THE EFFECT OF INSENSITIVE AGENTS-EMULSIFIERS ON THE THERMAL HAZARD OF 2,4,6-TRINITROPHENOL WAS EVALUATED BY DSC AND THERMOKINETIC METHODS

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With the increasing application of energetic materials across various fields, their associated safety concerns have become prominent. 2,4,6-Trinitrophenol, a compound containing three nitro groups, is particularly dangerous due to its unique chemical properties, yet there is limited research on effective methods to reduce its transportation and storage hazards and control its exothermic energy within a manageable range. This study proposes a novel method of modifying 2,4,6-trinitrophenol using a combination of wax-based blunting agents and emulsifiers. The compatibility of the modifications was confirmed using SEM, FTIR, and XPS, and the thermal decomposition processes of the modified samples were studied using DSC and typical kinetic methods. A nonlinear fitting method was utilized to verify the type of thermal decomposition of the modified samples. The results indicate that the MCW–Span80–TNP significantly reduces the heat release and hazard level of the samples, increases the apparent activation energy, and changes the decomposition process of TNP from autocatalytic reaction to two n-order reactions, making the decomposition process more controllable. However, calculations of the thermal risk parameters TMR, TCL, and SADT reveal that the modified samples should be stored in packages of less than 5 kg and maintained at temperatures below 60 °C to ensure stability and extend their shelf life.

Key words*: Energetic material; Composite modification; Thermokinetics; Thermal stability; Thermodynamic method.*

1. Introduction

Energetic materials represent a class of metastable compounds or mixtures that have found widespread applications over the past several centuries. Characterized by their ability to store significant amounts of energy and release it in a controlled manner, typically through combustion or detonation processes, these materials have garnered considerable attention in the scientific community. Among the various energetic materials, 2,4,6-trinitrophenol (TNP), also known as picric acid, stands out for its wide range of applications and unique chemical properties and is widely used in fields as diverse as explosive manufacturing [1, 2], rocket fuel production, dyes [3] and leather industries, pesticide preparations [4], fireworks [5] and the pharmaceutical industry. TNP is a compound that features three nitro-functional groups and exhibits a characteristic yellow color when dissolved in aqueous solution. Its high energy content, with a theoretical detonation velocity of up to 7350 m s^{-1}, surpasses that of trinitrotoluene (TNT) [6], which has a theoretical detonation velocity of 6900 m s^{-1}. The presence of nitro groups in TNP not only imparts high energy but also renders the compound highly sensitive due to its strong oxidizing nature. These nitro groups undergo decomposition and explosive reactions at elevated temperatures, posing significant safety risks. The unique chemical properties of TNP have led to a heightened focus on its potential hazards, prompting comprehensive research efforts to understand its behavior and develop methods for safe handling and use. The intricate chemistry of TNP, particularly its sensitivity to external stimuli and its propensity to undergo explosive reactions, necessitates careful consideration in both its storage and transportation. Moreover, the development of novel materials and techniques for the safe and effective use of TNP remains an active area of research, with the aim of harnessing its energetic properties while mitigating the associated risks. Many scholars have also studied this high-energy substance. According to the data obtained by Idrees Khan et al from the Scopus database, the current research on trinitrophenol is also increasing [7]. The energy-containing material trinitrophenol was analyzed from the statistical point of view, which laid a foundation for the subsequent research of related energy materials. More and more research on the thermal hazards of energetic substances with potential explosive hazards. Liu et al. studied the thermal stability of nitro by-products including trinitrophenol, providing reliable data support for exploring the intrinsic stability of nitro by-products [8].

In the field of energetic material modification, common methods include sol-gel, solvent-non-solvent, and spray drying techniques. Chen T et al. prepared energy-containing nano-composites of CL-20 and 3, 3-di(azide polymethyl) oxyethyl tetrahydrofuran copolymer (BAMO-THF) by sol-gel freeze-drying method. However, the raw materials of the traditional sol-gel method are expensive and toxic, and the modified materials are prone to agglomeration [9]. If an inert gel matrix is selected, the energy properties will be weakened. Ke-Xin Wang et al. used a spray drying method to generate organic complex n-Al/$[Ni(CHZ)_3](ClO_4)_2$ and n-Al from highly explosive high-energy metal-organic complex $[Ni(CHZ)_3](ClO_4)_2$, but this method is easy to bind the product to mechanical equipment. This process also causes higher thermal and mechanical stresses on the material [10].

