



Non-isothermal decomposition kinetics, heat capacity and thermal safety of 37.2/44/16/2.2/0.2/0.4-GAP/CL-20/Al/N-100/PCA/auxiliaries mixture

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ABSTRACT

The specific heat capacity (C_p) of 37.2/44/16/2.2/0.2/0.4-GAP/CL-20/Al/N-100/PCA/auxiliaries mixture was determined with the continuous C_p mode of microcalorimeter. The equation of C_p with temperature was obtained. The standard molar heat capacity of GAP/CL-20/Al/N-100/PCA/auxiliaries mixture was $1.225 \text{ J mol}^{-1} \text{ K}^{-1}$ at 298.15 K. With the help of the peak temperature (T_p) from the non-isothermal DTG curves of the mixture at different heating rates (β), the apparent activation energy (E_k and E_o) and pre-exponential constant (A_k) of thermal decomposition reaction obtained by Kissinger's method and Ozawa's method. Using density (ρ) and thermal conductivity (λ), the decomposition heat (Q_d , taking half-explosion heat), Zhang-Hu-Xie-Li's formula, the values (T_{e0} and T_{p0}) of T_e and T_p corresponding to $\beta \rightarrow 0$, thermal explosion temperature (T_{be} and T_{bp}), adiabatic time-to-explosion (t_{Tlad}), 50% drop height (H_{50}) of impact sensitivity, and critical temperature of hot-spot initiation ($T_{cr,hot spot}$) of thermal explosion of the mixture were calculated. The following results of evaluating the thermal safety of the mixture were obtained: $T_{be} = 441.64 \text{ K}$, $T_{bp} = 461.66 \text{ K}$, $t_{Tlad} = 78.0 \text{ s}$ ($n = 2$), $t_{Tlad} = 74.87 \text{ s}$ ($n = 1$), $t_{Tlad} = 71.85 \text{ s}$ ($n = 0$), $H_{50} = 21.33 \text{ cm}$.

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1. Introduction

α -Hydro- β -hydroxy-poly[oxy((azidomethyl)-1,2-ethanediyl)] (GAP) is an azide polymer and is characterized by the functional group of N_3 [1]. Owing to the highly exothermic decomposition of GAP [2], high burning rate and surface temperature were normally observed during the combustion of GAP [1–3], while its fuel-rich composition results in a low flame temperature [3]. The high burning rate and low flame temperature make GAP an excellent candidate for pressure or gas generators [4]. In addition, GAP is also used to replace inert binders in nitramine composite propellants resulting in increased specific impulse and burning rate. Propellants based on GAP and cyclic nitramines such as octahydro-1,3,4,7,8,10-hexanitro-5,2,6-(iminomethenimino)-1H-imidazo[4,5-b]pyrazine (CL-20), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) [5] or octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are characterized by a fairly high specific impulse while generating little smoke [5,6]. Although many of the combustion properties of nitramine/GAP propellants [7–10] have been investigated, to our knowledge, little

attention has been paid to the thermochemistry of this energetic material.

Thermal analysis study of energetic materials (EMs) is important not only for understanding of the kinetics of their thermal decomposition but also for assessing the effect of their exothermic decomposition on the potential hazardous in their handling, processing and storage. Kinetic studies also provide useful information on thermal stability and life expectancy (reliability) of EMs under different thermal environment in storage. Usually, the thermoanalytical methods employed for the study of thermal decomposition of EMs (like propellants and propellants ingredients) are thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimeter (DSC). Recently, differential scanning calorimetry became a main techniques to evaluate the thermal stability of polymers [11–13] and EMs [14–22].

In the work described here, GAP/CL-20/Al/N-100/PCA/auxiliaries mixture, which was used as one candidate of high energy composite solid propellants, was prepared, and its thermal behaviors, nonisothermal decomposition reaction kinetics, thermal safety were investigated. Using the original data of DSC, TG-DTG, the critical temperature of thermal explosion (T_b) and the adiabatic time-to-explosion (t_{Tlad}) were estimated. The 50% drop height of impact sensitivity (H_{50}), the critical temperature of hot-spot initiation caused by impact ($T_{cr,hot spot}$) were obtained.

