The effect of polymer matrices on the thermal hazard properties of RDX-based PBXs by using model-free and combined kinetic analysis

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Abstract: In this paper, the decomposition reaction models and thermal hazard properties of 1,3,5-trinitro-1,3,5-triazinane (RDX) and its PBXs bonded by Formex P1, Semtex 1A, C4, Viton A and Fluorel polymer matrices have been investigated based on isoconversional and combined kinetic analysis methods. The established kinetic triplets are used to predict the constant decomposition rate temperature profiles, the critical radius for thermal explosion and isotherms under a low temperature. It has been found that isoconversional and combined kinetic methods could yield equivalent reliable kinetic triplets, whereas it's easier to use the latter one to determine reaction models of energetic materials. The effect of the polymer matrices on the decomposition mechanism of RDX is significant, where Formex P1, Semtex and C4 could make initial decomposition of RDX follow a phase boundary controlled reaction mechanism, while under the effect of Viton A and Fluorel, its reaction model shifts to a random two dimensional nucleation and growth model. It has also been shown that the energetic materials that have longer induction period on constant reaction rate curves would have greater impact energy. According to isothermal simulations, the threshold cookoff time until loss of functionality at 82 °C for RDX-C4 and RDX-FM are less than 500 days, while it is more than 700 days for the others. Unlike simulated isothermal curves, when considering the charge properties and heat of decomposition, RDX-FM and RDX-C4 are better than RDX-SE in storage safty at arbitrary surrounding temperature.

Keywords: RDX; PBXs; Reaction models; Thermal explosion; Isothermal condition; Thermal stability;

1 Introduction

In order to produce safe munitions capable of surviving unwanted mechanical stimuli such as shocks from explosions and impacts by projectiles, the initiation sensitivity of explosives has to be significantly reduced. Such sensitivity could be reduced by employing the solid secondary high explosives including cyclic nitramines into polymeric matrices that are chemically stable and compatible with the explosive fillers [1, 2], forming one of the representative insensitive products "polymer bonded explosive" (PBX). 1,3,5-trinitro-1,3,5-triazinane (RDX) or sometime reduced sensitivity RDX (Rs-RDX), which is a well-known cyclic nitramine, is currently the most important military high explosive in the world [3]. RDX is usually used in mixtures with some other explosives, including TNT, PETN and HMX. The combinations of RDX and HMX have been the chief ingredients in approximately 75 products, mostly of which are plastic bonded explosives (or plastic explosives) and solid propellants [4]. The most common plastic explosive combining RDX and PETN is Semtex H (the original commercial Semtex® was based only on PETN). Besides, RDX was always combined with TNT to be used in PBXs of Composition A, B and C based on mononitrotoluol, wax, dinitrotoluol, polyisobutylene polymers [2]. It can also be mixed with plasticizers and polyisobutylene (PIB) to make C-4 explosive. However, in some newly developed PBX compositions, TNT has been completely replaced by RDX, where polystyrene, Kel-F (vinylidene-chlorotrifluorethene copolymer), polyurethane rubber, Estane (thermoplastic polyurethane elastomer), and nylon are usually used as polymer matrices. Some innovative RDX based mixtures have also been investigated, e.g. the RDX-based nanocomposite microparticles were produced by a simple but novel spray drying method [5]. With regard to thermal properties of RDX and its mixtures, a number of papers have been published [6], and it has been proved that the decomposition process of RDX could be greatly affected by the contact materials.

The theory of thermal explosion, firstly expressed in quantitative forms by Semenov and Frank-Kamenetskii, has been extensively developed in recent decades [7]. It can provide a model for self-heating and explosion in certain gas reactions, explosives, propellants and unstable chemical substances [8]. This theory is of great practical importance in treating problems of self-heating and ignition of energetic materials in storage and transport. The kinetic parameters, together with the reaction model (mechanism function for thermal decomposition) are very important in calculation of critical temperature for thermal explosion and the critical diameter for safe storage. The kinetic parameters of several RDX based PBXs have been obtained and published, where the Formex P1 [9], Viton A [10], C4 [11], Fluorel [12] and Semtex 1A [13] have been used as the polymer matrices. The initiation reactivity of RDX in Formex P1 and C4 matrix was also attempted by our workgroup [14, 15]. The decomposition reaction model of RDX has been widely accepted as first order (F1) [16]. However, the decomposition kinetic models of most its mixtures have never been published. Both the kinetic parameters and reaction model are the key factors for the prediction of the thermal hazard properties if knowing the physical parameters (heat capacity, heat conductivity) and charge conditions (dimensions, density, etc.) [17], it is, therefore, necessary to obtain the reliable kinetic parameters and accurate reaction model. This paper is principally concerned with the interpretation of the experimental kinetic models obtained by both isoconversional [18] and combined kinetic analysis methods [19], where a necessary comparison has been carried out. Then the kinetic triplets are used to predict the constant decomposition rate temperature profiles, the critical diameter for thermal explosion and isotherms under extreme conditions. On this basis, the effect of polymer matrices on the thermal hazard properties of RDX will be compared and clarified.

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2 Experimental

2.1 Samples

The preparation of the samples "RDX, RDX-FM, RDX-C4, RDX-SE, RDX-VA and RDX-FL", are decribed in our previous papers [9-13]. The sample names are based on involved polymers, where SE is Semtex binder, containing 15% of acrylonitrile-butadinene rubber (NBR) plasticized by a non energetic plasticizer with aromatic unit in its moleule; C4 means C-4 binder, containing wt. 25 % of polyisobutylene (PIB), wt. 59 % of dioctyl sebacate (DOS) and wt. 16 % of HM46 oil; FM: Formex, containing wt. 25% styrene-butadiene rubber (SBR) plasticized by wt. 75% oily material; VA means Viton A binder (Viton A 200), which is a copolymer of vinylidene fluoride and hexafluoro-propylene with a fluorine content of 66%; FL denotes Fluorel binder (Dyneon FT 2481), which is a terpolymer of tetrafluoroethylene, vinylidene fluoride and hexafluoropropylene containing also non-fluorinated aromatic building units.