An insensitive agent is a substance that reduces sensitivity. It can cover the surface of the energetic material, fill the gap, reduce friction, disperse external forces, absorb heat, and blunt the energetic material. Insensitive agents commonly used to reduce the sensitivity of energetic materials include waxes, polymers, and nitro compounds. Microcrystalline wax (MCW), also known as ground wax, is harmless to the environment and the human body and is commonly used in the cosmetics and food industries [11]. Due to its excellent water resistance, MCW is often used as a water-repellent agent in the paper industry or to improve the hydrophobicity of other materials [12]. Therefore, it can be used during TNP storage and transportation to prevent deterioration when encountering moisture. Peng Bao et al. used microcrystalline wax emulsion and energetic material CL-20 to prepare composite particles, to improve the stability of composite materials and reduce the sensitivity of CL-20 [13].

An emulsifier is a substance that enables a mixture of two or more insoluble ingredients to form a stable emulsion. In the field of emulsification, the most used emulsifier is sorbitan oleate [14], commonly known as Span-80. It has been widely studied that components with different properties can be encapsulated in different phases of a variety of emulsions to provide isolation, protection, and directed release [15]. Wu et al. studied the effect of emulsifier Span-80 on the thermal risk of fireworks [16], and their study raised the runaway threshold of fireworks propellant from 181.82 ℃ to 218.18 ℃, proving that emulsifier can effectively reduce the thermal risk.

Current research on the thermophysical properties of energetic materials modified with insensitive agents/emulsifiers is scarce, presenting a significant gap in the literature. This study investigates the use of microcrystalline wax in conjunction with Span-80 as a means to reduce the thermal hazard of energetic TNP. The compatibility of microcrystalline wax with emulsifiers has already been confirmed in numerous studies, establishing the feasibility of their synergistic use for modification and laying a foundation for future research. This work employs a physical mixing method to modify TNP with an insensitive agent/emulsifier, examining changes in parameters such as microscopic morphology, chemical composition, and thermal risk. Subsequently, a composite modification is conducted using MCW, which possesses favorable plasticity, and Span-80, the most commonly used oil-in-water emulsifier in the field of emulsion explosives, to explore the potential enhancements in the performance of the modified material. In this paper, the physical mixing method is used, the cost is low, the material is simple and harmless to the environment and human body, and it is a relatively economical modification method.

2. Experimental sample and methods

2.1. Sample preparation

The raw materials used include microcrystalline wax (MCW, melting point 67–72 ℃, purchased from Shanghai Aladdin Biochemical Technology Co., Ltd.), 2,4,6-trinitrophenol (TNP, self-made in the laboratory, the purity of the self-made samples has been proven in previous research by the research group [17]), Span-80 (CAS: 1338–43–8; Purity ≥ 99.7%, purchased from Ya tai United Chemical Co., Ltd. (Wuxi, Jiangsu, China). The instruments used for physical mixing, drying, and other processes include a heat-collecting magnetic stirrer, a vacuum drying oven and an Ultrasonic disperser (SCIENTZ-750F).

The preparation of the MCW–TNP sample and its further modification with Span-80 is described herein. Initially, 1 g of MCW was accurately weighed and placed in a beaker, which was then placed in a forced-air oven at 80 °C for complete melting of the wax. Meanwhile, 1 g of TNP was weighed. The melted MCW (0.5 g) was swiftly added to the TNP-containing beaker, followed by the addition of 10 g of carbon tetrachloride, which facilitated the dispersion of the components. The mixture was stirred at 75 °C for 30 minutes. After complete evaporation of the solvent, the mixture was cooled to room temperature and subsequently dried in a vacuum oven at 60 °C for 12 hours. The resulting material was ground in an agate mortar to obtain the MCW-TNP sample, as illustrated in Fig. 1.

For the preparation of the MCW–Span80–TNP sample, 0.5 g of Span-80 was added to the beaker containing 1 g of TNP. The components were ultrasonically mixed at 300 W for 30 minutes. Thereafter, 0.5 g of the melted MCW was added, followed by the introduction of 10 g of carbon tetrachloride to disperse the remaining components. The mixture was placed on a magnetic stirrer and stirred at 75 °C for 30 minutes. Upon complete evaporation of the solvent, the temperature was gradually reduced, and the obtained sample was dried in a vacuum oven at 60 °C for 12 hours. Finally, the sample was ground in an agate mortar to yield the MCW–Span80–TNP composite, as depicted in Fig. 1. This detailed preparation process ensures the homogeneity and stability of the modified energetic materials, which are critical for their subsequent characterization and performance evaluation.

