Non-isothermal decomposition behavior of Fluorel bonded explosives containing attractive cyclic nitramines

4 AUTHORS, INCLUDING:

Qi-Long Yan
Tel Aviv University

46 PUBLICATIONS   **326** CITATIONS

SEE PROFILE

Tong-Lai Zhang
Beijing Institute of Technology

271 PUBLICATIONS   **1,131** CITATIONS
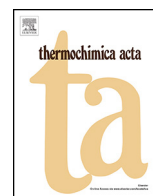
SEE PROFILE

Ahmed Elbeih
Military Technical College

45 PUBLICATIONS   **333** CITATIONS

SEE PROFILE

Non-isothermal decomposition behavior of Fluorel bonded explosives containing attractive cyclic nitramines

Qi-Long Yan[a], Svatopluk Zeman[a,*], Tong-Lai Zhang[b], Ahmed Elbeih[c]

[a] Institute of Energetic Materials, University of Pardubice, 532 10 Pardubice, Czech Republic
[b] State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China
[c] Military Technical College, Cairo, Egypt

ARTICLE INFO

ABSTRACT

The thermal behavior and decomposition kinetics of Fluorel-bonded PBXs based on some attractive cyclic nitramines were explored by means of non-isothermal TG and DSC techniques. The exothermic onset temperatures on DSC curves of RDX-FL, BCHMX-FL, HMX-FL and CL-20-FL were noticed at 208.7, 235.6, 277.2 and 239.2 °C with the peak maximum of 233.8, 237.4, 278.8 and 239.5 °C, respectively. The corresponding heat releases are 1758, 1393, 1546 and 1893 J g^{-1}, which are much lower than that of the pure cyclic nitramines. According to DSC peak shift, similar to Viton A, Fluorel polymer is probably not chemically compatible with BCHMX resulting in much lower thermal stability and heat of decomposition compared with pure BCHMX. It is also proved that Both Fluorel and Viton A could decrease or inhibit the autocatalytic effect occurring during liquid-state decomposition of RDX. However, opposite to Viton A, the Fluorel polymer could enhance the autocatalytic effect of BCHMX due to bad chemical compatibility. The activation energies for thermolysis of RDX-FL and CL-20-FL are found almost independent on the conversion rate ($0.3 < \alpha < 0.7$) with the mean values of 170 ± 3, and 206 ± 3 kJ mol^{-1}, while those of BCHMX-FL and HMX-FL are largely dependent on the conversion rate with average values of 189 ± 4 and 117 ± 5 kJ mol^{-1}.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Polymer-bonded explosive (PBX) is an explosive powder bonded together in a matrix using typically 5–10% by mass of a synthetic polymer, and they are widely used in many military and civilian fields due to their high safety, processing ease and superior strength [1,2]. The next generation of PBX materials will be improved in terms of insensitivity and high energetic density properties combined with an enhanced mechanical integrity [3]. Relatively new cyclic nitramines *cis*-1,3,4,6-tetranitroocta-hydroimidazo-[4,5-d] imidazole (BCHMX) and ε-2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (ε-CL-20) are found 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 β-1,3,5,7-tetranitro-1,3,5,7-tetrazocane (β-HMX) [4–6]. In fact, BCHMX and ε-CL-20 have already been used and evaluated in several kinds of PBXs [7–10].

The polymer matrix plays an important role in the thermal initiation of many solid propellants and also high energy PBXs

[11,12]. In order to study the compatibility, thermal reactivity and detonation performances of abovementioned new energetic fillers when introduced in PBXs, it is essential to study them firstly in currently used polymer bases including fluoropolymers, whose formulation can be tailored to a reasonable extent to meet the needs of individual end-uses, such as vinylidene–chlorotrifluorethene copolymer (Kel-F800) and Fluoroelastomer (Viton®, Fluorel®). They normally have high heat, oil and chemical resistance but mediocre low temperature performance [13]. Fluoroelastomer is the most highly temperature resistant of all commercially available elastomers. Its elemental composition is relatively low in oxidizable elements such as carbon and hydrogen, so it has a low demand as oxidizer, and can be used in high enough proportion to allow extrusion processing of PBX compositions. Viton A is a copolymer of Vinylidene Fluoride and Hexafluoro-propylene with a fluorine content of 66% and a density of 1.78–1.82 g cm^{-3} [14]. Viton A has been widely used in LX series compositions in the United States (e.g. LX-04, LX-10) [15]. Fluorel (or named as "Dyneon FT2481" by 3 M) is a terpolymer of Tetrafluoroethylene, Vinylidene Fluoride and Hexafluoropropylene containing also aromatic building units; its fluorine content is 68.6%, density is 1.86 g cm^{-3}. It also has been used in several PBXs as a comparison of Viton A with regard to detonation [16] and sensitivity properties [17]. Felix et al. have studied the effect of Kel F800 and Viton A on thermal degradation

kinetics of corresponding plastic bonded explosives [18]. It has been shown that mechanically robust pressed booster compositions with superior divergence characteristics could be formulated using the fluoropolymer binders [14,19]. The thermal decomposition kinetics of Formex P1, C4 and Viton A bonded PBXs containing abovementioned cyclic nitramines had been evaluated by means of DSC and TG techniques [20–24] and their low temperature thermolysis behavior have been studied by STABIL method [25,26]. The effect of C4 matrix on the thermal stability of ε-CL-20 has also been attempted [27,28]. 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 by our workgroup [17].

As described above, the previous investigations with regard to Fluoroelastomer bonded PBXs were conducted mainly on their sensitivity and detonation properties. However, as very important factors for safety evaluation, the effects of Fluorel binder on thermal behavior, stability and decomposition kinetics of cyclic nitramines are still not well known. Therefore, a comparative study on thermal behavior of Fluorel and Viton A bonded explosives containing BCHMX, HMX, RDX and CL-20 nitramines will be presented in this paper.

2. Experimental

2.1. Materials

BCHMX, as a relatively new polycyclic nitramine, was prepared by a two-step laboratory synthesis in our workgroup [6]. About 91% (m/m) of BCHMX, β-HMX, RDX and ε-CL-20 were bonded by 9% binder Fluorel by method described in paper [16], i.e. by a modified water-solvent slurry method: The nitramines are slurried in water (aqueous phase) and Fluorel was dissolved in methylethyl ketone, 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 Fluorel binder will be named as BCHMX-FL, HMX-FL, RDX-FL and CL-20-FL in this paper.