2.2 Experimental techniques

The involved PBXs are studied with regard to the decomposition models and related thermal hazard properties, using non-isothermal TG data. The experiments were carried out on a Netzsch 209F3 instrument (Al$_2$O$_3$ crucible) under the heating rate of 5, 7 (with data collecting rate of 40 points per Kelvin) and 10, 15 °C.min^{-1} (with data collecting rate of 60 points per Kelvin). The test temperature range for TG was 30~400 °C, with the sample mass of about 2.05-2.45 mg under 30 ml.min^{-1} dynamic nitrogen atmospheres.

3 Theoretical backgrounds

3.1 Determination of kinetic parameters

The kinetic parameters (triplets), including activation energy (E_a), pre-exponential factor (A) and kinetic model ($f(\alpha)$) of each individual process, should be determined for a complete kinetic description of the overall reaction. It is recommended to use an isoconversional (model-free) method first, which state that at constant extent of conversion the reaction rate is only a function of the temperature, to obtain the dependence of the activation energy on the extent of conversion. The activation energies of the involved materials have been obtained by a popular isoconversional method, the so-called modified Kissinger-Akahira-Sunose (KAS) equation (see details in Ref. [18]). Due to the large influence of experimental conditions on the data quality of the induction and ending processes, it is a common practice to consider only values of E_a obtained for the interval α = 0.3-0.7 when calculating the average value. One can also use a combined kinetic analysis method to determine the kinetic triplets at the same time, which will be simply introduced in the following section.

3.2 Determination of kinetic models

For an isoconversional method, the determination of an appropriate kinetic model and the activation energy are separated. For the kinetic model selection procedure, Málek [20] suggested a useful algorithm based on the shape of characteristic functions $z(\alpha)$ and $y(\alpha)$, which are obtained by a simple transformation of experimental data [21]. The most suitable kinetic model is then determined based on both, value of conversion degree $\alpha_{max,y}$ corresponding to the maximum of the $y(\alpha)$ function and value of $\alpha_{max,z}$, which corresponds to the maximum of the $z(\alpha)$ function. In the present work, two of the most popular models could be used: the physically meaningful Johnson-Mehl-Avrami model (JMA, Eq. 1) and empirical autocatalytic model (AC, see Eq. 2), which is also known as Šesták-Berggren model [19].

$$f(\alpha) = m(1-\alpha)[-\ln(1-\alpha)]^{[1-(1/m)]} \qquad (1)$$

$$f(\alpha) = \alpha^M (1-\alpha)^N \qquad (2)$$

where the parameters m, M and N can be calculated from the value of $\alpha_{max,y}$ by the following equations:

$$m = \frac{1}{1 - \ln(1 - \alpha_{max,y})} \qquad (3)$$

$$\frac{M}{N} = \frac{\alpha_{max,y}}{(1 - \alpha_{max,y})} \qquad (4)$$

$$\ln\left[\phi \exp\left(\frac{E}{RT}\right)\right] = \ln(\Delta H \cdot A) + N \cdot \ln\left[\alpha^{M/N}(1-\alpha)\right] \qquad (5)$$

The Šesták model is usually considered empirical, i.e. the model itself or its parameters do not have any physical basis or meaning, the description is purely phenomenological. In most cases, $\alpha_{max,z}$ is greater than $\alpha_{max,y}$ and $\alpha_{max,y} \neq 0$ for thermal decomposition of energetic materials. According to Málek's algorithm, one could select a JMA model when $\alpha_{max,z}$ is close to 0.632, otherwise select an AC model. Based on Eq. (3) and Eq. (4), one could plot $\alpha_{max,y}$ with m or M/N values, and $z(\alpha)$ at the function of α for JMA model (shown as Fig. 1).
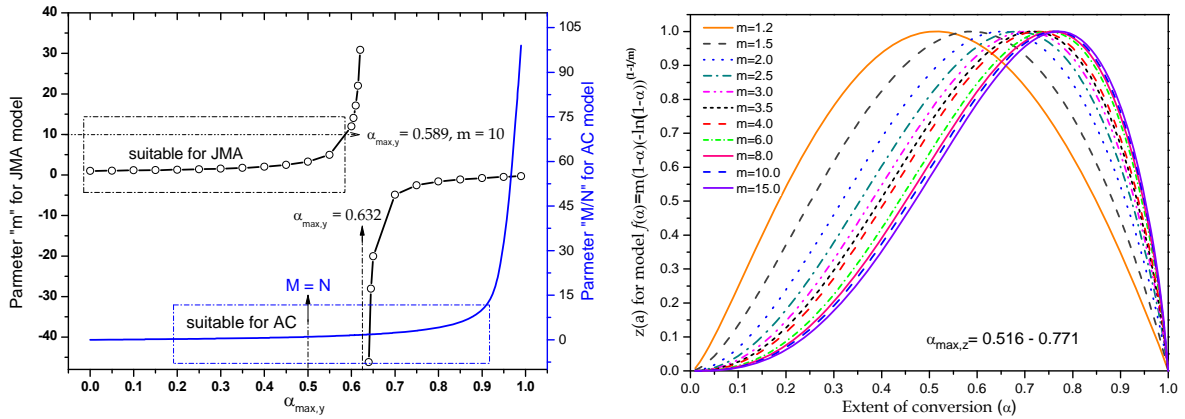

Fig.1, the dependence of m and M/N values on the $\alpha_{max,y}$ and $\alpha_{max,z}$ for JMA and AC model

For thermal decomposition of energetic material, Málek's algorithm could be extended in a more detail. It is clear from Fig. 1 that, in case of $\alpha_{max,y} \neq 0$, when $\alpha_{max,y} > 0.58$ (where m> 10 or m<0), usually it's better to choose AC model. If $\alpha_{max,y} < 0.58$, then it will depend on $\alpha_{max,z}$. When $0.50 < \alpha_{max,z} < 0.70$, it is more suitable to use a JMA model, otherwise AC model could be used. In some critical cases, both models could apply with comparable correlation coefficients. When m is greater than 10, the shape of JMA model will not sensitive to m. The parameter m for JMA model is usually easier to obtain, whereas parameters M and N for AC model are sometimes difficult to obtain due to bad linear correlation between caused by large errors in induction period. If $\alpha_{max,y}$ is very close to zero, one could follow Málek's algorithm to select some other models including reaction order model and diffusion model (D2-D4). After determining the kinetic model, the pre-exponential factor (A) can be established by fitting the experimental data using this model.