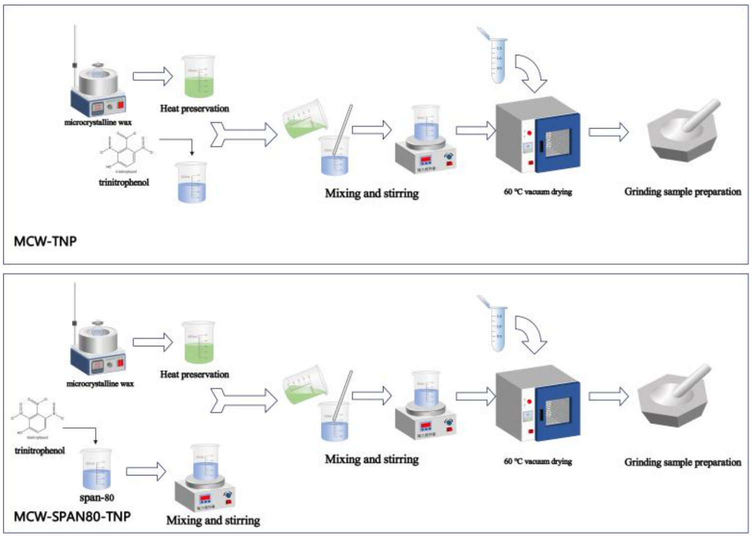

Figure 1. Preparation of modified MCW–TNP and MCW–Span80–TNP

2.2. Sample characterization

The microstructure of the material was observed by Scanning electron microscopy (SEM), Fourier infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were used to determine the analytical structure and chemical composition of the samples. 2,4,6-trinitrophenol (TNP) was a yellow or white acicular crystal. After microcrystalline wax/Span-80 composite modification of TNP, the sample showed yellow waxy solid particles. The micromorphologies of the two observed by electron microscopy (SEM) are shown in Fig. 2 below. It can be seen from the microscopic morphology before and after the composite modification of MCW and Span-80 that the surface of the sample before modification was broken into scales, the surface of the material was relatively rough and there were fine particles, while the surface cracks of the MCW–TNP sample disappeared after modification, which was due to the microcrystalline wax filling the surface cracks, which reduced the friction between the energetic materials to a certain extent. After the modification of the MCW–Span80–TNP sample, the sample showed irregular smooth clumps, and the surface was covered with a film, which was more three-dimensional. This was due to the changes in the morphology of the material due to the emulsification of the energetic material, and at the same time, the microcrystalline wax formed a film on the surface of the energetic material after emulsification.

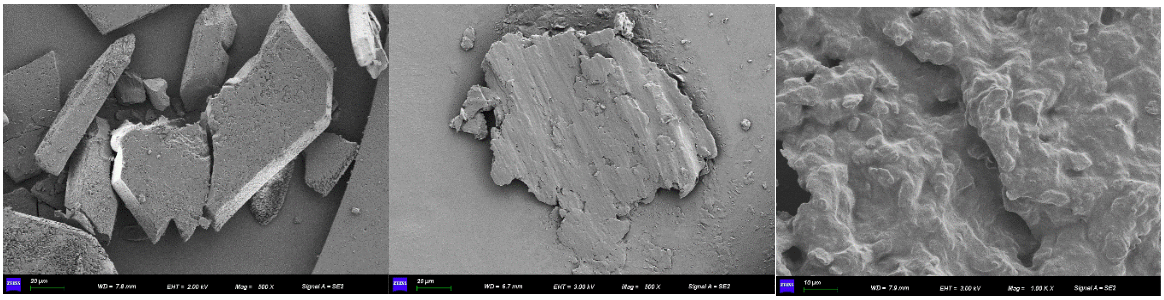

Figure 2. Microstructure of 2, 4, 6-trinitrophenol, MCW–TNP and MCW–Span80–TNP

Infrared absorption spectroscopy is a quantitative method to identify the composition and structure of molecules by using the absorption of infrared light and the generated infrared absorption spectrum. The US Thermo Scientific Nicolet iS50 was used to scan the surface functional groups of the sample, and the scanning range was 400–4000 cm^{-1}. The infrared spectra and corresponding chemical functional group composition of the MCW–TNP and MCW–Span80–TNP are shown in Fig. 3 and Tab. 1 below.

