Mechanism of Two Typical Binders BR and F2604 on Thermal Decomposition of HMX

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ABSTRACT: DSC–TG–FTIR–MS coupling technology was used to study the mechanism of two typical binders, that is, BR and F2604, on the thermal decomposition behavior of the HMX crystal. The results show that both BR and F2604 can induce premature decomposition of HMX and increase the activation energy of HMX. Especially in the case of HMX/BR particles, the decomposition temperature is the lowest, but the activation energy is the highest. Based on the results of DSC–TG–FTIR–MS, it is found that the rapid mechanism of binder and active intermediate products inhibits the reaction of relatively inert intermediate products and prolongs the continuous generation time of gas products in the composite particles, which delays the decomposition of HMX to a certain extent. This study is helpful for us to better understand the thermal decomposition behavior of HMX composite particles and provides reference for the application of high-energy composites.

1. INTRODUCTION

With the continuous development of weapon systems, modern warfare has developed from the previous one-way direct damage strike to the complex system confrontation combining penetration defense and strike bunkers. The combat mode is presented in a more and more multi-dimensional manner. Because of the deterioration of the battlefield environment, a large part of the loss of weapons and ammunition comes from self-explosion of ammunition caused by accidental ignition, which in turn leads to disastrous consequences for combat platforms such as ships. Therefore, ammunition in modern weapon systems is expected to not only have higher damage power but also higher reliability and safety when it is impacted by unexpected external dangerous stimuli. Therefore, mixed insensitive explosives, represented by polymer-bonded explosives (PBX) explosives, are gradually emerging.

PBX explosives are mainly composed of high-energy density energetic materials and polymer binders. High-energy density energetic materials include RDX, HMX, CL-20, and so forth, which have high energy but sensitive to external stimuli. The polymer binder including C–H-based polymers, such as HTPB and BR, and C–F-based fluoropolymer, such as Viton A, have been developed for PBX and propellant formulations. Binder, as an indispensable component of insensitive explosives, provides PBX with good mechanical properties and good safety. However, because of various heterogeneous decomposition reactions in PBX explosives, the solid–state reaction of high-energy composite materials is very complex, and the decomposition reaction mechanism is also be affected by a very small amount of polymer matrix. Therefore, studying the thermal decomposition behavior and kinetics of composite explosives is an essential part to evaluate the safety performance.

The thermal decomposition behavior and kinetics of HMX-based PBX have been extensively studied through non-isothermal thermogravimetry (TGA) or differential scanning calorimetry (DSC). In the published literature, more attention has been paid on the thermal decomposition behavior and kinetics of PBX based on HMX mixed with a binder, yet fewer articles focus on different reaction mechanisms caused by the basic reaction between binder and HMX. Wu et al. studied the thermal decomposition behavior of CL-20/HMX eutectic with nano-Fe2O3 and rGO-Fe2O3 by DSC–TG–MS coupling technology and proposed the thermal decomposition mechanism of CL-20/HMX eutectic. Lalit et al. used TGA and CRT combined with FTIR to obtain the mole fraction distribution of gas decomposition products evolved from liquid-phase HMX and studied the basic liquid-phase reaction combining with quantum chemical calculation. Studying the decomposition mechanism of composite high-energy materials can provide a better understanding of its thermodynamic behavior and more fundamental mechanism research for composite high-energy materials.

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In this paper, we study the effects of two typical binders BR and F\textsubscript{2604} on the thermal decomposition of HMX. The kinetic parameter activation energy of HMX and composite materials is calculated by the Kissinger method based on DSC data, and the kinetic model of the sample was analyzed by the Malek method. The DSC−TG−MS−FTIR coupling technology is used to test the evolution process of gas products in the thermal decomposition process. Based on the analysis of the thermal decomposition process and gas products of HMX, the action mechanism of BR and F\textsubscript{2604} is proposed, which provided a reference for the application of the two binders in HMX-based explosives.