2.2. Experimental techniques

The samples were studied with regard to their thermal decomposition kinetics and heat flow properties, using Thermogravimetry (TG, Netzsch 209F3 instrument) and Differential Scanning Calorimetry (DSC, Netzsch 200F3 instrument). The experimental conditions are as follows:

TG: 1.75–2.35 mg sample was placed in Al_2O_3 crucible, and heated under 30 ml min^{-1} dynamic nitrogen atmosphere with the heating rates of 0.3, 0.6, 1, 1.5, 2, 3, 4, 5, and 7 (with data collecting rate of 40 points per Kelvin), 10 and 15 °C min^{-1} (with data collecting rate of 60 points per Kelvin).

DSC: around 1.5 mg sample was placed in an Aluminum pan with a pin-hole cover, and heated at a constant heating rate of 5 °C min^{-1} under 0.1 MPa dynamic nitrogen atmospheres from 40 to 350 °C.

3. Results and discussion

3.1. TG/DTG studies

TG/DTG curves of RDX-FL, BGHMX-FL, and HMX-FL under several heating rates were recorded (see Fig. 1a–d). It has been shown that only a single decomposition process has been observed for all

involved materials. With the increase of heating rate, the reaction mechanism will obviously change for HMX-FL and BCHMX-FL. In particular, their kinetically controlled decomposition will change to fast burning process especially when the heating rate is above 4.0 °C min^{-1} (see Fig. 1b), which has also been observed for some other polymer bonded explosives containing HMX and BCHMX [22–24]. 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, the peak mass loss rates of Fluorel bonded PBXs are comparable when the heating rate is less than 2 °C min^{-1}. However, as mentioned above, the peak temperature and mass loss rate of HMX-FL depend greatly on the heating rate, which are very close to corresponding Viton A bonded explosives [24]. With regard to the mass loss during the main decomposition step, RDX-FL and HMX-FL could decompose more complete (over 85%) than the other two samples. It has been found by Singh [29] that the mass loss during the main stage for Viton A bonded PBX containing 90% of RDX was around 87% at the heating rate of 10 °C min^{-1}, which is in good agreement with our previously published results [24]. According to these results, there should be another decomposition process at above 460 °C for Fluorel bonded explosives, because Fluorel with higher Fluorine content (around 68%) is considered more thermal stable than Viton A, which has an initial decomposition temperature of 462 °C at the heating rate of 10 °C min^{-1} [19].

The corresponding α–T curves are plotted and shown in Fig. 2. It can be seen that all of the decomposition curves basically obey the sigmoidal trend. However, in case of the HMX-based materials [22–24], the shape of determined dependencies of α–T largely changes with the heating rate due to the fact that the mechanism controlling the proceeding reaction was not identical for all applied heating rates, which means that kinetically controlled decomposition reaction at lower heating rates (mostly < 4.0 K min^{-1}) and fast burning reaction resulted from self-heating at higher heating rates. For HMX-FL, the fast self-heating reaction even starts from the heating rate of 2.0 °C min^{-1} (see Fig. 1c). Much lower heating rate has to attempt for HMX-FL (e.g. as low as 0.3 °C min^{-1}). In fact, the polymer matrix affects the thermal behavior of cyclic nitramines in very different ways. According to our previous findings [22], a very sharp DTG peaks could be observed for CL-20-Formex [22] under the heating rates of above 3.0 °C min^{-1}, while kinetically controlled slow decomposition reaction was obtained for CL-20-VA [24] at the same heating rate. The α–T curves are very important for kinetic calculation. Usually, in order for reliable kinetic evaluation, it is necessary to apply the multiple heating rates with a wider dynamic range [11]. However, in most cases, For PBXs especially those containing high energy fillers (e.g. BCHMX, HMX and ε-CL-20), the situation will be different and complicated. Firstly, decomposition processes of such PBXs depend largely on the heating rate (e.g. HMX based PBXs and BCHMX-FL). Secondly, the kinetically controlled thermal decomposition could not be realized at slightly higher heating rates (e.g. above 5.0 °C min^{-1} for CL-20-Formex, BCHMX-C4, BCHMX-VA, HMX-C4, etc.). Hence the kinetic evaluation for such energetic materials would be limited to a very narrow dynamic range (e.g. 0.3–4.0 °C min^{-1} and even 0.3–1.5 °C min^{-1} for HMX-FL). In particular, with regard to HMX-FL, according to Fig. 2, only data from the curves of 0.3–1.5 °C min^{-1} could be used for kinetic calculation for the sake of acceptable correlation coefficients.

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 similar conditions for both, pure energetic materials and their Fluorel bonded
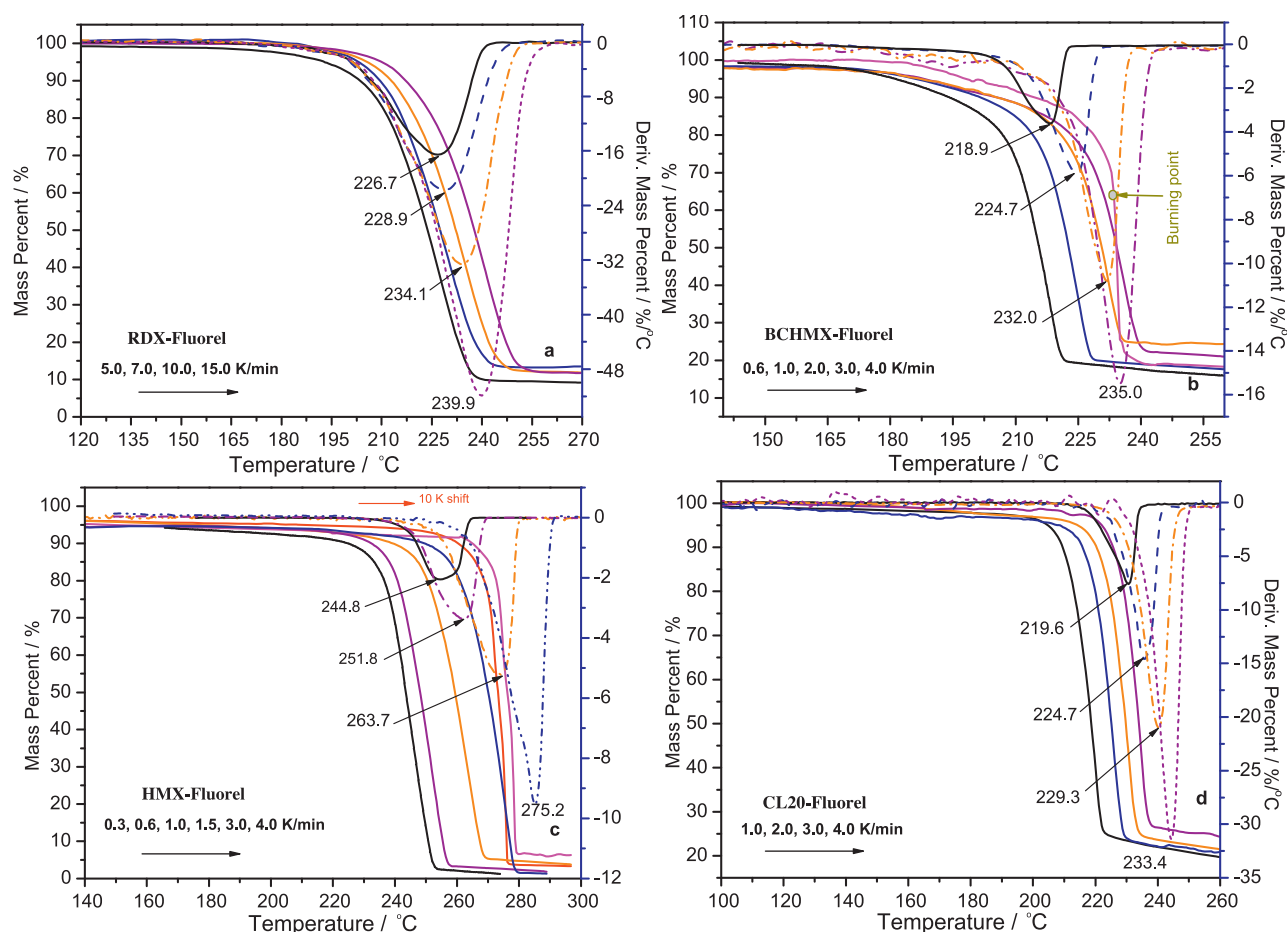
Fig. 1. TG/DTG curves of RDX-FL, BCHMX-FL, HMX-FL and CL-20-FL under heating rates of 1.0, 2.0, 3.0, 4.0, 5.0, 7.0, 10.0 and 15 °C min⁻¹.