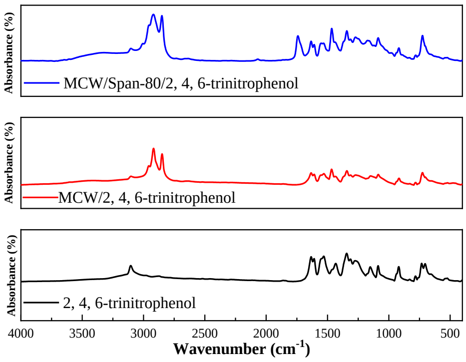

Figure 3. Comparison of Fourier infrared spectra

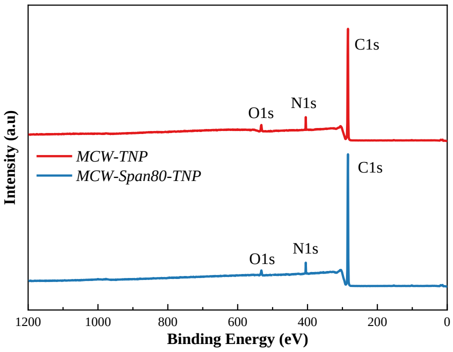

Figure 4. XPS spectra of modified materials

Table. 1. Infrared spectral peak and corresponding functional groups

Wavenumber range of TNP standard sample (cm^{-1})	Corresponding functional groups	MCW–TNP	MCW–Span80–TNP
3104	ν C–H	3102.21	3102.76
1633	ν C–C	1633.42	1633.56
1527	$\nu_{as}(NO_2)$	1529.69	1551.64
1432	$\nu_{as}(NO_2)$	1435.49	1438.75
1342	$\nu_s(NO_2)$	1342.13	1342.36
1314	$\nu_s(NO_2)$	1311.55	1312.20
1265	δ C–H	1271.18	1272.10
1176	δ C–H	1148.54	1173.04
1108	δ C–H	1085.94	1086.70
919	δ C–H	916.83	918.12
832	δ O–H–out of plane	829.17	834.57
783	ϕ NO_2	781.60	780.63
729	Ω NO_2	725.34	725.27
704	δ ring	701.81	-
521	δ ring	521.46	522.68

ν_{as}- asymmetric stretching; ν_s- symmetric stretching; δ-deformation; ϕ-scissoring; ω-wagging.

The main components are saturated straight paraffin contained in microcrystalline wax and Span-80, nitro and phenolic functional groups contained in nitrophenol. The chemical composition of MCW–TNP and MCW–Span80–TNP was determined by XPS, and the results are shown in Fig. 4. 2,4,6-trinitrophenol contains C, H, O, and N four elements, and the reagent used for modification also contains C, H, and O basic elements, so observing the presence of N element can be used as a standard to measure whether the modified reagent is introduced.

2.3. Thermal analysis kinetics method: DSC

The thermal hazard of the energetic materials was analyzed by Mettler DSC 3. The mass of the MCW–TNP sample was 1.5 mg±0.5 mg, the mass of the MCW–Span80–TNP sample was 1.7 mg± 0.5 mg, and the temperature was increased from 30 ℃ to 350 ℃ under 50 ml min^{-1} nitrogen atmosphere. 25 μL closed gold-plated crucible was tested at the temperature rise rate of 1, 3, 5, 8, 10 ℃ min^{-1}.

2.4 Thermokinetic modeling methods

Thermokinetic modeling methods are methods of kinetic analysis calculating dependence of activation energy E on the degree of conversion α for dynamic experiments with different constant heating rates β. The kinetic equation for non-isothermal heterogeneous reactions is given by eq. (1), where β is the heating rate (usually a constant), and α is the conversion percentage. Arrhenius [18] proposed the relationship between rate constant and temperature by drawing on the form of the equilibrium constant-temperature relationship, eq. (2), where A is the pre-exponential factor, E is the activation energy, R is the molar gas constant, and T is the thermodynamic temperature.

$$\frac{d\alpha}{dt}=\frac{1}{\beta}k(T)f(\alpha) \tag{1}$$

$$k=A\exp(-\frac{E}{RT}) \tag{2}$$

Substituting eq. (2) into eq. (1), we can obtain the non-isothermal heterogeneous kinetic eq. (3).

$$\frac{d\alpha}{dt}=\left(\frac{A}{\beta}\right)\exp(-\frac{E}{RT})f(\alpha) \tag{3}$$

Linear regression methods have been used to establish the Kissinger method, KAS method, Starink method, Vyazovkin method, and Ozawa–Flynn–Wall method. The reliability of the reaction kinetics method depends on the accurate selection of the mathematical model and the effectiveness of the kinetic evaluation methods.

The Kissinger kinetic method was initially developed for DTA curves but later proved to be applicable to DSC curves. The equation results in the Kissinger eq. (4), where T_p is the temperature corresponding to the maximum heat flow.

$$\ln\left(\frac{\beta}{T_p^2}\right)=\ln\frac{AR}{E_a}-\frac{E_a}{R}\frac{1}{T_p} \tag{4}$$

The KAS method improves the Kissinger kinetic model for determining the activation energy of a substance. The KAS equation is given by the eq. (5), In the above equation, $g(\alpha)$ represents the integral form of the reaction mechanism function, and T_α corresponds to the temperature associated with the conversion rate α.

$$\ln\left(\frac{\beta}{T_p^2}\right)=\ln\frac{A}{E_a g(\alpha)}-\frac{E_a}{R}\frac{1}{T_p} \tag{5}$$

Starink suggests that it can be represented by a general formula. The Starink kinetic model is used to calculate E_a and get thermodynamic results. The Starink kinetic process can be represented as eq. (6), where C is a constant, and represents an approximation of the temperature integral. In this study, the values of *i* and *C* are 1.80 and 1.0037, respectively.