In fact, another method so-called "combined kinetic analysis" could be used for this purpose [19], which is more convenient than the abovementioned isoconversional method. The combined kinetic analysis implies a simultaneous analysis of experimental data representative of the forward solid-state reaction under any experimental conditions. The procedure is based on the fact that only the true kinetic model fits simultaneously all experimental data yielding a unique $f(T)$ function. Here a modified Šesták-Berggren equation (Eq. 6) has been used to fit the experimental data. It can fit every kinetic function corresponding to the ideal models used in the literature and one could easily find its probable deviations from the ideality.

$$f(\alpha) = c\alpha^m (1-\alpha)^n \qquad (6)$$

One could refer to Ref. [19] for the detailed procedure to obtain Activation energy (E_a), together with the parameters of m, n and cA (here the pre-exponential factor being merged with c). This method has been widely used for thermal degradation of polymers [25, 26], but it has seldom been used to investigate thermal decomposition of energetic materials. It will be more convenient to investigate the complex decomposition reactions of energetic mixtures including propellants and PBXs, which could not be fully described by the ideal

kinetic models. After determination of the model by abovementioned methods, one could test the reliability of each selected model by using them to simulate the experimental data and then do some kinetic prediction.

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4 Results and discussions

4.1 The decomposition reaction model of RDX based PBXs

Based on abovementioned theory, the characteristic functions $z(\alpha)$ and $y(\alpha)$ have been plotted for studied materials, and only selected $y(\alpha)$ curves are presented here for the sake of space saving (see Fig. 2). It has been found that, the $y(\alpha)$ curves under different heating rates almost overlap with each other even there are slightly shifts for those of RDX-SE and RDX-FM. It indicates that the decomposition mechanism of RDX-SE and RDX-FM is slightly dependent on the heating rate. The corresponding $\alpha_{max,y}$ and $\alpha_{max,z}$ values are obtained and listed in Table 1. It has been shown that RDX, RDX-SE, RDX-VA, RDX-FL and RDX-C4 have the $\alpha_{max,z}$ values between 0.51-0.77, while corresponding $\alpha_{max,z}$ values are greater than $\alpha_{max,y}$ ($\alpha_{max,y} \neq 0$), which is a characteristic "fingerprint" suggesting good applicability of JMA model. RDX-C4 could be either described by AC model or JMA model, while AC model is better for RDX-FM. The corresponding parameters are calculated and summarized in Table 1.
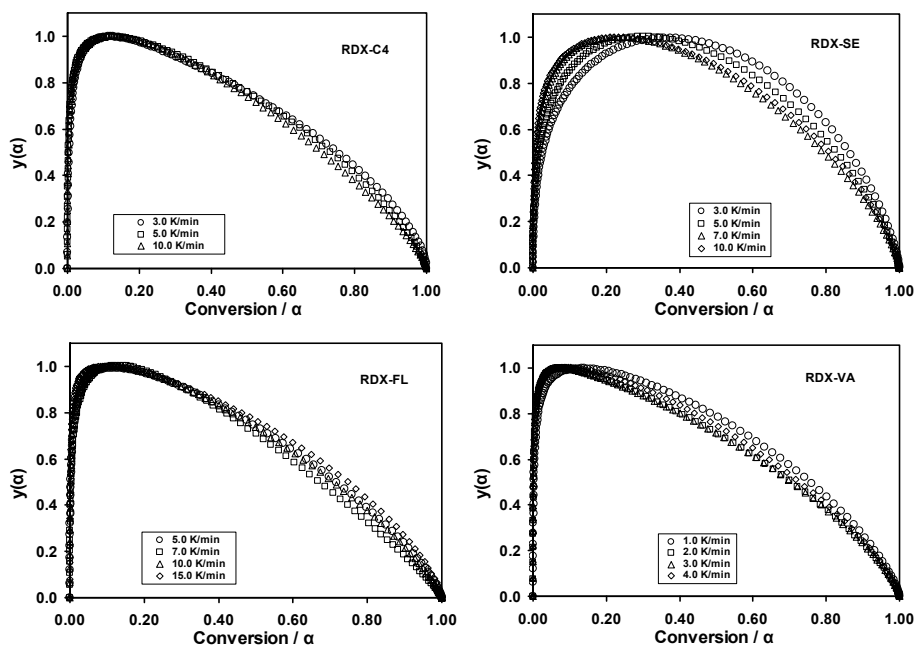

Fig. 2 The $y(\alpha)$ plots for the non-isothermal decomposition data of selected RDX based PBXs

Table 1 Parameters for reaction models of RDX and its PBXs evaluated by non-isothermal TG experiments

Samples	For $y_m(\alpha)$ and $z_m(\alpha)$		Model	Heating rate	Parameters for mechanism functions					
	$\alpha_{max,y}$	$\alpha_{max,z}$			m	M	N	E_a	$Log(A)^{(mo)}$	$Log(A)^{(ex)}$
RDX [16]	-	-	JMA	7.5-20	1.00	-	-	157.0[a]	-	14.76
RDX [27]	-	-	JMA	-	1.00	-	-	197-206[b]	-	18.4-19.9
	0.374	0.662	JMA	3.0	1.98				15.92	
RDX-SE	0.284	0.662	JMA	5.0	1.75	-	-	142.0±7	15.94	13.15
	0.178	0.662	JMA	7.0	1.63				15.95	
RDX-VA	0.125	0.675	JMA	3-10	1.15	-	-	174.4±3	19.81	16.57
RDX-FL	0.130	0.698	JMA	5-15	1.16	-	-	170.3±3	19.48	16.06
RDX-C4	0.198	0.703	AC	3.0	-	0.68	0.62	165.2±5	17.35	15.57
	0.142	0.703	AC	7-10		0.42	0.74		17.33	
RDX-FM	0.308	0.819	AC	2.0	-	0.35	0.54	147.9±11	17.24	13.49
	0.122	0.754	AC	5-10		0.42	0.71		17.33	

Notes: mo), model fitting values by Málek's method; ex), experimental values; the kinetic triplets are taken from our privious papers [15-23], which are the mean values calculated by KAS method; a, decomposes in gas state; b, the average values when RDX decomposes in a liquid state; The heating rates are in K.min^{-1}.

