Thermal Decomposition and Kinetics of Cast Plastic Bonded Explosives Based on NTO and HMX

Xinyu Kou, Shaohua Jin and Yu Chen*

School of Material Science and Engineering, Beijing Institute of Technology, Beijing, China

*Corresponding author email: bityuchen@bit.edu.cn

Abstract. In this work, we studied the influence of the ratio of NTO and HMX on the thermal decomposition performance of the series of cast PBXs. DSC was used to study the non-isothermal thermal decomposition performance of different PBXs, and ARC was used to study the adiabatic thermal decomposition. Both DSC and ARC results show that among the five different PBXs, N30 is the cast PBX with the best thermal stability.

Keywords: NTO; HMX; Thermal decomposition.

1. Introduction
On the modern battlefield, ammunition is required to have high power and high safety during combat, production, storage, and transportation. Countries around the world gradually regard high-energy insensitive explosives as the focus of ammunition development. NTO (3-nitro-1,2,4-triazol-5-one), as a typical representative of new high-energy and insensitive explosives, can be applied to prepare insensitive cast plastic bonded explosives (PBXs) and is active in the field of insensitive ammunition charges. HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane) is an elemental explosive with higher energy level and better comprehensive performance so far. It is a cast PBX that can be used in high-explosive, fragmented killing warheads. Cast PBXs based on HMX or NTO with hydroxyl terminated polybutadiene(HTPB) have been formulated in the literature[1-8]. However, there is a lack of discussion on the content ratio of NTO and HMX and the performance of cast PBX. Thermal decomposition performance is one of the safety features of pouring PBX, it is very important to do in-depth research on it. Therefore, this work studies the influence of the ratio of NTO and HMX on the thermal decomposition performance of the series of cast PBXs, which is of great significance to the formulation design of NTO/HMX-based PBX.

2. Experimental

2.1. Materials
NTO, HMX and TDI were produced by Gansu Yinguang Chemical Industry Group Co. Ltd. Al powers were manufactured from Angang Industrial Fine Aluminum Powder Co., Ltd. HTPB was obtained from Liming Chemical Research Institute Co., Ltd. Dioctyl Sebacate(DOS) was Tianjin Kaixin Chemical Industry Co., Ltd. TDI and DOS were the AR purity.

2.2. Preparation of the PBX Samples
Before the experiment, the different components were dried and the water content was strictly controlled. NTO, HMX, aluminum powder, HTPB and other ingredients were weighed according to the formula...
requirements. The weighed components are sequentially poured into a 5 L vertical sigma mixer, so that the different components are uniformly mixed under vacuum and heating conditions. Pour the material quickly into the vacuum casting equipment, and pour the material into the prepared mold at a certain speed under the condition of heat preservation, heating and vacuum. Heat and solidify the mould filled with explosives at 60°C for 7 days. After solidification, cool to room temperature, remove the explosives from the mould, and prepare the required PBXs samples as required. In this way, PBXs from a mixture of NTO and HMX at varying mass ratios (10:55, 20:45, 30:35, 40:25, 50:15 respectively) with 20% mass Al powders and 15% mass HTPB-binder system. They were designed as N10, N20, N30, N40 and N50.

2.3. Experimental Method
The DSC 200F3 produced by NETZSCH in Germany was applied to study the non-isothermal thermal decomposition performance of different PBXs. Using aluminum crucible to hold the sample; the sample size is 0.7~1 mg; the whole process adopts nitrogen atmosphere, the gas flow is set to 50 mL·min⁻¹; the heating rate is set to 1, 2, 5, 8 °C·min⁻¹. The adiabatic decomposition process of five kinds of PBXs was tested using the Type 254 adiabatic accelerating calorimeter (ARC) produced by NETZSCH in Germany. The test is conducted in the heating-waiting-search (HWS) mode, and the test conditions are listed in Table 4.2.

2.4. Kinetic Research Methods
The American Standard Test Methods ASTM E1641-07 and ASTM E1641-05 have used Kissinger as the standard method for thermal analysis. The Kissinger method formula [9] is as follows:

\[
\ln \left( \frac{\beta}{T_p^2} \right) = \ln \left( \frac{A R}{E_a} \right) - \frac{E_a}{RT_p}
\]

In the formula: \( \beta \) is the heating rate, \( T_p \) is the peak temperature of thermal decomposition, \( E_a \) is the activation energy of the thermal decomposition reaction, \( A \) is the pre-factor, and \( R \) is the gas constant. Use \( \ln(\beta/T_p^2) \) as the ordinate and \( 1/T_p \) as the abscissa to plot. \( E_a \) and \( A \) can be calculated according to the intercept and slope of the fitted straight line. Because the Kissinger method can only obtain the value of the apparent activation energy, it is more fit for analyzing the kinetics of the one-step thermal decomposition reaction[10].