$$\ln\left(\frac{\beta}{T_p^i}\right)=C_s-C(\frac{E_a}{RT}) \tag{6}$$

The Vyazovkin kinetic method determines the E_a during chemical processes. This method is commonly employed in studying chemical processes. As shown in eq. (7), where $t_{\alpha,t}$ represents the time required to achieve different conversion rates.

$$-\ln t_{\alpha,t}=\ln\left[\frac{A_\alpha}{g(\alpha)}\right]-\frac{E_a}{RT} \tag{7}$$

The FWO method eq. (8) can be simplified to the equation, and by plotting the vertical axis as lgβ and the horizontal axis as T^{-1}, the E_a can be determined. In eq. (8) , β represents the heating rate, *R* is the gas constant, and T_α corresponds to the temperature associated with the conversion rate α.

$$\lg\beta=-0.4567(\frac{E_a}{RT_\alpha})+\lg(\frac{AE}{RG(\alpha)})-2.315 \tag{8}$$

The utilization of dynamic evaluation methods in conjunction with nonlinear model parameter estimation methods applies to a wide range of dynamic models, regardless of their level of complexity. It can accurately determine dynamic variables in challenging circumstances. The nonlinear regression technique is frequently employed in scientific research to analyze experimental data obtained from DSC and to ascertain the thermal characteristic parameters of substances. This method conducts thermal hazard analysis for different states of substances, verifies the precision of the established kinetic model by simulating the thermal decomposition process of materials, and determines the corresponding kinetic parameters of the model based on the fitting results. Nonlinear regression is superior to linear regression in predicting the thermal decomposition process of modified samples.

3. Results and discussion

3.1 DSC result analysis

According to United Nations (UN) guidelines, DSC is recommended as a technique for identifying thermal hazards of energetic materials. Differential scanning calorimetry (DSC) is widely used to assess the thermal stability of energetic materials and the potential hazards of fire and explosion. Fig. 5 shows the DSC curve before and after TNP modification. According to the DSC curves of the two samples before and after modification, the initial temperature, the end temperature, the peak temperature, and the enthalpy of heat release in the process of thermal decomposition can be obtained. The comparison of thermal parameters of samples before and after modification is shown in Tab. 2 and Tab. 3. It can be seen that the decomposition heat of the sample is significantly reduced before and after modification, which may be related to the proportion of modified reagents added.

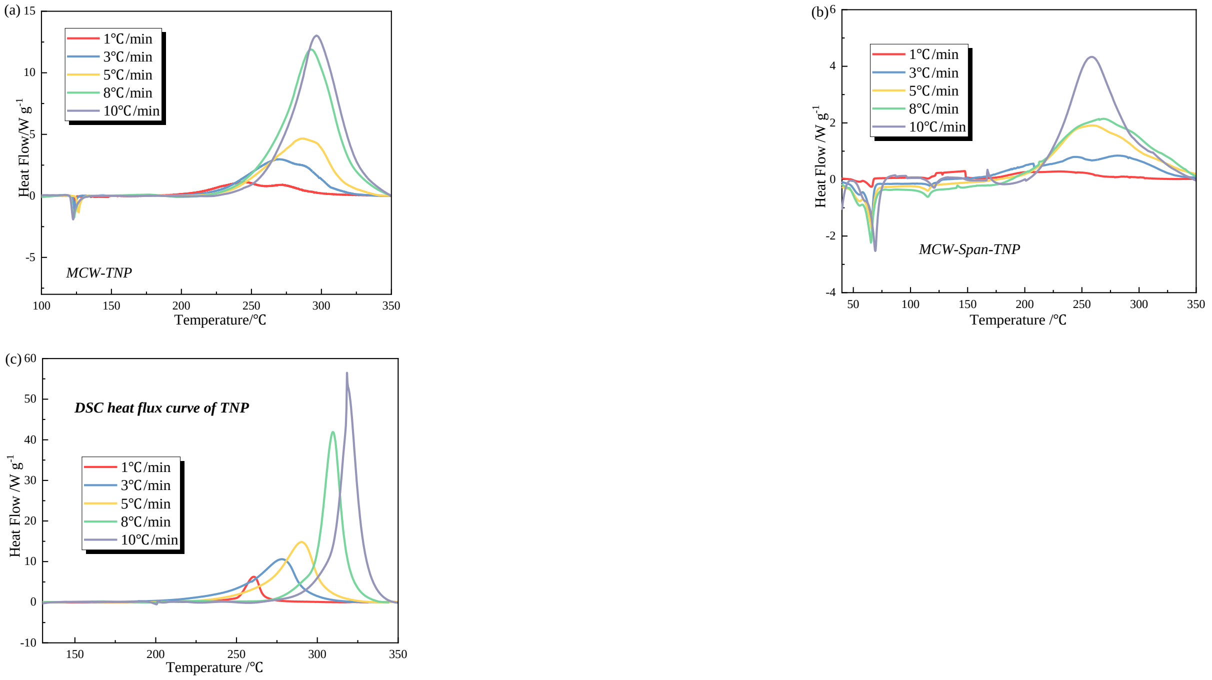

Figure 5. DSC heat flux curve of (a) MCW–TNP (b) MCW– Span80–TNP and(c) TNP

Table 2. Measure TNP and MCW-TNP at temperature rise of 1.0, 3.0, 5.0, 8.0, and 10.0 ℃min^{-1}.