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Thus the thermal safety of the mixture was evaluated which is useful for evaluating the process of the explosion from the thermal decomposition.

2. Experimental

2.1. Materials

CL-20 was supplied by Beijing Institute of Technology and had a purity of more than 99.5%. GAP was supplied by Li Ming Research Institute of Chemical Industry, the hydroxyl value was 35.14 mg KOH g⁻¹, the average molar mass was about 3380. The granularity of the spherical aluminum powder was 12.8 μm. The GAP/CL-20/Al/N-100/PCA/auxiliaries mixture samples used in the experiment were composed of 37.2% (mass fraction) GAP, 44% CL-20, 16% Al, 2.2% Desmodur N 100 (Hexamethylene diisocyanate, N-100) as curative, 0.2% polyether cyclic amide (PCA) as the bonding agent, and 0.4% other auxiliaries. The mixture samples were prepared by mixing and vacuum pouring. The mixture was cured in an air oven at 50 ± 2 °C for 7 days. The density of the mixture was 1.93 g/cm³.

2.2. Thermal decomposition condition

The DSC and TG–DTG experiments for the mixture were performed using a Model TA 910S differential scanning calorimeter (DSC) and a Model TA2950 TGA instrument. The heating rates used were 2.5, 5, 10, 15 and 20 K min⁻¹ from ambient temperature to 773 K with a sample mass of ca 1 mg for TG–DTG and DSC experiments under a nitrogen atmosphere at a flow rate of 60 mL min⁻¹. DSC and TG–DTG curves obtained under the same conditions overlapped with each other, indicating that the reproducibility of the tests was satisfactory.

2.3. The determination of the specific heat capacity

The specific heat capacity of the mixture was determined by a continuous C_p mode within 283–353 K at a heating rate of 0.15 K min⁻¹ on a Micro-DSCIII apparatus (Seteram, France) with the sample mass of 450 mg. The Micro-calorimeter was calibrated with α-Al₂O₃ (calcined), its math expression was C_p/J g⁻¹ K⁻¹ = 0.1839 + 1.9966 × 10⁻³T within 283–353 K and the standard molar heat capacity C_{p,m}[⊖](α-Al₂O₃) at 298.15 K was determined as 79.44 J mol⁻¹ K⁻¹ which was in an excellent agreement with the value reported in the literature [23] (79.02 J mol⁻¹ K⁻¹).

3. Results and discussion

3.1. Thermal behaviors of the mixture

The TG–DTG curve and DSC curve of the mixture are shown in Figs. 1 and 2. From Fig. 1, one can find that there are three mass-loss stages (stages I–III) in TG curve, corresponding to three peaks in DTG curve. For TG curve when β = 10 K min⁻¹, stage I begins at about 370.15 K and stops at about 469.15 K, accompanying with 28% mass-loss, it likely attributes to the decomposition of GAP or CL-20, with the summit peak in the DTG curve at about 460.66 K. Stage II begins followed by stage I and stops at about 513.15 K, with the summit peak in the DTG curve at about 495.73 K, accompanied by about 32% mass-loss, and it attributes to GAP, CL-20 and other auxiliary decomposition in the stage. Stage III stops at about 707.15 K, with the summit peak in the DTG curve at about 522.63 K, accompanied by about 21% mass-loss.