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, showing signs of kinetically controlled decomposition

processes except post process of ε-CL-20. However, if we look at the Fluoropolymer (Fluorel and Viton A) based mixtures of these compounds under the heating rate of 5 °C, only the RDX-FL and RDX-VA exhibit a similar kinetically controlled slow decomposition (see Fig. 3, their DSC curves almost overlapped). The sharp exothermic

Table 1
the parameters from non-isothermal TG/DTG data of Fluorel bonded PBXs containing different cyclic nitramines.

PBXs Gradients	β (°C min⁻¹)	TG curves			DTG peaks		
		T_{ot} (°C)	T_{id} (°C)	Mass loss (%)	L_{max} % (min⁻¹)	T_p (°C)	T_{oe} (°C)
RDX-FL	5.0	209.1	163.1	88.94	−16.5	226.7	245.2
	7.0	210.9	167.4	87.54	−21.8	228.9	251.3
	10.0	216.4	171.1	87.43	−32.6	234.1	253.9
	15.0	222.6	173.8	87.86	−51.8	239.9	260.8
BCHMX-FL	0.6	211.3	172.3	78.94	−3.6	219.2	230.2
	1.0	214.7	176.6	79.09	−5.9	224.7	232.4
	2.0	222.2	176.9	81.15	−10.8	232.0	239.9
	3.0	225.3	177.5	76.59	−15.5	235.0	245.4
	4.0	226.7	179.1	78.79	–	–	–
HMX-FL	0.3	234.6	214.2	88.20	−1.6	244.8	256.1
	0.6	242.3	222.1	86.02	−3.4	251.8	260.6
	1.0	250.9	227.9	86.56	−5.2	263.8	270.7
	1.5	265.3	229.3	88.33	−9.6	275.2	283.0
	2.0	268.2	235.3	85.95	−37.1	270.6	276.4
	3.0	268.3	241.9	88.78	−68.6	273.9	277.6
	4.0	270.3	246.4	86.41	−104.2	276.6	280.3
CL-20-FL	1.0	212.2	198.6	71.71	−7.6	219.6	224.9
	2.0	218.9	199.3	79.85	−14.7	224.7	232.9
	3.0	222.8	199.9	76.28	−21.0	229.3	238.6
	4.0	227.5	200.6	71.87	−31.5	233.4	241.4

Note: T_{ot}, onset temperature of decomposition; T_{oe}, the temperature of the end decomposition; T_{id}, 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.
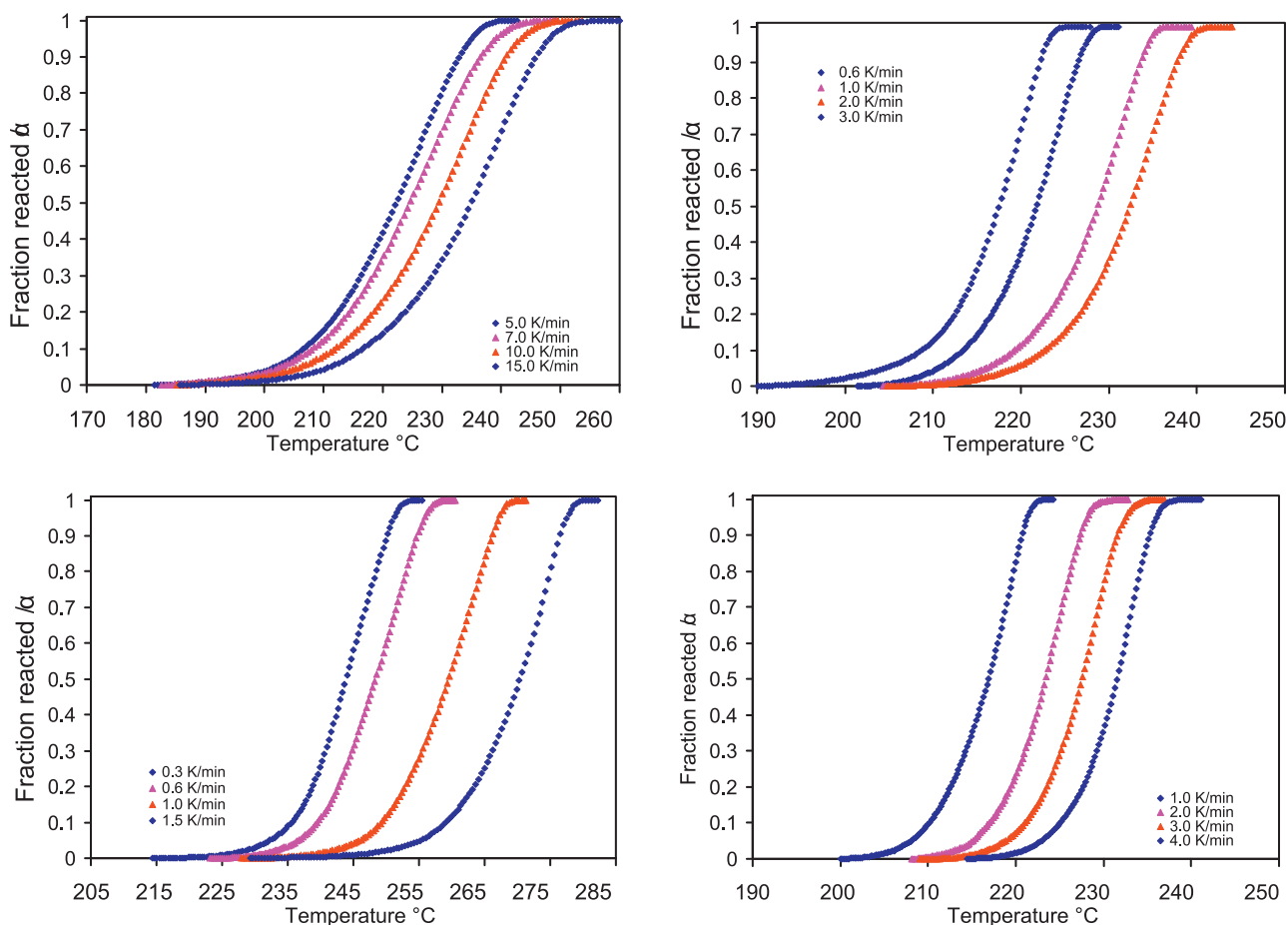
Fig. 2. The α–T curves of RDX-FL, BCHMX-FL, HMX-FL and CL-20-FL under the heating rates of 1.0, 2.0, 3.0, 4.0, 5.0, 7.0 and 10.0 °C min^{-1}.