β/ ℃min^{-1}	TNP				MCW–TNP			
	m_s/ mg	T_0/T_e/ ℃	T_p/ ℃	ΔH_d/ J g^{-1}	m_s/ mg	T_0/T_e/ ℃	T_p/ ℃	ΔH_d/ J g^{-1}
1	1.11	268.90/285.79	279.35	4271.47	1.98	167.41/290.53	243.93	2207.01
3	1.95	247.18/294.34	278.87	4166.50	1.89	226.63/277.31	269.84	1693.86
5	1.43	264.50/305.89	291.24	4313.52	1.89	246.53/317.53	287.31	1535.66
8	1.38	303.76/325.39	317.40	3971.35	2.47	263.23/323.32	293.26	1568.61
10	1.39	314.65/328.99	319.58	3809.74	1.84	267.77/328.12	296.97	1727.05

Table 3. Measure MCW–Span80–TNP at temperature rise of 1.0, 3.0, 5.0, 8.0, and 10.0 ℃min^{-1}.

β/ ℃min^{-1}	m_s/ mg	T_0/T_e/ ℃	T_p/ ℃	ΔH_d/ J g^{-1}
1	2.00	171.26/292.17	230.20	595.77
3	2.40	180.58/340.91	247.31	610.86
5	1.67	213.71/316.49	254.40	797.35
8	1.65	265.84/335.51	267.86	841.86
10	2.08	214.48/297.36	273.95	986.15

According to the DSC test data, the exothermic enthalpy of TNP decreased significantly during the modification process. According to the average enthalpy value, the average enthalpy of TNP, MCW–TNP and MCW–Span80–TNP were 4112.516 J g^{-1}, 1746.438 J g^{-1} and 766.398 J g^{-1}. The decomposition of exothermic enthalpy decreased by 57.53% and 81.36%, indicating that the effect of MCW–Span80–TNP was more significant.

3.2 Evaluation of thermodynamic methods

Non-isothermal kinetic tests were performed by DSC. Linear fitting was established by the Kissinger method, Kissinger–Akahira–Sunose method, Starink method, Vyazovkin method, and Ozawa–Flynn–Wall method. E_a calculated by the Kissinger method is shown in Fig. 6, and the degree of fitting is above 0.96. The apparent activation energy calculated by Kissinger reflects that the activation energy of the MCW–TNP alone increased by 2.006 kJ mol^{-1}, while the activation energy of the MCW–Span80–TNP increased by 20.621 kJ mol^{-1}, indicating that the addition of microcrystalline wax can promote the thermal decomposition process of materials. The composite modification of microcrystalline wax (MCW) and Span-80 can increase the reaction energy barrier, improve the thermal stability of the substance, and inhibit the reaction. Therefore, the E_a of the MCW–Span80–TNP was validated using the remaining four methods and compared with the E_a of the TNP.

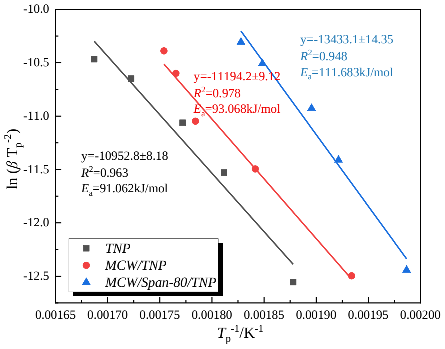

Figure 6. Linear regression analysis of TNP, MCW–TNP, and MCW–Span80–TNP based on the Kissinger model

The thermodynamic method with an equal conversion rate needs to select a value of the same conversion rate α, so it is selected between 0.05–0.90. The linear fitting curve of the TNP and MCW–Span80–TNP is shown in Fig. 7, and the fitting degree and specific activation energy values are shown in Tab. 4. According to the E_a calculated by five typical kinetic methods, the activation energy value of the composite modification increases by 20.621–43.592 kJ mol^{-1}, which indicates that the composite modification method has a significant effect on increasing the activation energy value and reducing the reaction risk.