2. MATERIALS AND EXPERIMENTAL SECTION

2.1. Materials. HMX was purchased from Gansu Yinguang Chemical Industry Group Co., Ltd. (Baiyin, Gansu, China) cis-1,4-polybutadiene (BR, density is 0.91 g/cm\textsuperscript{3}, and the relative molecular weight is 50,000−70,000) and fluoropolymer (F\textsubscript{2604}, density is 1.80 g/cm\textsuperscript{3}, and the relative molecular weight is 150,000−200,000) were all industrially produced. The molecular structure is shown in Figure 1.

2.1.1. Preparation of Composite Particles. The binder and HMX were weighed according to the mass ratio of 5:95. HMX was mixed in water and stirred, and the binder was dissolved in a low boiling point organic solvent, which is not miscible with water. Then, the binder solution was poured into the HMX aqueous solution, which was stirred violently, and the solvent was removed by distillation under continuous stirring. HMX-based composite particles were obtained after filtration. The detailed sample preparation process of HMX/BR is shown in Figure 2. The preparation process of HMX/F was similar, where only ethyl acetate was used to replace petroleum ether. For convenience, the composite particles were named HMX/BR and HMX/F. In the supporting documents, Figure S1 shows that the two binders are uniformly coated on the surface of the HMX crystal, and the FTIR results of Figure S2 indicate that there is only a certain physical interaction between the binder and HMX at room temperature.

2.2. Experimental Section. The DSC (NETZSCH DSC 204 F1 Phoenix, Germany) differential scanning calorimeter was used to test the thermal decomposition performance of energetic materials under Argon atmosphere. The sample weight was about 0.7 mg, and the heating rate was 5, 10, 15, and 20 K min\textsuperscript{−1}. The TGA-DSC3+ (METTLER TOLEDO)-FTIR (Nicolet iS50-GC/MS (Agilent 7890B-5977B) coupling technology was used for decomposition mechanism analysis; the sample mass was about 1 mg; Argon atmosphere and heating rate were with 10 K min\textsuperscript{−1}.

Figure 3 shows the DSC curves of pure HMX crystal and composite particles of HMX/BR and HMX/F at different heating rates. When the heating rate is 5 K min\textsuperscript{−1}, the exothermic peaks of the pure HMX crystal, HMX/BR, and HMX/F in DSC curves are 277.9, 268.8, and 274.3 °C, respectively. BR and F\textsubscript{2604} reduced the thermal decomposition peak of pure HMX from 277.9 to 268.8 and 274.3 °C, respectively. At the heating rates of 10, 15, and 20 K min\textsuperscript{−1}, a similar reduction effect is also shown. The results indicated that both binders have an induction effect on the thermal
decomposition of HMX, and the induction effect of BR is obvious. Figure S2 shows the DSC curves of pure BR and F2604 at a heating rate of 10 K min\(^{-1}\). It can be seen that the decomposition temperatures of BR and F2604 are 373.8 and 488.6 °C respectively, which is higher than the decomposition temperatures of HMX. Therefore, we inferred that the chemical reaction of BR and F2604 with the HMX decomposition products induced the decomposition of HMX. In particular, BR with a long C−H chain has a strong adsorption effect on H and O ions, which induces O and H to separate from HMX molecules and react with them.

3. RESULTS AND DISCUSSION

3.1. Thermal Decomposition Behaviors. The effect of binder on the non-isothermal thermal decomposition kinetics of HMX is studied by Kissinger equation which can be expressed as

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

(1)

In these equations, \(E_a\) is the activation energy, \(A\) is the pre-exponential factor, \(\beta\) is the heating rate, \(R\) is the ideal gas constant, and \(T_p\) is the peak temperature.