peaks correspond to rapid heat evolution associated either with extremely fast decomposition or burning due to relatively higher heating rate as discussed in Section 3.1. On the one hand, it can be seen that under the effect of Viton A and Fluorel, the exothermic peak temperature of the cyclic nitramines except ε-CL-20 is obviously decreased. The peak difference between the BCHMX and its Fluorel bonded mixtures is around 13 °C, which is much higher than those of the others (around 2–6 °C). Based on the standard criterion for compatibility of energetic materials [30], it seems that BCHMX is less chemically compatible with Fluoropolymer than the other cyclic nitramines resulting in a lower thermal stability and thermolysis heat release (less than 50% of the pure BCHMX). The differences in the case of BCHMX might be due to its sterically crowded molecule [8] and, at the same time, due to presence of the aromatic building units (polar segments of macromolecule) in Fluorel. On the other hand, Fluorel polymer seems worse than Viton A as the binder of BCHMX if considering the chemical compatibility

and thermal stability. In fact, the color of BCHMX-FL sample would change from white to dark gray after storage of 2 years at room temperature. With regard to RDX and HMX, the influence of Fluorel and Viton A on their thermal properties is almost the same, resulting in a very close peak temperature and heat of reaction.

As shown in Table 2, if we compare the decomposition enthalpies, those for the Fluoropolymer mixtures are significantly lower than those for pure energetic materials – and not only due to the 9% of the inert polymeric material. This may be probably explained by the involved burning or deflagration, where the heat release is so rapid that it cannot be properly recorded by the DSC sensor. If we compare the heat of reaction with their heat of combustion, obviously, no direct dependence could be found between them. It has been concluded that with the increase of heat of combustion, the experimental detonation velocity will decrease [20]. According to the description of these two fluoropolymer products, compared with Viton A, Fluorel polymer is improved in retention

Table 2
DSC Parameters of Fluorel bonded PBXs containing different cyclic nitramines under the heating rate of 5.0 °C min^{-1}.

Samples	Endothermic peaks				Exothermic peaks				H_c (J g^{-1})
	T_{ot} (°C)	T_p (°C)	T_{ed} (°C)	ΔH_1 (J g^{-1})	T_o (°C)	T_p (°C)	T_e (°C)	ΔH_2 (J g^{-1})	
RDX-FL	203.3	205.4	207.5	−112.9	208.7	233.8	247.6	1758	9662
BCHMX-FL	–	–	–	–	235.6	237.4	238.2	1393	9379
HMX-FL	181.2	182.6	183.3	−2.7	277.2	278.8	281.5	1546	9647
	188.9	190–192.4	193.1	-27.3					
CL-20-FL	158.6	161.1	167.9	−17.0	239.2	239.5	240.2	1893	8634

Note: T_o, 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; a, the heating rate in this Ref. is 10.0 K min^{-1}; H_c, Heat of combustion, taken from Ref. [16].
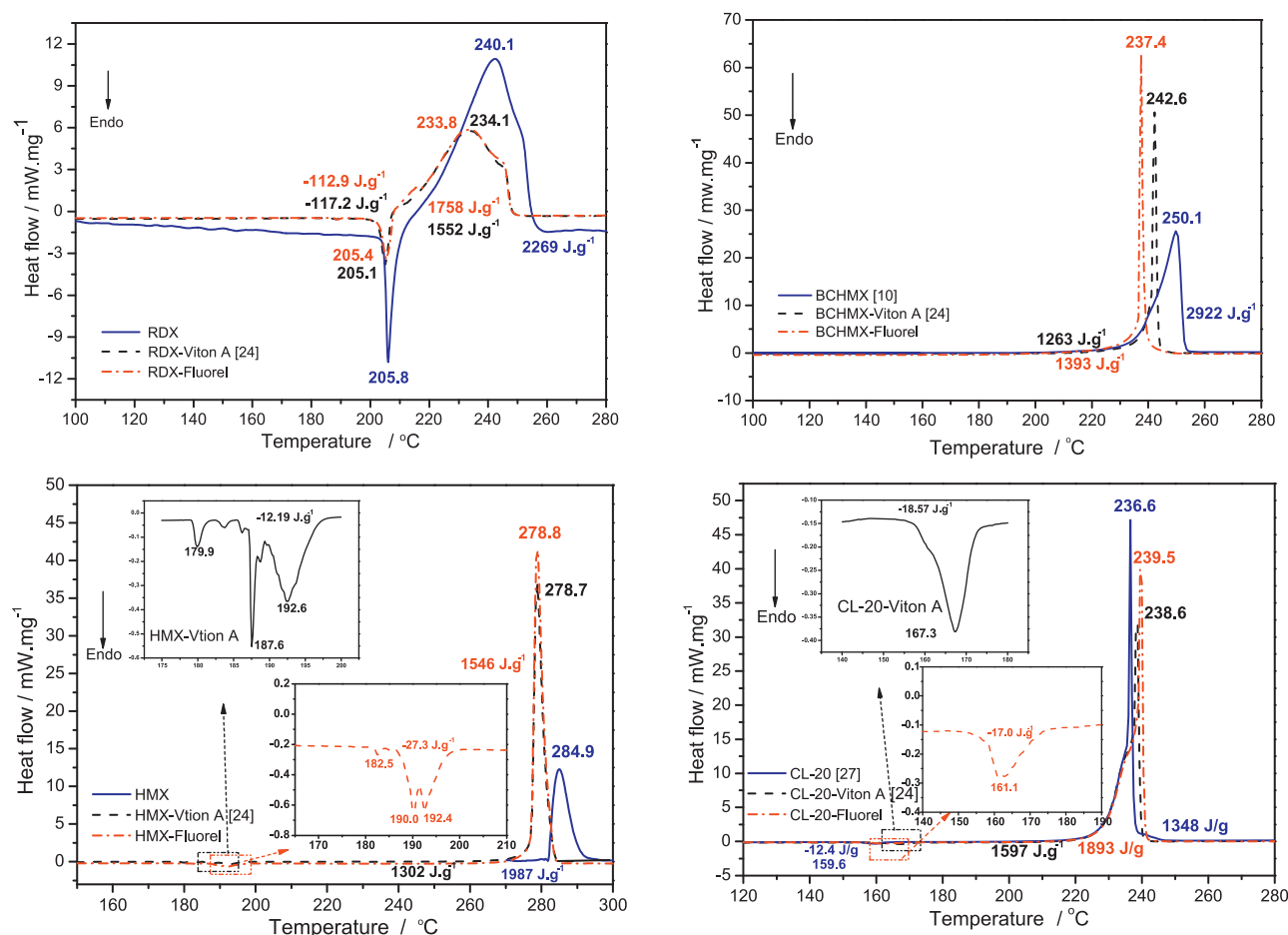
Fig. 3. The DSC curves of RDX-FL, BCHMX-FL, HMX-FL and CL-20-FL under the pressure of 0.1 MPa at a heating rate of 5.0 °C min⁻¹.

