, Z. Akštein, Preliminary study on several plastic bonded explosives based on cyclic nitramines, *Chin. J. Energ. Mater.* 19 (1) (2011) 8–12.
- [15] A. Elbeih, J. Pachman, S. Zeman, A.W. Trzcinski, Z. Akštein, S. Muhamed, Thermal stability and detonation characteristics of pressed and elastic explosives on the basis of selected cyclic nitramines, *Cent. Eur. J. Energ. Mater.* 7 (3) (2010) 217–232.
- [16] D.M. Hoffman, DMA signatures of Viton A and plastic bonded explosives based on this polymer, *Polym. Eng. Sci.* 43 (1) (2003) 139–156.
- [17] C.M. Elizabeth, F.D. Milton, M.N. Nanci, C.L.D. Rita de, Determination of polymer content in energetic materials by FT-IR, *J. Aero. Technol. Manag.* 1 (2) (2009) 167–175.
- [18] S. Vyazovkin, N. Sbirrazzuoli, Isoconversional kinetic analysis of thermally stimulated processes in polymers, *Macromol. Rapid Commun.* 27 (2006) 1515–1532.
- [19] T. Sell, S. Vyazovkin, C.A. Wight, Thermal decomposition kinetics of PBAN-Binder and composite solid rocket propellants, *Combust. Flame* 119 (1999) 174–181.
- [20] S.P. Felix, G. Singh, A.K. Sikder, J.P. Aggarwal, Studies on energetic compounds-Part 33: thermolysis of keto-RDX and its plastic bonded explosives containing thermally stable polymers, *Thermochim. Acta* 426 (2005) 53–60.
- [21] Q.-L. Yan, S. Zeman, J. Selesovsky, R. Svoboda, A. Elbeih, Thermal behavior and decomposition kinetics of Formex-bonded explosives containing different cyclic nitramines, *J. Therm. Anal. Calorim.* 111 (2013) 1419–1430.
- [22] Q.-L. Yan, S. Zeman, F.-Q. Zhao, A. Elbeih, Noniso-thermal analysis of C4 bonded explosives containing different cyclic nitramines, *Thermochim. Acta* 556 (2013) 6–12.
- [23] S. Zeman, A. Elbeih, Q.-L. Yan, Note on the use of the vacuum stability test in the study of initiation reactivity of attractive cyclic nitramines in Formex P1 matrix, *J. Therm. Anal. Calorim.* 111 (2013) 1503–1506.
- [24] S. Zeman, A. Elbeih, Q.-L. Yan, Notes on the use of the vacuum stability test in the study of initiation reactivity of attractive cyclic nitramines in the C4 matrix, *J. Therm. Anal. Calorim.* (2012), <http://dx.doi.org/10.1007/s10973-012-2710-y>.
- [25] Q.-L. Yan, S. Zeman, A. Elbeih, Z.-W. Song, J. Málek, The effect of crystal structure on the thermal reactivity of CL-20 and its C4 bonded explosives (I): thermodynamic properties and decomposition kinetics, *J. Therm. Anal. Calorim.* (2012), <http://dx.doi.org/10.1007/s10973-012-2711-x>.
- [26] Q.-L. Yan, S. Zeman, R. Svoboda, A. Elbeih, J. Málek, The effect of crystal structure on the thermal reactivity of CL-20 and its C4-bonded explosives (II): models for overlapped reactions and thermal stability, *J. Therm. Anal. Calorim.* (2012), <http://dx.doi.org/10.1007/s10973-012-2629-3>.
- [27] A. Elbeih, S. Zeman, M. Jungova, P. Vavra, Attractive nitramines and related PBXs, *Propell. Explos. Pyrotech.* (2012), <http://dx.doi.org/10.1002/prep.201200011>.
- [28] H.-S. Kim, B.-S. Park, Characteristics of the insensitive pressed plastic bonded explosive, DXD-59, *Propell. Explos. Pyrotech.* 24 (1999) 217–220.
- [29] Q.-L. Yan, S. Zeman, R. Svoboda, A. Elbeih, Thermodynamic properties, decomposition kinetics and reaction models of BCHMX and its Formex bonded explosive, *Thermochim. Acta* 547 (2012) 150–160.