It could be seen from Table 1, that under the effect of polymers, the reaction mechanism of RDX changes a lot. The Semtex matrix makes the decomposition mechanism slightly dependent on the heating rate. For C4 and

Formex matrix, the mechanism under lower heating rate is slightly different from higher heating rate due to evaporation effect, which will be discussed in detail later on. The advantage of the isoconversional method is that different model could be used to different heating rate where the same activation energy has been used, yielding different exponential factor. The exponential factors obtained by model fitting are greater than the calculated ones by isoconversional method, where the kinetic model has been neglected.

If we apply the combined method to the same experimental data (triplets of T, $d\alpha/dt$, α), the plots of $\text{Ln}[(d\alpha/dt)/f(\alpha)]$ vs. reciprocal of temperature $(1/T)$ under different experimental conditions could be obtained as shown in Fig. 3. In order to exclude the errors of the induction period, only the data in the range of $0.1 < \alpha < 0.9$ has been considered.
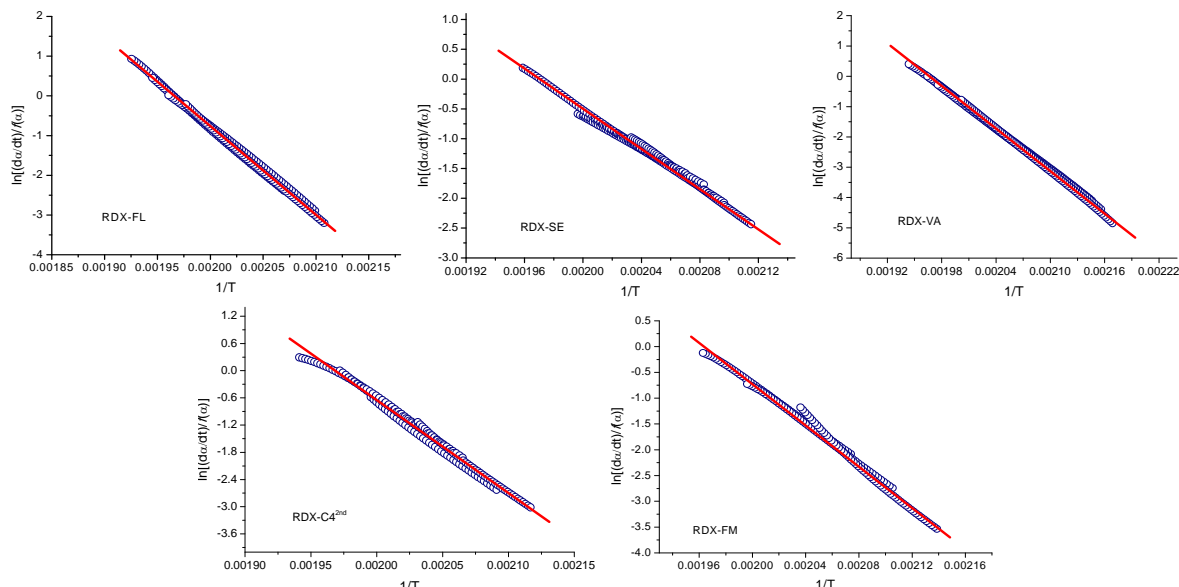

Fig. 3 The combined kinetic analysis plots for non-isothermal decomposition data of RDX based PBXs

It is clear from Fig. 3, that all of the materials could be fitted by a single mechanism function, although there are still some deviation for RDX-FM, RDX-SE and RDX-C4 with acceptable correlation coefficient (>0.98) due to slight mechanism change on heating rate, which agrees well with the minor inconsistencies of their $z(\alpha)$ and $y(\alpha)$ functions shape. In this way, the kinetic triplets are obtained and compared with those obtained by isoconversional method in Table 3.

Table 2 Comparisons of kinetic triplets of RDX based PBXs obtained by isoconversional method and combined kinetic analysis using non-isothermal TG data

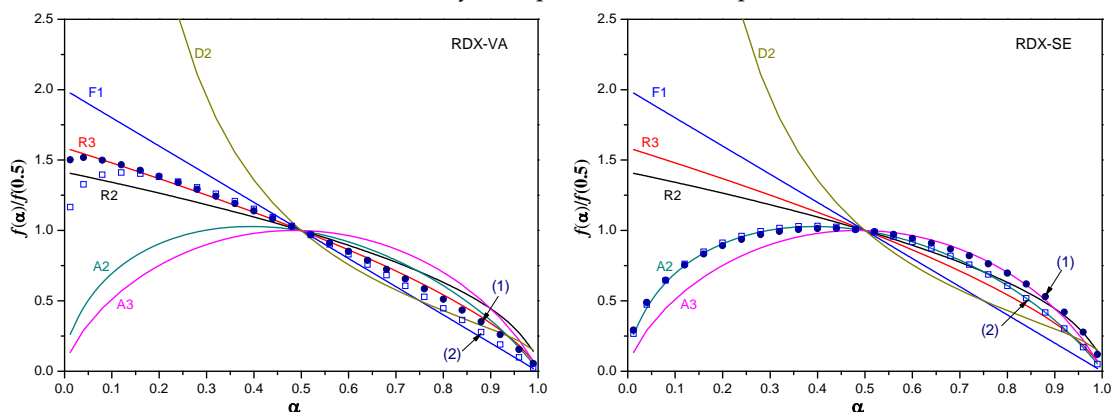| Samples	By combined kinetic analysis method				By isoconversional method[b]			
	m	n	E_a	$cA^{(mo)}$	m	M	N	E_a
RDX[a]	0.021	0.997	159.6±0.7	3.7±0.4E15	-1.98	0.02	1.03	157.0
RDX-SE	0.444	0.622	131.2±0.8	2.9±0.6E13	1.75 / 1.63	-	-	142.0±7
RDX-VA	0.027	0.745	190.3±0.3	3.2±0.3E19	1.15	-	-	174.4±3
RDX-FL	0.087	0.832	185.3±0.8	1.0±0.2E19	1.16	-	-	170.3±3
RDX-C4	0.143	0.874	163.1±1.8	5.7±0.3E16	-	0.68 / 0.42	0.62 / 0.74	165.2±5
RDX-FM	0.167	0.456	165.5±1.0	9.7±2.5E16	-	0.35 / 0.42	0.54 / 0.71	147.9±11

Notes: a), values are calculated from the TG data provided in the literature [25]; mo), model fitting values by combined kinetic analysis method; b) the kinetic triplets are taken from our privious papers [9-13] as mentioned in Table 1;