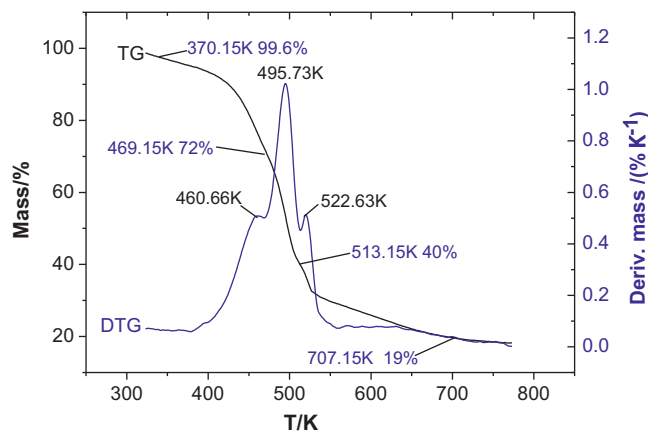


Fig. 1. TG–DTG curve of the mixture at a heating rate of 10 K min⁻¹.

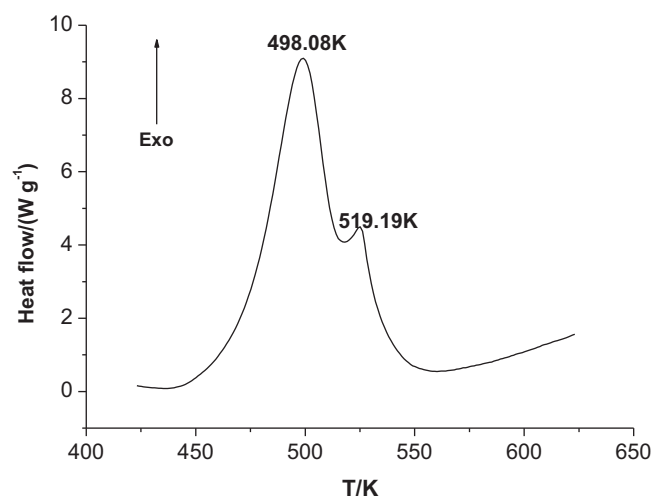


Fig. 2. DSC curve of the mixture at a heating rate of 10 K min⁻¹.

From Fig. 2 one can see that there are two exothermic peaks in the DSC curve, the main exothermal decomposition peak with the summit peak at about 498.08 K, corresponds to the stage I and stage II in the TG curve, and the subordinate one with the summit peak at about 519.19 K, corresponds to the stage III in the TG curve.

3.2. Analysis of kinetic data for the exothermic main decomposition reaction of the mixture

In order to obtain the kinetic parameters (the apparent activation energy (E_a) and pre-exponential constant (A)) of the exothermic main decomposition reaction for the mixture, two iso-conversional methods [Eqs. (1) and (2)] were employed.

Kissinger equation [24]

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E_a} - \frac{E_a}{RT_p} \quad (1)$$

Ozawa equation [25]

$$\lg \beta + \frac{0.4567E_a}{RT_p} = C \quad (2)$$

where C is the constant, E_a the apparent activation energy, β the heating rate, R the gas constant, T_p the peak temperature of DSC curve, A the pre-exponential factor.

Table 1

The peak temperatures (T_p) of decomposition reaction for the mixture determined by the DTG curves at various heating rates (β).

	β (K min ⁻¹)				
	2.5	5	10	15	20
T_{p1} (K)	431.19	445.31	460.66	472.97	478.01
T_{p2} (K)	473.15	484.12	495.73	502.10	507.50

From the original data in Table 1 (DTG), for peak1, E_k obtained by Kissinger's method [24] is determined to be 66.96 kJ mol⁻¹. The pre-exponential constant (A) is 10^{5.38} s⁻¹. The linear correlation coefficient (r_k) is 0.9985. The value of E_0 obtained by Ozawa's method [25] is 70.85 kJ mol⁻¹. The value of r_0 is 0.9988. For peak 2, E_k obtained by Kissinger's method [24] is determined to be 114.20 kJ mol⁻¹. The pre-exponential constant (A) is 10^{10.01} s⁻¹. The linear correlation coefficient (r_k) is 0.9999. The value of E_0 obtained by Ozawa's method [25] is 116.34 kJ mol⁻¹. The value of r_0 is 0.9999.