of elongation after long-term heat aging, resistance to acid and volume swell by organic solvents. It means Fluorel polymer is better than Viton A in terms of high temperature storage properties, which could be proved by the fact that the thermal stability of CL-20-FL is better than CL-20-VA. However, as the binder of BCHMX, Viton A is better than Fluorel due to greater chemical compatibility as mentioned above. Overall, the fluoropolymer has almost the same effect on the planar molecules such as RDX and HMX, the fluoropolymer with different chain structure (monomer) has different effect on crowded molecules such as BCHMX and ε-CL-20. This difference needs more investigations to clarify. Therefore, the thermal stability of the polymer bonded explosives will not only depend solely on the stability of the polymer itself, but also on the physicochemical interactions between the polymer bases and the explosive fillers.

For Fluorel bonded explosives, another effect that can be observed in Fig. 3 is the small endothermic peak corresponding to polymorphic transformation of ε-CL-20 and β-HMX at 161.1 and 190.0 °C, respectively, while at 167.3 and 187.6 °C for Viton A bonded mixtures. It means that ε-CL-20 crystal form is more stable in Viton A than Fluorel, while β-HMX is more stable in Fluorel polymer. Peak temperatures for this effect differ considerably due to totally different crystal structure for ε-CL-20 and β-HMX. It is well-known that two major conversions occur for decomposition of 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 [31]. Under the effect of Fluorel, the phase transition of ε-CL-20 shifted from 159.6 to 161.1 °C and it is also very interesting that the exothermic peak temperature of CL-20-FL is slightly higher that of the pure Rs-ε-CL-20 which is 238.4 °C [26],

indicating that the thermostable inert Fluorel has the equivalent effect as reducing sensitivity by recrystallization, which is also the case for Viton A polymer [23]. HMX exists in 4 polymorphic forms (α, β, δ and γ), and β-HMX is the most stable crystal form at room temperature. It has been found that a phase transition from β- to δ- can be clearly observed at about 170–190 °C for the fine β-HMX [32]. Here the fine β-HMX has been used, and hence it is reasonable that this conversion occurred at around 190 °C. It is very strange that there are several small shoulder endothermic peaks for this transformation for both Fluoropolymers. In fact, when β-HMX was coated by Formex or C4 matrices, the same effect could be observed with only one endothermic peak [21,22]. These phenomena need more detailed investigations to interpret. Besides, in case of RDX-FL mixture, an endothermic effect can also be observed at 205.4 °C, which corresponds to the melting of RDX (similar effect can be found for the pure RDX nitramine at almost the same temperature 205.8 °C, which confirms that both RDX and RDX-based PBX decompose at the liquid state).

3.3. Thermal decomposition kinetics

3.3.1. Kinetic parameters obtained by Kissinger method

The kinetics of the thermal decomposition of Fluorel bonded PBXs at different temperatures ranges were studied by non-isothermal TG (the mass loss was recorded as a function of temperature). As our previous study did on Viton A [24], the kinetic triplets were calculated firstly according to the traditional Kissinger method based on the shift of the peak temperatures presented in Table 1. The corresponding calculation results are summarized in

Table 3

Comparisons of the decomposition kinetic parameters of Viton A and Fluorel bonded PBXs containing different cyclic nitramines obtained by Kissinger method.

Sample names	Temp. range (°C)		Arrhenius parameters				Charge properties [16]		
	T_{ic}	T_{ec}	E_a	log A	r	k	ρ	p_r	D_e
RDX [29][a]	220	240	157.0	14.76	0.9901	2.85E−02	1.76	–	8750
RXV9505 [29][a]	215	230	201.0	19.76	0.9906	7.69E−02	–	–	–
RDX-VA [24]	202	253	177 ± 13	16.4 ± 2.7	0.9948	1.02E−02	1.79	2.89	8270
RDX-FL	226	240	161 ± 17	14.7 ± 3.3	0.9886	0.89E−02	1.74	4.28	8087
β-HMX [34][c]	171	314	227.1	19.70	–	13.0E−05	1.90	–	9100
β-HMX-VA [24][c]	251	281	245 ± 28	21.1 ± 4.4	0.9873	4.24E−05	1.92	2.85	8855
β-HMX [35][d]	226	268	135.6	10.1	-	10.0E−04	1.90	–	9100
HMX-FL[d]	244	276	110.7 ± 8	7.6 ± 0.9	0.9794	15.0E−04	1.80	4.77	8324
BCHMX (1st) [10]	84	205	242 ± 17	24.2 ± 3.3	0.9942	9.12E−02	1.79[b]	–	8650[b]
BCHMX (2nd) [10]	205	256	192 ± 10	17.2 ± 2.4	0.9990	2.01E−03			
BCHMX-VA [24]	217	253	186 ± 10	16.7 ± 2.4	0.9969	2.15E−03	1.81	2.56	8474
BCHMX-FL	214	226	196 ± 11	18.3 ± 2.6	0.9966	7.84E−03	1.76	3.91	8285
ε-CL-20 [27]	196	242	168.6	15.60	0.9988	12.9E−03	1.98	–	9473
ε-CL20-VA [24]	211	244	194 ± 16	17.8 ± 3.1	0.9936	4.20E−03	1.94	4.02	9023
ε-CL20-FL	219	234	199 ± 21	18.4 ± 3.9	0.9888	4.82E−03	1.84	5.33	8602

Notes: T_{ic} and T_{ec}, the initial and the end temperature for calculation; Rs-ε-CL20, ε-CL-20 with reduced sensitivity by recrystallization; k, rate constant at 230 °C; E_a, activation energy, in kJ mol^{-1}; A, pre-exponential factor, in s^{-1}; ρ, density of the charge, in g cm^{-3}; p_r porosity, in %; D_e, experimental detonation velocity, in m s^{-1}.