It can be seen from Table 3, that the parameters of m and n are very different obtained by different method even the same Šesták model has been used. However, the activation energies obtained by these two methods are very close to each other if considering larger derivations of the mean values by isoconversional method. It has been summarized by Long etc. [16], that the reported activation energy for RDX decomposition in liquid state without evaporation is in the scope of 197-206 kJ.mol^{-1}. As it's widely known, RDX is slightly volatile with the evaporation activation energy of around 100 kJ.mol^{-1} and then decompose in a gas-state with activation of around 140 kJ.mol^{-1}. In dynamic TG experiments, the evaporation occurred simultaneously with the decomposition especially under lower heating rate, whereby the activation energy of RDX obtained here is around 159 kJ.mol^{-1}. In open pan experiments (TGA) the decomposition kinetics of RDX are greatly affected by vaporization, while conducting experiments in closed pans would significantly suppresses vaporization and favors liquid state decomposition as the dominant process. Both pierced and closed pan DSC experiments show a decrease in the activation energy with the extent of conversion that is ascribed to a competition between liquid and gas phase decomposition [29]. Under the package of thermal stable polymers, the activation energy was increased, especially for highly thermal stable Fluoroelastomer (Viton A and Fluorel), due to great hindrance of evaporation.

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4.2 Reliability of obtained reaction models and their physical interpretation

Now that the decomposition models for the same material obtained by two methods seem very different, the comparison of their shape with the ideal models has to be done. The normalized curves of obtained kinetic models for RDX-VA and RDX-SE with the ideal models have been compared in Fig. 4. The corresponding mathematical expressions of the ideal models could be found in many literatures [2, 18, 19]. As it could be seen, the shape of the models obtained by these two methods is very close to each other even they have different parameters. It means that both of the methods yield equivalent kinetic triplets.
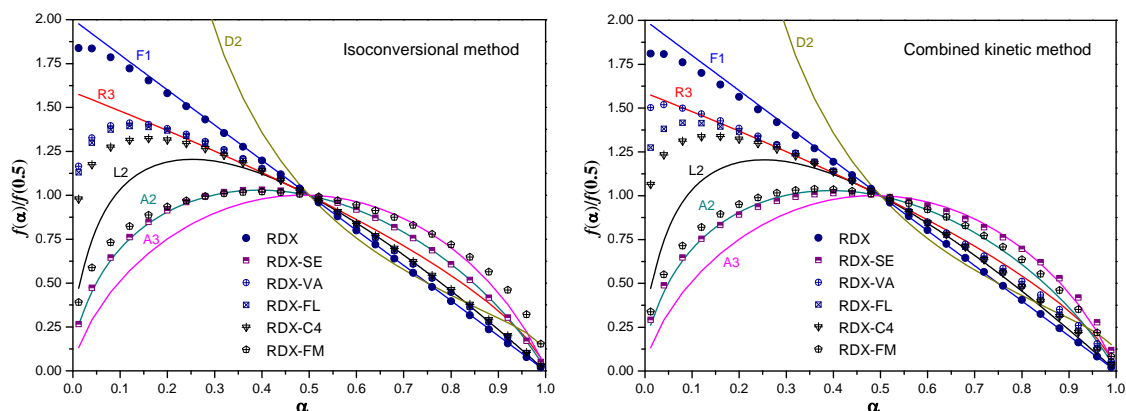

Fig. 4 A comparison of normalized curves of obtained kinetic models for RDX-VA and RDX-SE with the ideal models: (1) by isoconversional method and (2) by combined kinetic analysis method; Notes: "D2: Two-dimensional diffusion; R2: Phase boundary controlled reaction (contracting area), R3: Phase boundary controlled reaction (contracting volume); F1, First order reaction, so-called unimolecular decay law, where random nucleation followed by an instantaneous growth of nuclei; A2, A3: Random nucleation and two and three dimensional growth of nuclei through different nucleation and nucleus growth models", which is also the case for Fig. 6.
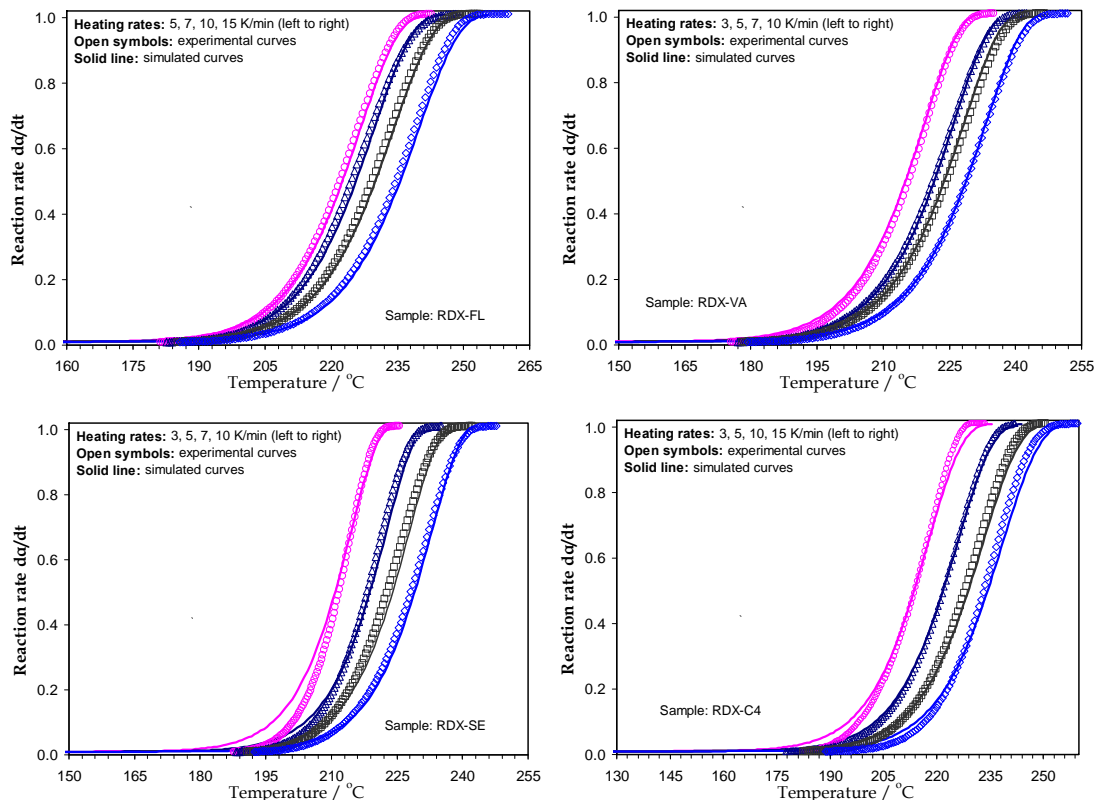
Fig. 5 The reconstruction of the experimental curves for RDX based PBXs by using kinetic triplets from combined kinetic analysis