From the original data in Table 2 (DSC), for the exothermic peak 1, E_k obtained by Kissinger's method [24] is determined to be 102.23 kJ mol⁻¹. The pre-exponential constant (A) is 10^{8.64} s⁻¹. The linear correlation coefficient (r_k) is 0.9999. The value of E_0 obtained by Ozawa's method [25] is 105.00 kJ mol⁻¹. The value of r_0 is 0.9999. For the exothermic peak 2, E_k obtained by Kissinger's method [24] is determined to be 169.45 kJ mol⁻¹. The pre-exponential constant (A) is 10^{15.01} s⁻¹. The linear correlation coefficient (r_k) is 0.9676. The value of E_0 obtained by Ozawa's method [25] is 169.36 kJ mol⁻¹. The value of r_0 is 0.9706.

3.3. The critical temperature of thermal explosion (T_b)

By using DSC data for peak 1, $E_0 = 105.00$ kJ mol⁻¹, $R = 8.314$ J mol⁻¹ K⁻¹, $T_{e0} = 439.39$ K, $T_{p0} = 458.85$ K. The values of T_{be} and T_{bp} were obtained by Zhang–Hu–Xie–Li's equation [26] [Eq. (3)] as 441.64 K and 461.66 K, respectively. The high values of T_{be} and T_{bp} for the mixture show that the transition from thermal decomposition to thermal explosion is not easy to take place.

$$T_{be \text{ or } bp} = \frac{E_0 - \sqrt{E_0^2 - 4E_0RT_{e0 \text{ or } p0}}}{2R} \quad (3)$$

3.4. The specific heat capacity of the mixture

Fig. 3 shows the determination result of the mixture using a continuous specific heat capacity mode of the Micro-DSC III apparatus. The specific heat capacity of the mixture presents a good quadratic equation relationship with temperature in the determining temperature range. Specific heat capacity equation is shown as:

$$C_p \text{ (J g}^{-1} \text{ K}^{-1}\text{)} = -1.062345 + 1.26295 \times 10^{-2}T - 1.662694 \times 10^{-5}T^2 \text{ (285 K} < T < 355 \text{ K)} \quad (4)$$

Table 2

The peak temperatures (T_p) of the exothermic decomposition reaction for the mixture determined by DSC curves at various heating rates (β).

β (K min ⁻¹)	T_e (K)	T_{p1} (K)	T_{p2} (K)	T_{e0}^a (K)	T_{p0}^a (K)	E_k (kJ mol ⁻¹)	$\lg(A_k)$ (s ⁻¹)	Q_d (J g ⁻¹)
2.5	455.21	473.55	506.78	439.39	458.85	102.23	8.64	690.4
5	465.18	485.39	516.25					
10	475.41	498.08	519.19					
15	479.57	505.84	530.88					
20	489.94	511.42	531.11					

^a The T_{e0} and T_{p0} are the values of T_e and T_p corresponding to $\beta \rightarrow 0$, respectively.

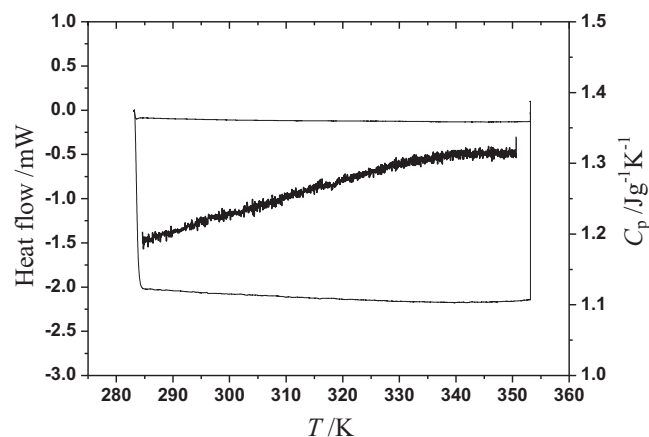


Fig. 3. Determination results of the continuous specific heat capacity C_p of the mixture.