The calculated results of kinetic parameters are shown in Table 1. Compared with pure HMX, the addition of BR and F2604 increased \(E_a\) of HMX from 338.9 to 497.5 kJ mol\(^{-1}\) and 396.0 kJ mol\(^{-1}\), respectively, which means that the two binders could inhibit the thermal decomposition of HMX. The higher activation energy of HMX/BR indicates that the inhibition effect of BR is more obvious than that of F2604. In addition, we use AKTS software to analyze the DSC results and draw the \(T−\alpha\) curve, as shown in Figure S4. The reaction rate was calculated according to the \(T−\alpha\) curve, and the kinetic models of the three samples at a heating rate of 10 K/min were analyzed by the Malek method.\(^{41−43}\) As shown in Figure 4, it

![Figure 3. DSC curves at various heating rates for (a) pure HMX, (b) HMX/BR, and (c) HMX/F.](image)

| Sample   | \(\beta/\text{K/min}^{-1}\) | \(T_p/°\text{C}\) | \(E_a/\text{kJ mol}^{-1}\) | lnA/s\(^{-1}\) | \(r^2\) |
|----------|-----------------|----------------|-----------------|-------------|-------|
| HMX      | 5               | 277.9          | 338.9           | 80.0        | 0.987 |
|          | 10              | 281.6          |                 |             |       |
|          | 15              | 285.1          |                 |             |       |
|          | 20              | 288.2          |                 |             |       |
| HMX/BR   | 5               | 268.8          | 497.5           | 116.7       | 0.998 |
|          | 10              | 272.5          |                 |             |       |
|          | 15              | 274.1          |                 |             |       |
|          | 20              | 275.7          |                 |             |       |
| HMX/F    | 5               | 274.3          | 396.0           | 93.1        | 0.988 |
|          | 10              | 278.3          |                 |             |       |
|          | 15              | 280.1          |                 |             |       |
|          | 20              | 283.3          |                 |             |       |
can be seen that the kinetic models of the three samples are most similar to curves 39 and 40. Therefore, the kinetic models of HMX and its composite particles are $f(\alpha) = \alpha/2$ or $f(\alpha) = \alpha$, which follows the exponential rule. Generally, DSC results showed that BR and F$_{2604}$ could reduce the decomposition temperature of HMX and induce HMX to decompose earlier; however, with the decomposition process, it gradually shows the inhibition effect on HMX decomposition.

3.2. DSC–TG–FTIR–MS Results. To further understand the influence of two binders on the thermal decomposition of HMX, we investigated the thermal decomposition process of three particles at a heating rate of 10 K min$^{-1}$ by DSC–TG–FTIR–MS coupling technology. The DSC–TG results are shown in Figure S5, and the DSC test is similar to the results in Section 3.1, which will not be discussed here. The TG results show that the mass decay of HMX/BR and HMX/F particles is faster than that of pure HMX, and that of the HMX/BR is the fastest, which means that both BR and F$_{2604}$ binders can accelerate the conversion of HMX to gaseous products. At the same time, FTIR is used to detect the gas products generated during the thermal decomposition of high-energy particles. The infrared spectrum is shown in Figure 5a. The results revealed that the main decomposition gas products of HMX are CO$_2$ (715 and 2310 cm$^{-1}$), CHN (760 and 3315 cm$^{-1}$), N$_2$O (1285, 2220 and 2550 cm$^{-1}$), NO$_2$ (1550 cm$^{-1}$), CH$_2$O (1745 and 2802 cm$^{-1}$), NO (1910 cm$^{-1}$), and H$_2$O (3500 cm$^{-1}$), and more CO$_2$ is produced with the addition of BR and F$_{2604}$. In the infrared spectrum detection, CO has a relatively small dipole moment and N$_2$ has a symmetrical structure and no dipole moment. Therefore, CO and N$_2$ signals are not detected in the FTIR test.