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

[b] The sample was pressed with 3% of Viton B binder.

[c] Calculated at the heating rate range of 1.0–4.0 K min^{-1}.

[d] Calculated at the heating rate range of 0.1–1.5 K min^{-1}.

Table 3. On the one hand, for thermal kinetic study of energetic materials, in order to exclude the influence of self-heating process on apparent activation energy, it is a common practice to use less sample mass, lower heating rate (non-isothermal) and lower temperature (isothermal). On the other hand, with very low heating rate, the error would be raised for volatile materials (e.g. nitric esters and some nitramines). Based on Kissinger method, lower heating rate (<1.0 K min^{-1}) could also make the activation energy (intercept) very sensitive to the heating rate. It means slightly improper baseline subtraction will result in very different kinetic parameters. For TGA experiments, the sample mass cannot be less than 1 mg, which is very sensitive to flow rate of inert gas and gas release process from the sample, resulting in a larger error. Instead, one could use relatively larger sample mass (around 2 mg) by placing a thin layered sample on the bottom of the pan for the sake of better heat dissipation.

According to Table 3, it could be found that the errors for thermolysis kinetic parameters of PBXs HMX-FL, RDX-FL, CL-20-FL and HMX-VA are much higher than those of the others. Such large errors (over 10%) may be caused by the variability of decomposition mechanism at different heating rate. If burning or deflagration occurred within the applied interval of heating rates, the kinetic results for their decomposition will not be considered physically meaningful (e.g. HMX-Formex [22] and HMX-C4 [23]). In addition, as will be shown later, the activation energy obtained by the traditional Kissinger method is very close to the activation energy at the half conversion obtained by isoconversional method. Under the effect of Formex [22], Viton A [24] and Fluorel, the a two-step decomposition process of BCHMX changes to a one-step mechanism, while a single step mechanism for ε-CL-20 changes to a two-step decomposition process under the effect of C4 binder [23]. Comparing the rate constants (at 230 °C) of the pure nitramines with those of their fluoropolymer bonded PBXs, it could be found that the thermostable fluoropolymer, which decomposes at much higher temperatures than cyclic nitramine fillers [13], could decrease the rate constants of RDX and ε-CL-20, where BCHMX is an exception due to bad chemical compatibility as mentioned in Section 3.2. It means, if a thermostable polymer were chemical compatible to the nitramine fillers, it would promote the activation energies (energy barrier) and decrease the decomposition rate constant of corresponding PBXs. The rate constant of RDX is much higher than those of the others, because the attempted temperature (230 °C) is above its

onset temperature, while lower than those of the others. Different from our previous papers [22–24], here much lower heating rates has been attempted for HMX-FL, in order to avoid the self-heating effect and thermal runaway of the sample. A much lower activation energy has been obtained (110 kJ mol^{-1}) comparing with our previous results. It has been reported that [35] the mean activation energy for β-HMX decomposition is in the vicinity of 150 kJ mol^{-1} by DSC method and 135.6 kJ mol^{-1} by non-isothermal TGA method under heating rates of lower than 1 °C min^{-1}. Such low activation energy may be caused by partial sublimation during slow heating rate and errors from mechanism change on heating rate. It has been found that both ε-CL-20 and β-HMX were volatile especially under dynamic vacuum, where β-HMX sublimates much more rapidly than ε-CL-20 [36]. It proves that the variation of decomposition mechanism on the heating rate for HMX based PBXs results from both sublimation and self-heating effect.

With regard to their detonation properties, it has been found that there are minor differences in measured detonation velocities for Viton A and Fluorel bonded explosives [16]. The samples with Viton A as a binder performed slightly better than those based on Fluorel (see Table 3). The increase of the experimental detonation velocities was 198 m s^{-1} for RDX, 204 m s^{-1} for β-HMX, and 168 m s^{-1} for HNIW based explosives. The porosity of Fluorel bonded explosives is much higher than those of Viton A bonded explosives, resulting in a lower charge density and detonation velocity. Therefore, overall, it is better to use Viton A other than Fluorel as a binder of cyclic nitramines in order for greater charge properties and higher detonation performance, and here BCHMX is an exception for both fluoropolymers due to worse chemical compatibility.

3.3.2. Dependence of Kinetic parameters on extent of conversion

As described in our previously published paper [10], 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 for involved materials, 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 case of the DTG peak tails. The corresponding calculation results ($\alpha = 0.1, 0.2, 0.3,... 0.9$) are summarized in Table 4.

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

α reacted	RDX-FL			BCHMX-FL			HMX-FL			CL-20-FL		
	E_a	Log A	r	E_a	Log A	r	E_a	Log A	r	E_a	Log A	r
0.10	199.6	19.93	0.9946	177.0	16.55	0.9986	127.82	9.94	0.9825	254.7	24.86	0.9970
0.20	178.4	17.34	0.9966	179.5	16.73	0.9980	124.30	9.48	0.9808	217.3	20.64	0.9990
0.30	170.4	16.29	0.9937	182.7	17.00	0.9971	120.50	9.03	0.9833	210.7	19.84	0.9993
0.40	168.1	15.91	0.9935	189.7	17.70	0.9970	117.64	8.62	0.9835	208.1	19.48	0.9997
0.50	166.2	15.61	0.9926	192.3	17.94	0.9974	116.12	8.44	0.9861	205.3	19.12	0.9995
0.60	170.9	16.07	0.9935	187.3	17.39	0.9965	116.50	8.51	0.9853	202.0	18.74	0.9998
0.70	175.8	16.43	0.9957	194.0	18.03	0.9974	116.94	8.49	0.9859	203.6	18.82	0.9998
0.80	178.5	16.62	0.9979	194.2	18.03	0.9989	117.96	8.57	0.9867	200.6	18.47	0.9997
0.90	175.7	16.20	0.9999	194.3	17.98	0.9990	120.02	8.74	0.9878	194.6	17.78	0.9998
Mean	170 ± 3	16.06 ± 0.3		189 ± 4	17.6 ± 0.4		117 ± 5	8.6 ± 1.2		206 ± 3	19.2 ± 0.4	

Note: E_a, calculated from non-isothermal TG data in kJ mol^{-1} and Log A, in s^{-1}; Mean value, obtained in the range of $\alpha = 0.3$–0.7.

