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

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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}.

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-tetranitrooctahydroimidazo-[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

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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