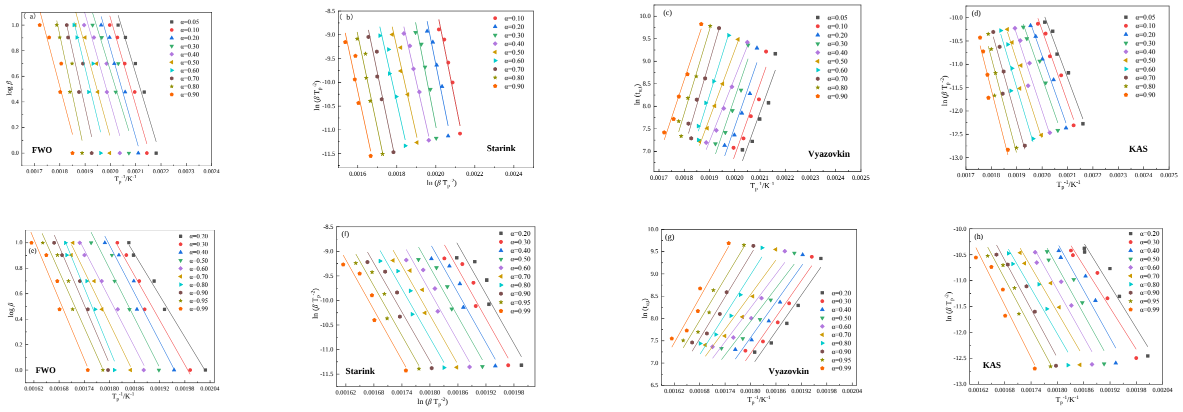

Figure 7. Linear fitting curve of TNP (a: FWO; b: Starink; c: Vyazovkin; d: KAS) and MCW–Span80–TNP (e: FWO; f: Starink; g: Vyazovkin; h: KAS)

Table 4. The E_a and R^2 were calculated by Kissinger, KAS, FWO, Vyazovkin, and Starink kinetic methods.

Method	E_a/ kJ mol^{-1}	R^2
Kissinger	0.972	111.683
KAS	0.8910	131.287
FWO	0.8626	133.082
Vyazovkin	0.8548	134.654
Starink	0.8698	133.837

3.3 Nonlinear fitting analysis and evaluation

The nonlinear regression method is frequently employed in for processing DSC experimental data for obtaining the substance's thermal characteristic parameters. This method performs thermal hazard analysis for different states of substances, verifies the correctness of the established kinetic method by simulating the thermal decomposition process of meanings, and obtains the relevant kinetic parameters of the method from the fitting results. Fig. 8 illustrates the scenario of non-linear fitting. Compared with linear regression, nonlinear regression can more accurately predict the thermal decomposition process of composite-modified samples. The results indicate that the thermal decomposition of TNP follows an *n*-order reaction and an autocatalytic reaction, which is consistent with the reaction types studied by previous scholars. The thermal decomposition of MCW–Span80–TNP follows two *n*-order reactions, as shown in Fig. 9. A nonlinear regression fitting method was used to simulate the original and the modified of composite materials to verify the rationality of linear regression. The curve obtained from nonlinear regression is in good agreement with the experimental data.