Since the shapes (inherent mechanism) of decomposition models obtained by two methods are equivalent, one could select any one of them to reconstruct the experimental curves for the sake of reliability. The reconstructed curves by using models from combined kinetic analysis are presented in Fig. 5 (only four typical materials have been selected as the representatives). It can be seen that the experimental curves could be well constructed by the obtained models, especially for RDX-FL and RDX-VA. The decomposition mechanism of

these materials is not dependent on the heating rates, whereas the experimental curves of RDX-SE and RDX-C4 under lower heating rates could not be well reconstructed due to the effect of evaporation. As mentioned in the last section, the evaporation of RDX is relatively stronger under lower heating rate. The reconstruction for RDX-FM is better than RDX-SE and slightly worse than RDX-VA, which is very acceptable if considering the experimental errors. Those models obtained herein are reliable and now they are ready for physical interpretation and kinetic prediction. A comparison of normalized curves of obtained kinetic models with some ideal models for involved materials has been carried out (see Fig.6).

Fig. 6 A comparison of normalized curves of obtained kinetic models with some ideal models for RDX based PBXs by both isoconversional and combined kinetic analysis methods;

It is very clear from Fig. 6, that both methods yield almost equivalent results for all of the involved materials. If we look at the graph obtained by combined kinetic method, the effect of the polymer matrices on the decomposition mechanism of RDX is significant. Similar to the literature [16], the decomposition reaction model of pure RDX is very close to F1 (first order chemical reaction). Under the effect of polymer matrices, the reaction model shifts to those with longer induction period. The polymer matrices containing mineral oil materials and plasticizers (Formex P1, Semtex and C4) almost have the same effect, making the beginning of RDX decomposition follow R3, which corresponds to phase boundary controlled reaction (contracting volume). However, their post decomposition processes ($\alpha > 0.5$) still follow F1 mechanism. For highly thermal stable Fluoroelastomer (Viton A and Fluorel), they could not only stabilize RDX by hindering its evaporation, but also change the decomposition mechanism from the first order reaction model to a random two dimensional nucleation and growth model. For pure RDX, as mentioned in the last section, its initial stage of decomposition in closed pans has activation energy of 200 kJ.mol^{-1}, which is consistent with liquid phase RDX decomposition [30]. Standard bond energy of N-N bond is of 38.4 kcal.mol^{-1} (160.65 kJ.mol^{-1}) while those energy of C-N bond represents of 73.0 kcal.mol^{-1} (305.43 kJ.mol^{-1}) [31]; that means that homolysis of the N-N bond is a primary fragmentation in the PBXs studied [16, 31]. However, the whole decomposition processes of RDX-VA and RDX-FL has almost identical activation energies is higher than 160 kJmol^{-1} [10, 12], indicating competition of N-N and C-N bond scission an as a rate-limiting step under packing of these polymers. There is another factor that might affect the activation energy of the mixtures, which is known as activation entropy ($\triangle S^{\#}$). It could be calculated on the basis of the following equation.

$$\Delta S^{\#} = R(\ln A - \ln T_b) - 205.86 \qquad (7)$$

where values of T_b and $\triangle S^{\#}$ are listed and intepreted in Table 3. The positive $\triangle S^{\#}$ values give evidence of homolytic primary process of the studied PBXs decomposition. It is clear that this value has similar trends like activation energy, where RDX-VA has the largest value and RDX-FM the lowerst. Polyfluorinated binders are as if inert coatings of the crystalline RDX [32]. However, nonfluorinated aromatic building units, presented as an admixture in Fluorel, could decrease activation entropy, and this is why Viton and Fluorel have different effects on the chemistry of detonation [33]. Dioctyl sebacate (DOS) the case of RDX-C4, might be a reason to increase $\triangle S^{\#}$ value in comparison with RDX and decrease in comparison with RDX-FM. Aromatic plasticizer in RDX-SE probably is the reason for a great decrease of $\triangle S^{\#}$ value. Aromatic units might have influence through their π-electron systems (complexes formation), while polar plasticizers here figure as solvents (excluding oily admixtures).

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4.3 The relationship between the kinetic model and impact sensitivity

The microscopic processes involved in initiation by impact are complicated and not very well understood. In general, it is believed that ignition by impact starts from pockets of hotspots generated from energy localization as a result of shear band formation [34]. A variety of mechanisms have been proposed for their formation, including adiabatic compression of trapped gas in voids, friction involving sliding or impacting surfaces, shear band formation caused by mechanical failure, sparks, triboluminescence and heating at crack tips. Real explosive formulations are defective (plastic bonded, porous, etc.) and these heterogeneities lead to hotspots and a complex multi-dimensional flow even in macroscopically unidirectional detonation. The initial temperature at the hotspot that could lead to a runaway chemical reaction is very important for the impact sensitivity of the explosives. The decomposition mechanism (reaction model) might have some relation with the impact initiation of explosives. If considering the explosive at the beginning decomposes at a constant rate, which could result in a thermal built-up. Hence the constant rate thermal analysis may provide some information for the initial temperature of low decomposition rate that could lead to a thermal runaway. Here we can use obtained kinetic triplets to simulate constant low reaction rate temperature profiles using the following equation [35].

$$C_r = cA\exp(\frac{-E_a}{RT})\alpha^m(1-\alpha)^n \qquad (8)$$

where C_r is the proposed constant reaction rate, E_a the apparent activation energy and cA the integrated preexponential factor. The decomposition processes under the rate of 2.5%.min^{-1} for involved materials have been simulated (see Fig. 7). The corresponding charge performance and sensitivity parameters of RDX and its PBXs are summarized in Table 3.