The standard molar heat capacity of the mixture is 1.225 J mol⁻¹ K⁻¹ at 298.15 K.

3.5. The determination of the adiabatic time-to-explosion of the mixture

The adiabatic time-to-explosion (t_{Tad} , s) of EMs is the transiting time of an EMs from thermal decomposition to explosion under the adiabatic conditions, and is an important parameter for assessing the thermal stability and the safety of EMs. The estimation formulae of calculating the adiabatic time-to-explosion (t) of EMs used are Eqs. (5)–(7) taken from Refs. [27,28].

$$C_p \frac{dT}{dt} = Q_d A \exp\left(\frac{-E}{RT}\right) f(\alpha) \quad (5)$$

$$\alpha = \int_{T_0}^T \frac{C_p}{Q_d} dT \quad (6)$$

$$t = \frac{1}{Q_d A} \int_{T_0}^T \frac{C_p \exp(E/RT)}{f(\alpha)} dT \quad (7)$$

where C_p is the specific heat capacity (J g⁻¹ K⁻¹); $f(\alpha)$ is the differential mechanism function; E is the apparent activation energy; A is the pre-exponential constant; Q_d is the heat of decomposition; R is the gas constant (8.314 J mol⁻¹ K⁻¹) and α is the conversion degree.

By substituting the original data of $C_p = 1.225$ J g⁻¹ K⁻¹, $f(\alpha) = 2(1 - \alpha)^{3/2}$, $E = 102230$ J mol⁻¹, $A = 10^{8.64}$ s⁻¹, $Q_d = 690.4$ J g⁻¹, $R = 8.314$ J mol⁻¹ K⁻¹, the integral upper limit $T = T_b = 461.66$ K and the lower limit $T_0 = T_{e0} = 439.39$ K into Eq. (7), the value of t of 78.0 s ($n=2$), 74.87 s ($n=1$) and 71.85 s ($n=0$) are obtained, respectively, which means that the mixture has a high resistance to heat and thermal safety.

3.6. The critical temperature of hot-spot initiation ($T_{cr,hot\ spot}$) of the mixture

The inner of the EMs creates a local thermal point when the EMs accepted energy and the EMs will explore from thermal decomposition when the hot-spot temperature reaches to the explosive temperature. The critical temperature of hot-spot initiation ($T_{cr,hot\ spot}$) is an important parameter for evaluating the thermal safety of EMs.

In order to obtain $T_{cr,hot\ spot}$ of the mixture, assuming that $T_{cr,hot\ spot}$ is a function of the size and duration of the hot-spot and of the physical and chemical properties, the equation for calculating the value of $T_{cr,hot\ spot}$ can be adopted as Bruckman–Guillet first-order decomposition reaction estimation equation [Eq. (8)] [29]

$$\begin{aligned} & \left(\frac{4}{3}\pi a^3\right) \rho Q_d \left\{1 - \exp[-(t - t_0)Ae^{-E/RT_{cr}}]\right\} \\ &= \int_a^\infty 4\pi r^2 \rho c_p \left[\frac{a\theta_0}{r} \operatorname{erfc}\left[\frac{r-a}{2\sqrt{Bt}}\right]\right] dr \\ &= \int_a^\infty 4\pi r^2 \rho c_p \left[\frac{a(T_{cr,hot\ spot} - T_{room})}{r} \operatorname{erfc}\left[\frac{r-a}{2\sqrt{(\lambda/\rho c_p)t}}\right]\right] dr \end{aligned} \quad (8)$$

where a is the radius of the hot-spot in 10^{-3} cm, ρ is the density in g cm^{-3} , Q_d is the heat of reaction in J g^{-1} , $t - t_0$ is the time interval in 10^{-4} s, A is the pre-exponential constant in s^{-1} and $A = A_k$, E is the apparent activation energy in J mol^{-1} and $E = E_a$, R is the gas constant in $\text{J mol}^{-1} \text{K}^{-1}$, $T_{cr,hot\ spot}$ is the critical temperature of hot-spot initiation in K, C_p is the specific heat in $\text{J g}^{-1} \text{K}^{-1}$, T_{room} is the ambient temperature in 293.15 K, λ is the thermal conductivity in $\text{J cm}^{-1} \text{s}^{-1} \text{K}^{-1}$.