During the thermal decomposition of HMX, we extracted the gas products at multiple time points in FTIR detection, as shown in Figures 6, S6 and S7, in which the red arrow indicates the appearance of the products and the black arrow indicates the disappearance of the products. The infrared spectrum of pure HMX showed that N$_2$O (20 min) is the first gas product, followed by trace CO$_2$ (21 min) and CHN (22 min), and then other gas products (NO$_2$, NO, CH$_3$O, H$_2$O, and NO) appeared simultaneously in the infrared detection at 22.5 min. Figure S6 shows that when BR is added into HMX, some gas products will appear earlier, such as CHN (21.5 min), NO$_2$, NO, CH$_3$O, H$_2$O, and NO (22 min), while Figure S7 shows that the formation time of gas products of HMX/F particles is similar to that of the pure HMX crystal. With the progress of the decomposition reaction, the infrared results show that the gas products of pure HMX, except N$_2$O, almost disappear at about 24.5 min, while the disappearance time of HMX/BR and HMX/F gas products is about 26 and 27 min, respectively. Obviously, the addition of both binders prolonged the duration of gas product formation. Therefore, the FTIR results can be summarized as follows: BR induces HMX to

![Figure 5. FTIR spectrum of the evolved gases at 280 °C.](https://dx.doi.org/10.1021/acsomega.0c04985)
decompose in advance and prolong the continuous formation time of gas products, while F does not show an obvious induction effect, but also prolong the continuous formation time of gas products.

The gas chromatography−mass spectrometer (GC−MS) is used to further detect the composition and content of gas products, and the total particle flow spectrum is shown in Figure 7. Pure HMX showed strong ion flow peaks at 1.92, 2.55, 2.77, and 8.7 min and weak ion peaks at 11.5 and 14.5 min; because of the variety of HMX gas products, only fragments with relative ion flow intensity greater than 3% are selected for mass-core ratio (m/z) analysis. The mass spectrum corresponding to each ion flow peak is shown in Figure 8, and the possible structures corresponding to m/z are listed in Table 2. In the ion flow of 1.92 min, the main values of m/z are 14, 16, 28, 32, and 40; the corresponding fragments are CH₂N₂⁺, O⁺, CO, N₂, and CN₂⁺ respectively. Figure 8a shows that the addition of BR and F₂604 increased the contents of CO, N₂, and CH₂N₂⁺ and decreased the contents of O⁺, O₂, and CN₂⁺, which means that the binder could promote some oxygen-containing reactions and generate stable products CO and N₂. Figure 7 shows that the m/z of the fragment corresponding to 2.55 min is 44, and there is only one relatively stable fragment corresponding to CO₂, while the m/z corresponding to 2.77 min is 30 and 44, and the corresponding product fragments are CH₃O and N₂O, respectively, which can be produced by further pyrolysis of intermediate products CH₂N₂O₂. Moreover, Figure 7 shows that the relative ion flow peak values corresponding to 2.55 and 2.77 min are HMX/BR > HMX/F > HMX, which means that BR and F₂604 promote the production of CO₂, CH₃O, and N₂O.

![Figure 6. Evolution of gas products with decomposition time of the pure HMX crystal.](image)

![Figure 7. GC−MS spectrum of the evolved gases at 280 °C.](image)

For the weaker ion flow, the mass spectra of the composite particles and pure HMX are obviously different. At 11.5 min,
the main m/z are 26, 27, and 28, and the corresponding main ion fragments are CHN and its isotopic ions CN and CH2N. The slightly higher ion flow peak in Figure 7 and the more fragments with m/z of 27 in Figure S8a indicate that the presence of BR and F2604 will promote the formation of CHN. In the 14.5 min ion flow peak, the main product fragments are CHN, CH2N, C2N2H, C2N2H, and so forth, of which CH2N is the CHN isotope, C2N2H is the C2N2H isotope, and C2N2H, C2N2H, and C2N4H4 are products of group rearrangement. Figure S8b shows more CHN, CH2N rearrangement in HMX/BR and HMX/F to produce rearranged ions of C2N2H, C2N2H2, and C2N4H4. It is worth noting that among the three materials, only HMX/BR composite particles have an ion flow peak of 9.5 min, as shown in Figure S9, and the main fragments corresponding to the m/z are C4H4 and C2H2 indicate that BR has undergone fracture decomposition. No typical fluoride-containing fragment HF is detected in HMX/F particles, which may be because the F2604 has not been completely decomposed into HF or HF fragment quickly participates in the reaction, so it is not detected in the GC−MS test.