Ozawa method is also often used to calculate pre-exponential factors and the activation energy of thermal decomposition reactions. The Ozawa method equation [11] is:

\[
\lg \beta = \lg \left( \frac{AE_a}{RG(\alpha)} \right) - 2.315 - 0.4567 \frac{E_a}{RT_p}
\]

In the formula: \( \beta, A, E_a, R, T_p \) represent the same meaning as in formula (1), and \( G(\alpha) \) is the integral form of the reaction mechanism function. Studies have shown that for the DSC test, the thermal decomposition reaction conversion rate at the peak temperature is approximately equivalent at different heating rates, so \( G(\alpha) \) in equation (2) is a constant value, so there is \( \lg \beta \) and \( 1/T \) is linear. Use \( \lg \beta \) as the ordinate and \( 1/T \) as the abscissa to plot the graph. The activation energy \( E_a \) can be calculated from the slope of the straight line obtained by linear fitting.

The mechanism function method is a commonly used method to calculate the kinetic parameters of mixed explosives. According to the Achar-Brindley-Sharp method, take the logarithm of both sides of the equation to obtain:

\[
\ln \frac{m_f}{f(\alpha)} = \ln \left( A DT_{ol} \right) - \frac{E_a}{RT}
\]
Where: $m_T$ is the temperature rise rate, $f(\alpha)$ is the adiabatic decomposition mechanism function, $E_a$ is the activation energy of the thermal decomposition reaction, $A$ is the pre-factor, $\Delta T_{ad}$ is the adiabatic temperature rise, $T$ is the temperature, and $R$ is the gas constant.

3. Results and Discussion

3.1. Non-isothermal Thermal Decomposition Process Studies

The heat flow curves of the exothermic reaction process of five cast PBXs with different NTO/HMX ratios at different heating rates are shown in Figure 1. Table 1 shows the thermal decomposition parameters of NTO/HMX cast PBX with different ratios at different heating rates.

![Figure 1. DSC curves of different PBXs at different heating rates.](image)

Table 1. Thermal decomposition parameters of HMX/NTO cast PBX under different heating rates.

| Sample | $\beta/(^\circ\text{C} \cdot \text{min}^{-1})$ | $T_{ad}^a/^\circ\text{C}$ | $T_p^b/^\circ\text{C}$ | $T_p^c/^\circ\text{C}$ | $\Delta H/(\text{J} \cdot \text{g}^{-1})$ |
|--------|-------------------|-----------------|-----------------|-----------------|-------------------|
| N10    | 1                  | 214.06          | 230.92          | 263.29          | 818.31            |
|        | 2                  | 227.03          | 242.33          | 270.65          |                   |
|        | 5                  | 240.07          | 253.18          | 277.82          |                   |
|        | 8                  | 243.65          | 260.31          | 280.13          |                   |
|        | 1                  | 218.79          | 227.63          | 258.27          |                   |
|        | 2                  | 229.17          | 236.47          | 270.89          |                   |
|        | 5                  | 242.16          | 247.70          | 276.28          | 806.92            |
|        | 8                  | 240.04          | 253.18          | 280.67          |                   |
| N20    | 1                  | 218.79          | 227.63          | 258.27          |                   |
|        | 2                  | 229.17          | 236.47          | 270.89          |                   |
|        | 5                  | 242.16          | 247.70          | 276.28          | 806.92            |
|        | 8                  | 240.04          | 253.18          | 280.67          |                   |
| N30    | 1                  | 218.79          | 227.63          | 258.27          |                   |
|        | 2                  | 229.17          | 236.47          | 270.89          |                   |
|        | 5                  | 242.16          | 247.70          | 276.28          | 806.92            |
|        | 8                  | 240.04          | 253.18          | 280.67          |                   |
| N40    | 1                  | 218.79          | 227.63          | 258.27          |                   |
|        | 2                  | 229.17          | 236.47          | 270.89          |                   |
|        | 5                  | 242.16          | 247.70          | 276.28          | 806.92            |
|        | 8                  | 240.04          | 253.18          | 280.67          |                   |
| N50    | 1                  | 218.79          | 227.63          | 258.27          |                   |
|        | 2                  | 229.17          | 236.47          | 270.89          |                   |
|        | 5                  | 242.16          | 247.70          | 276.28          | 806.92            |
|        | 8                  | 240.04          | 253.18          | 280.67          |                   |

a The starting temperature of thermal decomposition reaction.

b The peak temperature of thermal decomposition in the first stage.

c The peak temperature of thermal decomposition in the second stage.
It can be seen from Figure 1 and Table 1 that the DSC heat flow curves of the five NTO/HMX cast PBXs have two exothermic peaks, indicating that there are two main decomposition stages in the entire thermal decomposition process. When the NTO content is below 30%, the exothermic peak in the first stage is relatively gentle, and the exotherm is mainly concentrated in the second stage at this time; and with the increase of the heating rate, the peak shape of the exothermic peak in the first stage does not change significantly. The exothermic peak in the second stage becomes sharper, indicating that the degree of reaction in the second stage is greatly affected by the heating rate. When the NTO content is 30% and above, the heat release is mainly concentrated in the first stage; and as the heating rate increases, the situation is similar to that of the NTO content below 30%. With the increase of NTO content, the heat release of the five PBXs showed a decreasing trend.