By submitting $\rho = 1.93 \text{ g cm}^{-3}$, $C_p = 1.225 \text{ J g}^{-1} \text{K}^{-1}$, $\lambda = 0.365 \text{ W m}^{-1} \text{K}^{-1}$, $Q_d = 690.4 \text{ J g}^{-1}$, $E = 102230 \text{ J mol}^{-1}$ and $A = 10^{8.64} \text{ s}^{-1}$, $T_{room} = 298.15 \text{ K}$, $R = 8.314 \text{ J mol}^{-1} \text{K}^{-1}$, $a = 10^{-3} \text{ cm}$ [30] $t - t_0 = 10^{-4} \text{ s}$ [30] to [Eq. (8)], the value of $T_{cr,hot\ spot}$ of (1232.65 K) is obtained.

3.7. 50% drop height (H_{50}) of impact sensitivity of the mixture

The impact sensitivity is an important parameter for evaluating the security and reliability of EMs and can be characterized by 50% drop height (H_{50}). Using data, $\lambda = 0.365 \text{ W m}^{-1} \text{K}^{-1}$, $\rho = 1.93 \text{ g cm}^{-3}$, $Q_d = 690.4 \text{ J g}^{-1}$, $E = 102230 \text{ J mol}^{-1}$, and $A = 10^{8.64} \text{ s}^{-1}$, the H_{50} of the mixture was estimated as 21.33 cm by Eq. (9) [31].

$$\begin{aligned} 0.282312 \lg(H_{50}) + \lg \sqrt{\frac{\lambda}{A\rho Q_d}} - 0.347174 \\ + \frac{0.02612E}{T_1 + 33.8765H_{50}^{0.564623}} = 0 \end{aligned} \quad (9)$$

4. Conclusions

The thermal behavior of the title mixture under the non-isothermal condition by DSC, TG–DTG methods was studied. There are three mass-loss stages in TG curve for the mixture, and they are likely attributes to the decomposition of GAP, CL-20 and other auxiliary. The apparent activation energy and pre-exponential factor of the exothermic decomposition reaction as well as the linear correlation coefficient are $102.23 \text{ kJ mol}^{-1}$ (E_k), $10^{8.64} \text{ s}^{-1}$, 0.9999 (Peak 1, DSC), $105.00 \text{ kJ mol}^{-1}$ (E_0) 0.9999 (Peak 1, DSC), respectively.

The specific heat capacity equation of the title mixture is $C_p (\text{J g}^{-1} \text{K}^{-1}) = -1.062345 + 1.26295 \times 10^{-2}T - 1.662694 \times 10^{-5}T^2$

($285 \text{ K} < T < 355 \text{ K}$). The critical temperatures of thermal explosion (T_{be} and T_{bp}) for the mixture are 441.64 K and 461.66 K, respectively, which show that the transition from thermal decomposition to thermal explosion for the mixture is not easy to take place. The adiabatic times-to-explosion of the mixture are 78.0 s ($n=2$), 74.87 s ($n=1$) and 71.85 s ($n=0$), respectively, which means that the mixture has a high resistance to heat. The critical temperature of hot-spot initiation (T_{cr}) for the mixture is 1232.65 K. The 50% drop height (H_{50}) of impact sensitivity for the mixture is estimated as 21.33 cm, and the mixture has a good thermal stability.

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