If we compare the results for the original Kissinger method (Table 3) and those obtained from the calculations according to the modified KAS equation (Table 4), it can be seen that almost perfect agreement was obtained for the BCHMX-FL and CL-20-FL materials. Slightly lower activation energy (around 6% difference) was obtained from the Kissinger method for the RDX-FL material. In case of the HMX-VA mixture there is of course a huge difference in the results obtained by the two employed methods. However, the activation energies obtained by KAS method for HMX-FL might be more physically meaningful because the huge change of the reaction

mechanism was alleviated (without using the data from heating rate of higher than 2.0 °C min^{-1}). In order to make a comprehensive comparison for the activation energies of pure nitramines with their fluoropolymer bonded PBXs, the dependence of activation energies for these materials on degree of conversion are plotted in Fig. 4.

The isoconversional activation energies for pure BCHMX [10], ε-CL-20 [27,28], RDX [31] and β-HMX [35] are obtained from our previous paper and the literature. According to the kinetic studies on RDX and HMX based PBXs [23–34,36–38], the activation energy
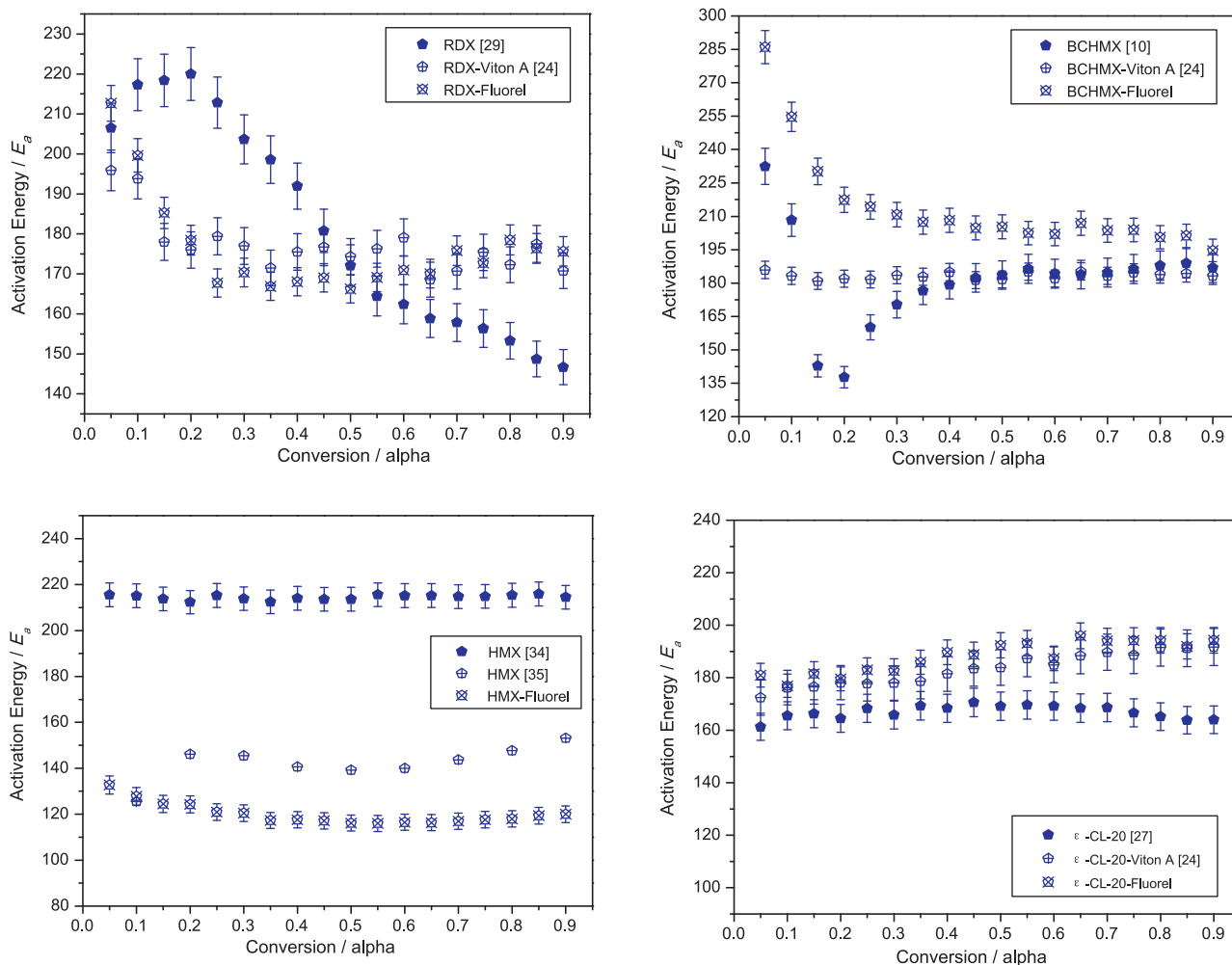

Fig. 4. Dependence of the apparent activation energy of Fluoropolymer (Fluorel and Viton A) bonded PBXs containing RDX, HMX, BCHMX and CL-20 on the degree of conversion determined by using KAS method.

of PBXs with non-energetic matrix is normally lower than that of the pure energetic fillers. According to Fig. 4, overall, unlike their pure nitramine fillers, the activation energies of fluoropolymer bonded explosives containing RDX and HMX, ε-CL-20 are almost independent on the extent of conversion, where the effect of Viton A and Fluorel is almost equivalent. The activation energy of CL-20-FL and CL-20-VA is higher than that of the pure ε-CL-20 especially after the conversion of 60%, resulting in lower rate constants and higher thermal stability. The activation energy for the initial decomposition step ($\alpha < 0.5$) of RDX is higher than that of its Fluoropolymer bonded PBXs while lower at the post step ($\alpha > 0.5$). Both Fluorel and Viton A could greatly affect the initial activation energy of RDX ($\alpha = 0.1$–0.3), making it less dependent on the conversion rate, indicating that the autocatalytic effect occurring during liquid-state decomposition of RDX has been decreased or inhibited. Similar results could also be found for C4 polymer bases [23]. However, opposite to Viton A, the Fluorel polymer enhanced the autocatalytic effect of BCHMX due to bad chemical compatibility.