3.2. Non-isothermal Thermal Decomposition Kinetic Studies

After the decomposition reaction of energetic materials begins, the reaction is uncontrollable, so the thermal decomposition reaction in the first stage plays a vital role in evaluating the safety of energetic materials. Based on the first stage peak temperature of different PBXs in Table 2, the apparent activation energy and pre-finger factor of different formulations were calculated by Kissinger method and Ozawa method. The linear fitting curve of \( \ln(\beta/T_p^2) \) with respect to \( 1/T_p \) obtained from Kissinger method and the linear fitting curve of \( \log\beta \) with \( 1/T_p \) obtained from Ozawa method are shown in Figure 2. Table 2 shows the calculation results of thermal decomposition kinetic parameters obtained from Kissinger and Ozawa method.

![Figure 2](image)

**Figure 2.** The a) Kissinger and b) Ozawa curves of the first-stage thermal decomposition of different PBXs.

| Sample | Kissinger | Ozawa |
|--------|-----------|-------|
|        | \( E_a/\text{kJ}\cdot\text{mol}^{-1} \) | \( A/\text{s} \) | \( R^2 \) | \( E_a/\text{kJ}\cdot\text{mol}^{-1} \) | \( R^2 \) |
| N10    | 152.60    | 4.87\times10^{14} | 0.9935 | 153.31 | 0.9941 |
| N20    | 177.49    | 2.49\times10^{17} | 0.9937 | 176.88 | 0.9942 |
| N30    | 189.00    | 3.38\times10^{18} | 0.9992 | 187.87 | 0.9993 |
| N40    | 169.07    | 3.01\times10^{16} | 0.9975 | 168.91 | 0.9977 |
| N50    | 143.55    | 7.92\times10^{13} | 0.9952 | 144.63 | 0.9956 |

The purpose of this stage of work is to illustrate the influence of the relative content of NTO and HMX on the thermal decomposition kinetics of the system. When the percentage of NTO in the system increases from 10% to 50%, the activation energy of the first stage thermal decomposition of PBXs varies from 143.55 to 189.00 kJ/mol. The activation energy of N30 is close to that of HMX/HTPB-based PBXs in the literature. Abusaidi et al. [12] conducted a DSC test of HMX/HTPB-based PBXs, and the activation energy calculated by Ozawa method was 188.26 kJ/mol. However, as the ratio of NTO/HMX...
in the mixed explosive increases in this article, the apparent activation energy of thermal decomposition of NTO/HMX cast PBX first increases and then decreases, showing the same trend as the initial temperature of thermal decomposition in the previous section. When their content is close, the inhibition is strong. The greater the apparent activation energy, the more difficult the thermal decomposition reaction is.

3.3. Adiabatic Thermal Decomposition Process Studies

The ARC instrument was used to investigate the adiabatic thermal decomposition behavior of NTO/HMX-based cast PBXs. The pressure and temperature changes over time during the entire test process are shown in Figure 3.

![Figure 3](image)

Figure 3. N10, N20, N30, N40, N50 temperature and pressure change curve with time.

Considering the two factors of pressure and temperature, different PBXs have two adiabatic thermal decomposition stages. However, due to the relatively small content of NTO or HMX in N10 and N50, a period of exothermic process proceeded relatively quickly, resulting in no detection by the instrument exothermic section. Based on the figure, it is not difficult to find that the adiabatic thermal decomposition reaction of N10 and N20 mainly occurs in the second stage, while N30, N40, and N50 mainly occur in the first stage.

3.4. Adiabatic Thermal Decomposition Kinetic Studies

According to the mechanism function method, the adiabatic decomposition kinetic parameters of different formulations were calculated, and the results are shown in Table 3.

