



Thermodynamic properties, decomposition kinetics and reaction models of BCHMX and its Formex bonded explosive

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ABSTRACT

As an attractive new energetic material, cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX) and its polymer bonded explosive (PBX) with styrene-butadiene rubber (SBR) binder (Formex type) have been investigated with regard to its thermal decomposition kinetics and reaction models by using DSC, TG and SEM techniques. It was found that the decomposition of BCHMX in dynamic nitrogen could be divided into two steps, while there is only one step for its Formex bonded explosive. The activation energy for decomposition of BCHMX/Formex was obtained to be $221.7 \pm 4.99 \text{ kJ mol}^{-1}$ by modified KAS method, while the mean activation energies for pure BCHMX are calculated as $233.0 \pm 2.1 \text{ kJ mol}^{-1}$ for first step and $186.0 \pm 0.92 \text{ kJ mol}^{-1}$ for the second step. It was further proved that the first decomposition step of BCHMX is autocatalytic, during which the crystal of BCHMX could dissolve in the liquid phase of its thermolysis products on the surface. Besides, the JMA and AC models were found to be appropriate to interpret the two-step decomposition of pure BCHMX and JMA model for BCHMX/Formex, the parameterized reaction models for BCHMX could be established as $f(\alpha) = \alpha^{0.45}(1-\alpha)^{1.51}$ and $f(\alpha) = 2.33 \times (1-\alpha)[- \ln(1-\alpha)]^{0.57}$, while for BCHMX/Formex as $f(\alpha) = 2 \times (1-\alpha)[- \ln(1-\alpha)]^{1/2}$.

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1. Introduction

A polymer bonded explosive (PBX) is an explosive material in which explosive powder is bound together in a matrix using typically 5–10% by weight of a synthetic polymer, they have been widely used due to their high safety, processing ease and superior strength [1]. The next generation of PBX materials will be improved in terms of insensitivity and high energetic density properties combined with an enhanced mechanical integrity [2]. There are always several aspects to investigate the performance and properties of such new PBXs, including their formulations and processability, initiation and sensitivity, thermal decomposition and stability, mechanical properties, as well as detonation parameters.

In general, thermal analysis is considered the best way of studying energetic materials decomposition, which was therefore vastly carried out by scientists all over the world [1,3,4]. During the past decades, there are much work has been done with regard to thermal decompositions of nitramines-based PBXs with regard to their kinetics and reaction mechanisms. As

one of prominent energetic candidates for 1,3,5-trinitro-1,3,5-triazinane (RDX) or 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), a new polycyclic nitramine cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX) was synthesized [5] and used in many polymer based explosives [5–8]. It has theoretical maximum density (TMD) of 1.86 g cm^{-3} , calculated detonation velocity of 9050 m s^{-1} , detonation pressure of 37 GPa and explosion heat of 6.518 MJ kg^{-1} [9,10]. However, no data is available with regard to its thermal dynamic properties, decomposition kinetics and reaction models. In particular, therefore, this paper will discuss some new findings on thermal behavior of BCHMX and its Formex bonded PBX, whose ingredients are provided in Section 2.

2. Experimental

2.1. Materials

BCHMX: cis-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (bicycle-HMX), which is a new polycyclic nitramine, was prepared by a two-step continuous laboratory synthesis in our workgroup [5]. About 87% of BCHMX by weight was bonded by 13% Formex matrix which containing 25% styrene-butadiene rubber (SBR) plasticized by 75% oily material to form PBX marked as BCHMX/Formex.

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2.2. Experimental techniques

It was studied with regard to the kinetics of thermal decomposition, using different heating rate Thermogravimetry (TG, Netzsch 209F3 instrument, Al₂O₃ crucible) and under the heating rates of 1.0, 2.0, 3.0, 5.0, 7.0 (with a data collecting rate of 40 points per Kelvin) and 10 °C min⁻¹ (with a data collecting rate of 60 points per Kelvin). Their heat flow properties was also evaluated by the technique of Differential Scanning Calorimetry (DSC, Netzsch 200F3 instrument, aluminum pan with a pin hole cover), which was introduced in the dynamic nitrogen atmosphere with a pressure of 0.1 MPa. The sample mass was about 1.1–1.9 mg for DSC under dynamic nitrogen atmosphere (30 ml min⁻¹), and it was tested at the temperature range of 40–350 °C (heating rate, 5 °C min⁻¹). The test temperature range for TG was 30–400 °C, with the sample mass of about 1.30–1.75 mg and under dynamic nitrogen atmosphere (30 ml min⁻¹).