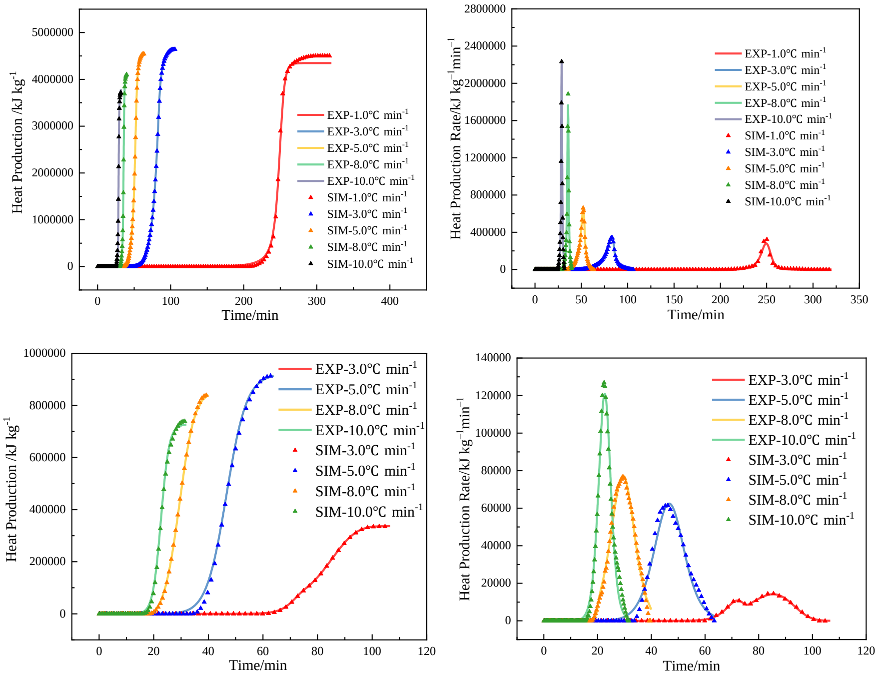

Figure 8. The nonlinear fitting curve of the TNP sample and MCW–Span80–TNP

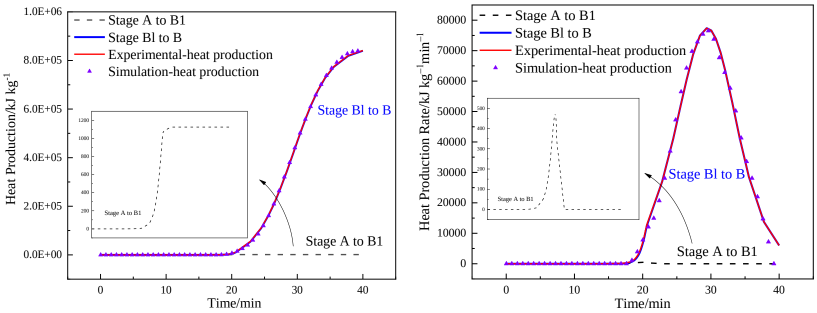

Figure 9. The nonlinear fitting curve of two *n*-order reactions (taking temperature rise 8 ℃min^{-1} as an example)

3.4 Using a nonlinear regression method to determine *TMR* and *TCL*

Energetic substances, due to their high energy functional groups, generate a large amount of heat in the event of bond breakage, resulting in hazardous storage and transportation temperatures. Due to the huge energy contained in TNP, it is prone to collision or friction during storage and transportation. To assess the thermal hazard of a substance, several thermal hazard parameters need to be considered, such as *TMR* (Maximum reaction rate arrival time) and *TCL* (Conversion limit Time) [19]. Taking the temperature rise rate of 10 ℃min^{-1} as an example, the thermal parameter results of the TNP and MCW–Span80–TNP are shown in Fig. 10. When the ambient temperature exceeds 135 ℃ and *TMR*<120 min, *TMR* represents the time required for a substance to reach its maximum conversion rate, that is, when the ambient temperature exceeds 135 ℃, the time for the material to reach the maximum conversion is less than 120 min. According to the evaluation of liberated heat in GB/T 42300–2022 formulated by the Ministry of Emergency Management of China, the modification of MCW–Span80 reduced the danger level of energy-containing substances from 4 to 2. When the modified sample reaches the corresponding temperature of maximum conversion rate, the *TMR* curve slowly declines, but when TNP reaches the corresponding temperature of maximum conversion rate, the curve rapidly declines, which may be uncontrollable. Therefore, in the process of storage and transportation, the ambient temperature should not exceed 60 °C.

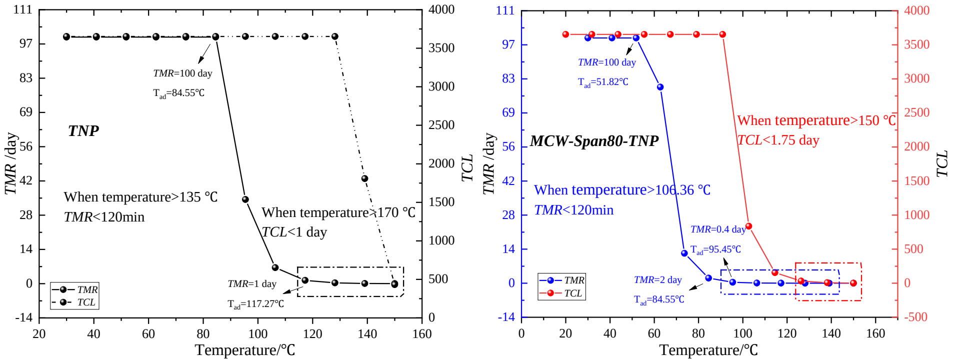

Figure 10. Comparison of thermal hazard parameters

4. Conclusions

In this study, microcrystalline wax (MCW) and Span-80 were employed to modify 2,4,6-trinitrophenol, with the compatibility verified using SEM, FTIR, and XPS techniques, and the thermal decomposition process of the MCW–Span80–TNP sample analyzed using DSC and typical kinetic methods. The results demonstrated that the modification significantly reduced the enthalpy of decomposition by 81.36%, while increasing the apparent activation energy by 20.621 to 43.592 kJ mol^{-1}, leading to a reduction in the hazard level from level 4 to 2. The kinetic analysis based on DSC data, using five typical methods (Kissinger, FWO, KAS, Vyazovkin, and Starink), confirmed that the type of thermal decomposition reaction changed from autocatalytic to *n*-order, enhancing the controllability of the sample's hazardousness. The thermal risk parameters *TMR* and *TCL*, derived from the experimental data, can predict the storage time of the modified samples at specific temperatures. These findings ensure the stability and extended shelf life of the modified nitro-containing energetic materials during storage and transportation, providing essential reference for the chemical management of these materials.

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