3.3. Thermal Decomposition Mechanism. During the thermal decomposition of HMX, the initial decomposition of HMX and the rapid oxidation mechanism in the decomposition process determine the thermal decomposition process of HMX. The thermal decomposition process of HMX mainly includes the breakage of the N−N bond, the separation of H and O, the fission of C−N ring, and the rapid oxidation of sensitive intermediate products into stable gas products. In this paper, the coupling analysis of DSC−TG−FTIR−MS detection results is carried out, the main action mechanisms of the two binders are summarized, and a simple schematic diagram is drawn, as shown in Figure 9. During the initial decomposition process, a large number of small molecular substances such as NO2, HONO, H, and OH and large molecular intermediate products such as C4H7O6N7 are generated. Intermediate products will react with each other to form relatively stable products. For example, HONO can react with itself to generate H2O and also can react with C4H7O6N7 to form unstable products, as shown in Figure S10. Moreover, with a hydroxyl group next to the adjacent nitroamine group in C4H7O6N7 molecule will more easily lead to C−N bond breaking and generate small-molecule intermediate products such as CH2O, N2O, and CHN. The existence of oxidizing active ions (O, HO, etc.) makes the interaction between intermediates easier, but there is a competition mechanism between relatively inert intermediates and oxidizing intermediates, as shown in Figure 9. In the thermal decomposition of the composite particles, the addition of binder BR and F can induce HMX to undergo N−N fracture and H, O dissociation reaction and promote the reaction of small-molecular intermediate products with active ions more quickly. However, the promotion of small-molecule reaction (step 1) by the binder will consume more active ions, which indirectly inhibits the further reaction of relatively inert substances such as C4H7O6N7 (step 2). Moreover, the reaction...
between binder and HMX intermediate products in the thermal decomposition process will also consume oxidizing active ions. Especially BR, the strong induced adsorption of O seriously affected the thermal decomposition behavior of HMX. This competition mechanism for active ions explains why the decomposition temperature of composite particles is lower, but the activation energy is higher, and the decomposition duration is longer.

4. CONCLUSIONS

DSC−TG−FTIR−MS coupling technology is used to study the mechanism of two different types of binders (BR and F2604) on the thermal decomposition behavior of HMX crystals. It is found that both binders can reduce the decomposition temperature of HMX, induce the decomposition of HMX, and promote the appearance of gas products earlier, while the composite particles have higher activation energy and longer duration of gas product generation. Based on the coupling analysis of DSC−TG−FTIR−GCMS detection results, the mechanism of action of BR and F2604 is proposed, that is, the two binders induce the decomposition of HMX in advance and promote the transformation of small-molecular intermediate fragments into gas products. However, in the oxidation reaction, the existence of the binder makes the small-molecule intermediate fragment more competitive than the inert macromolecular intermediate product, which can consume the active ions in the decomposition process faster, and the reaction of the binder rubber chain also consumes some active ions. Compared with pure HMX crystals, the excessive consumption of active ions in composite particles inhibits the further reaction of inert macromolecular intermediate products such as C4H7O6N7, thereby prolonging the continuous generation time of gas products and slowing down the thermal decomposition process of HMX.

■ ASSOCIATED CONTENT

+ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04985.

Morphology of the samples, FTIR test chart of samples at room temperature, thermal analysis test of the binder, reaction process of samples, DSC−TG results of the samples, FTIR diagram of composite particles during thermal decomposition, part GC−MS test results, and
possible chemical reactions between intermediates (PDF)

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**Author Contributions**

All authors discussed the results and commented on the manuscript.

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