Table 3 some charge performance and sensitivity parameters of RDX and its PBXs

Sample	Formula	M_e	VoD_{exp}	d	I_m	H_d	T_b	$\lrcorner S^\#$
RDX	$C_3H_6N_6O_6$	222.1	8750[a]	1.76[a]	5.6	2269.0	205.3	40.74
RDX-FM	$C_{4.14}H_{8.01}N_6O_{6.21}$	241.0	7711	1.56	21.4	1788.0	201.7	67.95
RDX-C4	$C_{4.66}H_{8.04}N_6O_{5.99}$	243.7	8055	1.61	21.1	1749.0	178.1	63.96
RDX-SE	$C_{5.31}H_{8.92}N_6O_{6.23}$	256.5	7468	1.54	23.6	1808.0	196.4	0.15
RDX-VA	$C_{3.63}H_{6.46}F_{0.77}N_6O_{5.95}$	244.0	8285	1.76	10.6	1552.0	191.4	116.34
RDX-FL	$C_{3.60}H_{6.32}F_{0.79}N_6O_{5.96}$	244.0	8087	1.74	10.8	1758.0	199.9	106.50

Notes: a) Values taken from Ref. [10], other values are tested by our workgroup and published elsewhere [43-45]. D, Charge density, in g.m^{-3}; M_e, Molecular weight, g.mol^{-1}; I_m, Impact energy, in J; H_d, Heat of decomposition, J.g^{-1}; T_b, Critical temperature for thermal explosion, in Celsius. T_b, the critical temperature extrapolated from the onset temperature of TGA curves when the heating rate decreases to zero, in Celsius; $\triangle S^\#$, activation entropy, in J.K^{-1}.mol^{-1}.
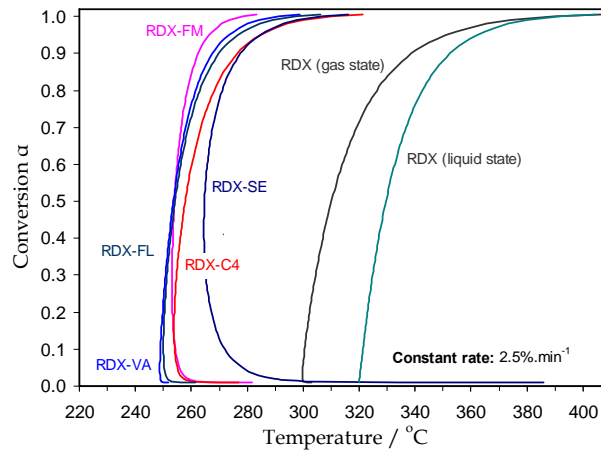
Fig. 7 A comparison of normalized curves of obtained kinetic models with some ideal models for RDX based PBXs by both isoconversional and combined kinetic analysis methods;

According to Table 3, the detonation velocity as well as heat of decomposition could be slightly brought down by C4, Fluorel and Viton A, whereas over 10% decrease occurred for Formex and Semtex matrices, due to great decrease of charge density and dilution of the energy. With regard to the impact sensitivity, the polymer could greatly increase the impact energy of RDX, making it much safer to handle. Interestingly, if we compare the sensitivity data with the shape of their constant rate decomposition curves (See Fig. 7), it is clear that the material that has longer induction period has greater impact energy (e.g. RDX-C4). Here the induction period of RDX (in liquid state) is almost zero. The induction period of RDX-FL and RDX-VA is very close, which is smaller than those of the RDX-SE and RDX-FM, resulting in lower impact energies (10.6 and 10.8 J). This phenomenon reveals that the impact initiation greatly depends on the induction period of thermal decomposition of energetic materials. A much higher temperature is needed for energetic materials with longer induction period to maintain the initial lower constant reaction rate.

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4.4 The effect of polymer on the threshold time of cookoff

Cookoff experiment is a widely-used technique to evaluate the thermal explosion threshold of energetic materials [39]. The 500-day cookoff temperature has been suggested that for the safety of a particular general purpose bomb [40, 41]. If the cookoff was carried out under isothermal conditions at 82 °C, the warm-up period until destroying its functionality (this roughly corresponds to a amount reacted of maximum 2% of the explosive) should be more than 500 days for the sake of storage safety. In practice, it is difficult to carry out such experiments under extreme conditions (record isotherms for years) due to limitation of corresponding test techniques. Instead, one could use the Arrhenius frequency factor (cA), activation energy (E_a) and reaction models to simulate small-scale isothermal curves under very low temperature without considering the charge properties and the confinement. The corresponding isotherms at 82 °C for involved materials have been simulated by using obtained kinetic triplets (shown in Fig. 8).

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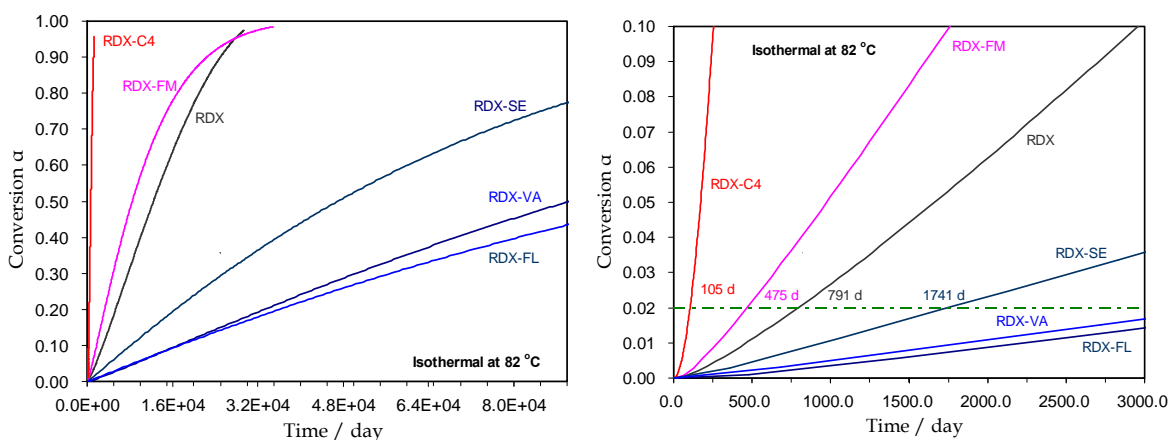
Fig. 8 the simulated isothermal curves of RDX based PBXs under the temperature of 82 °C using the kinetic triplets obtained by combined kinetic analysis method (for small samples)

Based on Fig. 8, one could easily get the time where 2% of the explosive has been reacted. It has been found that the threshold cookoff time until loss of functionality at 82 °C of RDX-C4 and RDX-FM are less than 500 days. The others have very good storage (aging) properties according to the results. It also reveals that the material that has better sensitivity does not necessarily have better storage properties (e.g. RDX-C4). RDX-VA and RDX-FL are of great storage properties and also acceptable sensitivity. RDX-SE has both good storage and lower sensitivity, and this is why Semtex H explosive has been worldwide used both in military and civil applications.