- [30] V.P. Sinditskii, V.Yu. Egorshv, V.V. Serushkin, A.I. Levshenkov, M.V. Berezin, S.A. Filatov, S.P. Smirnov, Evaluation of decomposition kinetics of energetic materials in the combustion wave, *Thermochim. Acta* 496 (2009) 1–12.
- [31] G. Singh, S.P. Felix, P. Soni, Studies on energetic compounds Part 31: thermolysis and kinetics of RDX and some of its plastic bonded explosives, *Thermochim. Acta* 426 (2005) 131–139.
- [32] Q.-L. Yan, X.-J. Li, L.-Y. Zhang, J.-Z. Li, H.-L. Li, Z.-R. Liu, Compatibility study of trans-1,4,5,8-tetranitro-1,4,5,8-tetraazadecalin (TNAD) with some energetic components and inert materials, *J. Hazard. Mater.* 160 (2–3) (2008) 529–534.
- [33] R. Turcotte, M. Vachon, Q.S.M. Kwok, R. Wang, D.E.G. Jones, Thermal study of HNIW (CL-20), *Thermochim. Acta* 433 (2005) 105–115.
- [34] C.K. Saw, Kinetics of HMX and phase transitions: effects of grain size at elevated temperature, in: 12th International Detonation Symposium, 11–16 August, San Diego, CA, 2002.
- [35] A.K. Burnham, K.W. Randall, Kinetics of thermal degradation of explosive binders Viton A, Estane, and Kel-F, *Thermochim. Acta* 426 (2005) 85–92.
- [36] G.B. Majelis, G.M. Nazin, Y.I. Rubtsov, V.A. Strunin, Thermal decomposition and combustion of explosives and propellants, Taylor and Francis Publisher, London, ISBN: 0-451-29984-5, 2003, pp. 80–85.
- [37] C.M. Tarver, T.D. Tran, Thermal decomposition models for HMX-based plastic bonded explosives, *Combust. Flame* 137 (1–2) (2004) 50–62.
- [38] G. Singh, S.P. Felix, P. Soni, Studies on energetic compounds. Part 28: thermolysis of HMX and its plastic bonded explosives containing Estane, *Thermochim. Acta* 399 (1–2) (2003) 153–165.
- [39] J. Lee, K.-S. Jaw, Thermal decomposition properties and compatibility of CL-20, NTO with silicone rubber, *J. Therm. Anal. Calorim.* 85 (2) (2006) 463–467.
- [40] S. Zeman, A study of chemical micro-mechanisms of initiation of organic polynitro compounds, in: T. Klapoetke (Ed.), *High Energy Density Materials, Series: Structure & Bonding*, vol. 125, Springer, New York, 2007, pp. 195–271.
- [41] S. Zeman, A study of chemical micro-mechanisms of initiation of organic polynitro compounds, in: P. Politzer, J. Murray (Eds.), *Theoretical and Computational Chemistry*, vol. 13, Energetic Materials, Part 2, Detonation, Combustion, Elsevier B.V., Amsterdam, 2003, pp. 25–52.
- [42] L.-Q. Liao, Q.-L. Yan, Y. Zheng, Z.-W. Song, J.-Q. Li, P. Liu, Thermal decomposition mechanism of particulate core-shell KClO₃-HMX composite energetic material, *Indian J. Eng. Mater. Sci.* 18 (5) (2011) 393–398.
- [43] T.B. Brill, R.J. Karpowicz, Solid phase transition kinetics. The role of intermolecular forces in the condensed-phase decomposition of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine, *J. Phys. Chem.* 86 (1982) 4260–4265.
- [44] A. Elbeih, J. Pachman, S. Zeman, P. Vavra, W.A. Trzcinski, Z. Akštein, Detonation characteristics of plastic explosives based on attractivenitramines with polyisobutylene and poly(methyl methacrylate) binders, *J. Energ. Mater.* 30 (4) (2012) 358–371.
- [45] M. Chovancová, S. Zeman, Study of initiation reactivity of some plastic explosives by vacuum stability test and non-isothermal differential thermal analysis, *Thermochim. Acta* 460 (2007) 67–76.
- [46] N.P. Loginov, S.N. Surkova, Effectiveness of the action of stabilizers in explosive compositions under mechanical loading, *Fiz. Goreniya Vzryva* 42 (1) (2006) 100.