The activation energy distribution of HMX is slightly higher than that of its Fluoropolymer bonded PBXs. As stated in previous literature [33,39], pure β-HMX will probably not melt during its heating process because this nitramine could gradually dissolve in the products of its thermal decomposition, which is also a reason for the discrepancy between kinetics parameters of the HMX thermolysis in its alleged liquid and solid states [40,41]. Under the package of thermostable Fluoropolymer, this effect could be enhanced resulting in much higher sensitivity to temperature gradient (heating rate) and hence a huge variation of decomposition mechanism on heating rate was observed, resulting in larger errors of kinetic parameters when isoconversion method has been used. In fact, rupture of the intermolecular forces rather than cleavages of covalent bonds within the molecule largely control the decomposition reaction rate of β-HMX and this might be also the case for BCHMX.

4. Conclusions

The thermal behavior and decomposition kinetics of Fluorel bonded PBXs based on some attractive cyclic nitramines were investigated by non-isothermal TG and DSC techniques. The following conclusions could be made:

(1) 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.
(2) The onset of the DSC exotherms were noticed at 208.7, 235.6, 277.2 and 239.2 °C with the peak maximum at 233.8, 237.4, 278.8 and 239.5 °C for RDX-FL, BCHMX-FL, HMX-FL and CL-20-FL, respectively. Their corresponding exothermic releases were covered by energy changes of 1758, 1393, 1546 and 1893 J g^{-1}, which are much lower than that of the pure cyclic nitramines; According to DSC peak shift, Similar to Viton A, Fluorel polymer is probably not chemically compatible with BCHMX resulting in much lower thermal stability and heat release compared with pure BCHMX.
(3) Both Fluorel and Viton A could decrease or inhibit the autocatalytic effect occurring during liquid-state decomposition of RDX. Opposite to Viton A, the Fluorel polymer could enhance the autocatalytic effect of BCHMX due to bad chemical compatibility. The activation energies for thermolysis of RDX-FL, BCHMX-FL, HMX-FL and CL-20-FL are found almost independent on the conversion rate ($0.3 < \alpha < 0.7$) with the mean values of 170 ± 3, 189 ± 4, 117 ± 5 and 206 ± 3 kJ mol^{-1}, respectively.

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. Energetic 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. Pachmán, 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, no. 2, Pułtusk, Poland, 2010, pp. 7–16.
[5] A. Elbeih, J. Pachmán, S. Zeman, W.A. Trzciński, Z. Akštein, Advanced plastic explosive based on BCHMX compared with Composition C4 and Semtex 10, New Trends in Research of Energetic Materials, Czech Republic, 2011, pp. 119–126.
[6] D. Klasovitý, 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, 2009, July 28th.
[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 Cryst. Sect. E58 (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. Pachmán, W.A. Trzciński, S. Zeman, Z. Akštein, J. Šelešovský, Study of plastic explosives based on attractive cyclic nitramines Part I, Detonation characteristics of explosives with PIB binder, Propellants 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] S. Vyazovkin, N. Sbirrazzuoli, Isoconversional kinetic analysis of thermally stimulated processes in polymers, Macromol. Rapid Commun. 27 (2006) 1515–1532.
[12] T. Sell, S. Vyazovkin, C.A. Wight, Thermal decomposition kinetics of PBAN-Binder and composite solid rocket propellants, Combust. Flame 119 (1999) 174–181.
[13] A. Ghosh, P.P. De, S.K. De, M. Saito, V. Shingankuli, Studies on flammability, thermal stability and hot oil resistance of silicone rubber, fluororubber and their blends, Kautschuk Gummi Kunststoffe 56 (3) (2003) 96–100.
[14] A. Taguet, B. Ameduri, B. Boutevin, Crosslinking of vinylidene containing flouoropolymers, Adv. Polym. Sci. 184 (2005) 127–211.
[15] A. Elbeih, S. Zeman, M. Jungová, P. Vávra, Attractive nitramines and related PBXs, Propellants Explos. Pyrotech. 38 (3) (2013) 379–385.
[16] A. Elbeih, J. Pachman, S. Zeman, W.A. Trzcinski, M. Suceska, Study of plastic explosives based on attractive cyclic nitramines, Part II: Detonation characteristics of explosives with polyfluorinated binders, Propellants Explos. Pyrotech. 38 (2013) 238–243.
[17] 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.
[18] S.P. Felix, G. Singh, A.K. Sikder, J.P. Aggrawal, 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.
[19] D.M. Hoffman, DMA signatures of Viton A and plastic bonded explosives based on this polymer, Polym. Eng. Sci. 43 (1) (2003) 139–156.
[20] S. Zeman, A. Elbeih, Z. Akstein, Preliminary study on several plastic bonded explosives based on cyclic nitramines, Chin. J. Energy Mater. 19 (1) (2011) 8–12.
[21] A. Elbeih, J. Pachmán, S. Zeman, A.W. Trzcinski, Z. Akstein, S. Muhamed, Thermal stability and detonation characteristics of pressed and elastic explosives on the basis of selected cyclic nitramines, Cent Eur. J. Energy Mater. 7 (3) (2010) 217–232.
[22] Q.-L. Yan, S. Zeman, J. Šelešovský, 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.
[23] Q.-L. Yan, S. Zeman, F.-Q. Zhao, A. Elbeih, Non-isothermal analysis of C4 bonded explosives containing different cyclic nitramines, Thermochim. Acta 556 (20) (2013) 6–12.
[24] Q.-L. Yan, S. Zeman, A. Elbeih, Thermal behavior and decomposition kinetics of Viton A bonded explosives containing attractive cyclic nitramines, Thermochim. Acta 562 (20) (2013) 56–64.

[25] 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.

[26] 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. 112 (3) (2013) 1433–1437.

[27] 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. 112 (2) (2013) 823–836.

[28] 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. 112 (2) (2013) 837–849.

[29] 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.

[30] 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.

[31] 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.

[32] C.K. Saw, Kinetics of HMX and phase transitions: effects of grain size at elevated temperature, in: 12th International Detonation Symposium, August 11–16, San Diego, CA, 2002.

[33] C.M. Tarver, T.D. Tran, Thermal decomposition models for HMX-based plastic bonded explosives, Combust. Flame 137 (1–2) (2004) 50–62.

[34] 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.

[35] A.K. Burnham, R.K. Weese, Thermal Decomposition Kinetics of HMX, in: 36th Intl. ICT Conf and 32nd Inl. Pyrotechnics Seminar Karlsruhe, Germany, June 28 to July 1, 2005.

[36] B.L. Korsounskii, V.V. Nedelko, N.V. Chukanov, T.S. Larikova, F. Volk, Kinetics of thermal decomposition of hexanitrohexaazaisowurtzitane, Russ. Chem. Bull. 49 (5) (2000) 812–818.

[37] 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.

[38] H.-S. Kim, B.-S. Park, Characteristics of the insensitive pressed plastic bonded explosive, DXD-59, Propellants Explos. Pyrotech. 24 (1999) 217–220.

[39] 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.

[40] 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.

[41] 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. S 18 (5) (2011) 393–398.