4.5 The effect of polymer on the critical radius of the cylinder charge

"ASTM E-1445" documented the standard method for estimation of the critical temperature of thermal explosion and critical half thickness of a sample at a certain initial temperature in a container where heat losses to the environment are less than the retained heat, resulting in build-up of internal temperature leading to thermal runaway. This figure of merit can be determined for a wide variety of shapes (sphere, infinite slab, cube, box, cylinder) assuming either an unstirred (Frank-Kamenetskii) or a stirred (Semenov) model for the container. Frank-Kamenetskii theory is usable for the substances with the low thermal conductivity (e.g. polymer bonded explosives), and thereby the surface temperature is the same as has the surroundings. However, the temperature range where decomposition occurs, and more importantly the shape of the exotherms obtained, is not indicative of the expected first order reaction for most involved materials. According to Frank-Kamenetskii theory, the critical half-thickness of the charge could be calculated using the following equation:

$$r_0 = \left(\frac{\delta_c \lambda R T_0^2}{Q E_a cA \rho \exp(\frac{-E_a}{RT_0})} \right)^{1/2} \tag{9}$$

where δ_c is the the shape factor (it equals to 0.88, 2.00 and 3.22 for infinite plate, cylinder and sphere, respectively), λ the heat conductivity, ρ the density, Q the heat of reaction, cA the integrated preexponential factor, T_0 the initial temperature, and E_a the apparent activation energy. One could use decomposition heat and charge density data in Table 3 for current materials. The heat conductivity of RDX is around 0.106 W.m^{-1}.K^{-1} while its PBXs is around 0.21-0.28 W.m^{-1}.K^{-1} [42, 43], which indicates that the polymer could increase the heat

conductivity to a similar extent (around 2 times). In this way, the dependence of critical half-thickness on the initial temperature was simulated and plotted in Fig. 9 considering a cylinder confinement.
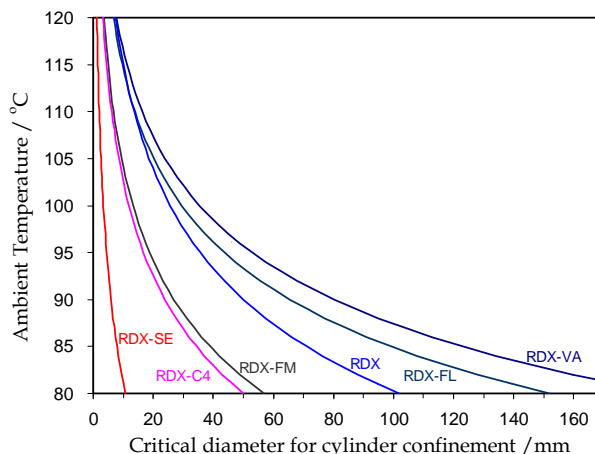

Fig. 9 the simulated isothermal curves of RDX based PBXs under the temperature of 82 °C using the kinetic triplets obtained by combined kinetic analysis method (for infinite cylinder charge)

It has been shown from Fig. 9, that under the same cylinder confinement, RDX-VA has the largest critical half thickness (radius), whereas RDX-SE has the lowest. Unlike simulated isothermal curves, when considering the charge properties and the heat release, RDX-FM and RDX-C4 are better than RDX-SE in storage safty at a certain temperature. There are several experimental investigations with regard to the thermal stability of RDX based PBXs. It has been found that the peak temperatures for the C4, Formex and Semtex mixtures prepared are lower than those of the pure RDX due to the presence of the polar plasticizer dioctyl sebacate (DOS) and dioctyl phthalate (DOP) in the binders. They may act as solvents for RDX during heating, leading to a lower decomposition temperature and smaller critical radius [44]. It was also found [10, 12] that the peak temperatures for all the prepared mixtures bonded by Viton A and Fluorel are slightly higher than those of pure explosives, which showed they could enhance the thermal stability of the RDX, resulting in greater critical radius. The Viton A and Fluorel are considered have greater thermal stability than Semtex and C4 matrix [45], hence a film of such inert materials may inhibit the thermal decomposition of RDX. It was further pointed out by Burnham [46] that the presence of an endothermic binder in a PBX could increase the times to thermal explosion, while the presence of an exothermic binder decreases the times to explosion.

5 Conclusions

The thermal decomposition kinetic models of RDX and its PBXs are obtained by both isoconversional and combined kinetic analysis methods with a necessary comparison. The established kinetic triplets are used to predict the constant decomposition rate temperature profiles, the critical radius for thermal explosion and isotherms under a low temperature. On this basis, the effect of polymer matrices on the thermal hazard properties of RDX are compared and clarified. The following conclusions could be made:

(1) Both isoconversional and combined kinetic methods are reliable, yielding almost equivalent kinetic triplets. The combined kinetic analysis method is more convenient to determine reaction models of energetic materials, if the activation energy was nearly constant throughout the decomposition process;

(2) The effect of the polymer matrices on the decomposition mechanism of RDX is significant. The decomposition reaction model of pure RDX is very close to first order chemical reaction, while Formex P1, Semtex and C4 could make the its initial decomposition following phase boundary controlled reaction mechanism, whereas under the effect of Viton A and Fluorel, its decomposition reaction model shifts to a random two dimensional nucleation and growth model;

(3) The energetic materials that have longer induction period on the constant reaction rate decomposition curves would have greater impact energy;

(4) According to isothermal simulations, the threshold cookoff time until loss of functionality at 82 °C for RDX-C4 and RDX-FM are less than 500 days, while it is more than 700 days for the others. Unlike simulated isothermal curves, when considering the charge properties and the heat release, RDX-FM and RDX-C4 are better than RDX-SE in storage safty at an arbitrary temperature.

Acknowledgements

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