![Table 3](image)

Table 3. Kinetic parameters of adiabatic thermal decomposition of five PBXs.

| Sample | $E_a$ /kJ·mol$^{-1}$ | $A$ /s$^{-1}$ | $f(\alpha)$ | $R^2$ |
|--------|----------------------|-------------|------------|-------|
| N10    | 275.11               | 2.46×10$^{25}$ | $3(1-\alpha)^{2/3}$ | 0.9838 |
| N20    | 296.48               | 7.06×10$^{27}$ | $3(1-\alpha)^{2/3}$ | 0.9675 |
| N30    | 566.71               | 9.48×10$^{56}$ | $2(1-\alpha)^{1/2}$ | 0.9875 |
| N40    | 485.07               | 3.16×10$^{56}$ | $2(1-\alpha)^{1/2}$ | 0.9769 |
| N50    | 460.96               | 2.05×10$^{48}$ | $2(1-\alpha)^{3/2}$ | 0.9946 |

From the table, the adiabatic decomposition mechanism function of N10 and N20 is $3(1-\alpha)^{2/3}$, N30 and N40 is $2(1-\alpha)^{1/2}$, and N50 is $2(1-\alpha)^{3/2}$. That indicates that the adiabatic decomposition mechanism function of cast PBXs has changed with the increase of NTO content. The mechanism function reflects the functional relationship between the material reaction process $\alpha$ and the reaction rate, and explains the mechanism of the thermal decomposition reaction. The mechanism function is that in an imaginary solid-phase reaction, a local active area exists on the interface between the product and the reactant. The
continuous advancement of this area is the characterization of the reaction process, and then according to the various basic steps that affect the reaction rate, such as the gas product diffusion, nucleus formation and growth, phase interface reaction are derived separately [13,14]. As the reaction progresses, the activation energy of adiabatic decomposition reaction increases first and then decreases with the increase of NTO content, indicating that the closer the NTO and HMX content are, the higher the activation energy and the better the adiabatic stability.

4. Conclusions
Using DSC and ARC to study the non-isothermal thermal decomposition performance and adiabatic decomposition performance of different NTO/HMX-based cast PBXs.
(1) With the increase of NTO content, the initial decomposition temperature showed a tendency of first increasing and then decreasing, while the peak temperature change trend of the two stages was opposite to the initial decomposition temperature. The apparent activation energy of thermal decomposition increases first and then decreases, showing the same trend as the onset temperature of thermal decomposition.
(2) When the content of NTO and HMX is closer, the reaction of NTO/HMX-based cast PBXs in the main adiabatic decomposition stage is more gentle, and the possibility of thermal explosion is smaller. The higher the activation energy, the better the adiabatic stability.

References
[1] Wilkinson, S. D., et al. (2017). A complete equation of state for non-ideal condensed phase explosives. *J. Appl. Phys.*, 122(22), 225112-225126.
[2] Bui, D. R., & Brady, V. (2004). Evaluation of reduced sensitivity RDX in PBXN-109 in GP bomb. *Karlsruhe:ICT*.
[3] Suzuki, Y., Matsuzaki, S., & Yano, E. (2007) Reduced sensitivity RDX(RS-RDX): Effect of crystal quality on the shock sensitivity of a cast cured PBX formulation based on RS-RDX. *Miami:NDIA IMEM Technology Symposium*.
[4] Nouguez, B., & Mahé, B. (2010) Achieving STANAG 4439 IM shaped charge requirements on 155mm shells: an update. *Munich Germany: IMEMTS2010*.
[5] Nouguez, B., & Eck, G. (2016) From synthesis to formulation and final application. *Propell. Explos. Pyrot.*, 41(3), 548-554.
[6] Wang, Y., et al. (2017) Preparation and characterization of cyclotrimethylenetrinitramine (RDX) with reduced sensitivity. *Materials*, 10(08), 974-983.
[8] Jangid, S. K., et al. (2019) Evaluation studies on partial replacement of RDX by spherical NTO in HTPB-based insensitive sheet explosive formulation. *J. of Energ. Mater.*, 37(3), 320-330.
[9] Kissinger, H. E. (1957) Reaction kinetics in differential thermal analysis. *Anal. Chem.*, 29(11), 1702-1706.
[10] Vyazovkin, S., et al. (2011) ICTAC kinetics committee recommendations for performing kinetic computations on thermal analysis data. *Thermochimica Acta*, 520(1-2), 1-19.
[11] MacCallum, J. R., & Tanner, J. (1970) The kinetics of thermogravimetry. *Eur. Polym. J.*, 6(7),1033-1039.
[12] Abusaidi, H., & Ghaeni, H. R. (2017) Thermal analysis and kinetic decomposition of Nitro-functionalized hydroxyl-terminated polybutadiene bonded explosive. *J. Therm. Anal. Calorim.*, 127(3), 2301–2306.
[13] Brown, M., Dollimore, D., & Galwey, A. K. (1980) *Reactions in the solid state*. Elsevier: Amsterdam.
[14] Šesták, J. (1980) *Thermal properties of solids*. Elsevier: Amsterdam.