3. Theoretical

3.1. Calculation of activation energy

A kinetic study is usually considered of either a practical or a theoretical purpose. A major practical purpose is the reliable prediction of process rates and material lifetimes when sound kinetic analysis methods are used [12]. Solid-state reactions of composite energetic material PBX are in many cases complex and may involve several overlapping processes. The kinetic analysis of such solid-state reactions is challenging, as far as the kinetic parameters, 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. Thus, while a large number of analytical methods are available for determining the kinetic parameters of discrete solid-state reactions, the number of procedures for the analysis of complex processes is much more limited. With regarding to a one-step process, we can use model-free methods, which state that at a constant extent of conversion the reaction rate is only a function of the temperature. In fact, the slight pressure dependence could be ignored in most of kinetic computational methods used in the area of thermal analysis. First, one can simply obtain the value of activation energy E_a of the major exothermic decomposition reaction of PBXs by using Kissinger's method (see Eq. (1)) [11].

$$-\frac{E_a}{R} = \frac{d \ln(\beta/T_p^2)}{d(1/T_p)} \quad (1)$$

where β is the heating rate, and T_p the peak temperature of DTG or DSC curve at that rate. When $\ln(\beta/T_p^2)$ is plotted against $1/T_p$, a straight line is obtained, and the activation energy is calculated from the slope $-E_a/R$. However, according to International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Committee recommendations [12], such crude temperature integral approximation might result in inaccurate values of E_a . A more accurate equation that has been frequently called the Kissinger–Akahira–Sunose (KAS) equation [13], based on which, according to Starink [14], a more accurate equation to estimate E_a was founded as follows:

$$\ln \left(\frac{\beta_i}{T_{\alpha,i}^{1.92}} \right) = \text{Const} - 1.0008 \frac{E_a}{RT_{\alpha}} \quad (2)$$

Compared to the Ozawa–Flynn–Wall (OFW) method, the modified KAS method offers a significant improvement in the accuracy of the E_a values. In fact, the theoretical purpose of kinetic analysis is interpretation of experimentally determined kinetic triplets. It has been stated that each of the components of a kinetic triplet is

associated with some fundamental theoretical concept, where E_a is associated with the energy barrier and A with the frequency of vibrations of the activated complex [15], and $f(\alpha)$ or $g(\alpha)$ with the reaction mechanism [16]. In order to evaluate thermal behavior and the decomposition kinetics of BCHMX and its Formex bonded explosive, the most accurate method namely modified KAS equation (Eq. (2)) was used herein to calculate their decomposition kinetic parameters.

3.2. Determination of reaction models

Second step of the kinetic analysis consist of choosing an appropriate kinetic model for the description of decomposition peaks. For this procedure, Málek [17,18] suggested an algorithm based on the shape of characteristic functions $z(\alpha)$ and $y(\alpha)$. These functions are obtained by a very simple transformation of experimental data, for non-isothermal conditions the characteristic functions are defined as follows:

$$y(\alpha) = \phi \cdot e^{E/RT} \quad (3)$$

$$z(\alpha) = \phi \cdot T^2 \quad (4)$$

As stated in a recent comprehensive review paper by Svoboda and Málek [19], the introduced functions are in fact a universal way for determination of an appropriate kinetic model applicable to any physical process including crystallization, glass transitions and thermal decomposition [20]. Determination of the most suitable kinetic model then utilizes both values of $\alpha_{\max,y}$ corresponding to the maxima of the characteristic functions and $\alpha_{\max,z}$ the overall shape of the functions. Based on this information, the optimal kinetic model can be chosen according to the algorithm in Ref. [17].

3.3. Calculation of pre-exponential factor

Last step in the kinetic analysis is determination of the pre-exponential factor A . It is advantageous to confirm the value of this parameter by independent valuation within the framework of different models (if possible). On the one hand, the values of A could be determined by curve fitting for specific reaction models such as JMA that will be used in this paper (Eq. (5)).

$$f(\alpha) = m(1 - \alpha)[- \ln(1 - \alpha)]^{1-(1/m)} \quad (5)$$

Value of the kinetic parameter m itself can then be calculated from the conversion corresponding to the maximum of the $y(\alpha)$ function $\alpha_{\max,y}$ according to [19]:

$$m = \frac{1}{1 - \ln(1 - \alpha_{\max,y})} \quad (6)$$

In addition, linear dependence of this equation is also often considered a satisfactory condition for applicability of JMA model. Another model applied within the framework of this article was the autocatalytic model AC (M, N) (Eq. (7)) as follows, which is also known as Šesták Berggren model [21].

$$f(\alpha) = \alpha^M(1 - \alpha)^N \quad (7)$$

This model is empirical, i.e. the model itself or its parameters do not have any physical basis or meaning, the description is purely phenomenological. Parameters of this model can be evaluated on the basis of the following two equations:

$$\frac{M}{N} = \frac{\alpha_{\max,y}}{(1 - \alpha_{\max,y})} \quad (8)$$

$$\ln \left[\phi \exp \left(\frac{E}{RT} \right) \right] = \ln(\Delta H \cdot A) + N \cdot \ln[\alpha^{M/N}(1 - \alpha)] \quad (9)$$

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