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Thermal decomposition behavior of ammonium perchlorate/nitrated microcrystalline cellulose carbamate/diethylene glycol dinitrate energetic composite

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ABSTRACT

This study reports the successful preparation of an energetic composite consisting of ammonium perchlorate (AP), nitrated microcrystalline cellulose carbamate (M3CN), and diethylene glycol dinitrate (DEGDN). The optimal composition was determined by theoretical performance calculations using the NASA-CEA2 program prior to preparation. Characterization techniques, including Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM), confirmed the uniform dispersion of AP within the M3CN/DEGDN matrix without altering its chemical structure. Thermal analysis revealed that the incorporation of AP facilitated the decomposition of both components, as indicated by shifts to lower decomposition peak temperatures. This suggests a catalytic interaction that enhances heat release and combustion energy. Kinetic models using isoconversional methods revealed a significant reduction in activation energy, further supporting the observed catalytic effects in the AP@M3CN/DEGDN composite during different stages of decomposition.

1. Introduction

Developing advanced energetic materials is a high-priority area in propellants, explosives, and pyrotechnics [1,2]. Researchers particularly focus on composite energetic materials that offer interesting features, such as modified double-base solid propellants (MDBs) [3,4]. These energetic formulations contain cellulose nitrate (NC) as a binder, oxidizers like ammonium perchlorate (AP), plasticizers and energetic additives including nitramines [5,6]. MDBs are recognized for their variable combustion rates, specific impulse values, and excellent mechanical properties. Their superior performance characteristics make them suitable for military applications in missiles, rocket motors, and boosters [7]. Ongoing research aims to enhance the safety and efficacy of these formulations while addressing challenges related to insensitive munitions, leading to an increasing demand for these materials in chemical propulsion systems [8,9].

Energetic plasticizers, particularly nitrate esters such as nitroglycerin (NG), diethylene glycol dinitrate (DEGDN), and ethylene glycol dinitrate (EGDN), are essential components in modified double base (MDB)

propellants [10–12]. These plasticizers perform a variety of functions, including acting as a fuel, improving the physical properties, and enhancing the overall energy and plasticity of the propellant formulations [13]. An efficient plasticizer should have a low melting point, compatibility with other components, acceptable sensitivity, and a favorable density [14]. Despite its widespread use, NG presents several challenges, including high sensitivity to friction and impact, low thermal stability, and phase transition issues during production and application [15,16]. Alternative nitrate esters including DEGDN and EGDN have been identified as promising candidates to replace NG and mitigate these drawbacks [13]. These alternatives offer improved wetting properties and allow softer boundaries at nitrocellulose interfaces, which helps to reduce the overall sensitivity of the resulting propellant blends. In addition, they can effectively lower the freezing point of NG [12]. EGDN is recognized as a particularly effective energetic plasticizer owing to its higher energy content compared to NG, although it is more sensitive to impact. Research suggests that incorporating functional groups such as -NH₂ or -CH₃ into energetic compounds may improve their safety profile [17,18]. Indeed, DEGDN is characterized by its ability to

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form homogeneous matrices with NC through hydrogen bonding and electrostatic interactions, making it an attractive option for improving the performance of energetic formulations. Propellants containing DEGDN can operate effectively at lower temperatures while achieving reduced barrel erosion compared to traditional formulations containing NG [19,20].

Nitrocellulose is known to be the most dominant cellulose-based energetic polymer due to its favorable mechanical properties, excellent energetic performance, and compatibility with many other substances [21–23]. However, conventional NC suffers from several shortcomings, such as high shock sensitivity and low combustion efficiency [24,25]. These drawbacks have motivated researchers to explore other cellulose-based energetic polymers that would offer a reasonable compromise between mechanical reactivity, thermal stability, and energy density [26,27]. Our research team has recently focused on synthesizing and evaluating new cellulose-based energetic materials through structural modification and chemical functionalization of cellulose precursors. This is because the molecular structure of cellulose is characterized by a high density of hydroxyl groups (OH), known for their high reactivity. This reactivity allows the introduction of different functional groups, helping to design modified biopolymers with specific performance criteria [28,29]. In this context, carbamated microcrystalline cellulose nitrate (M3CN) is noteworthy as a novel energetic polysaccharide with improved physicochemical properties, increased heats of combustion, and superior energetic performance over conventional NC [27].

The primary objective of this investigation was to elucidate the influence of AP on the properties and thermokinetic decomposition behaviour of the M3CN/DEGDN energetic composite. First, the AP@M3CN/DEGDN formulation was optimised using NASA-CEA software to calculate its specific impulse, which is a critical performance metric for energetic materials. A combination of analytical techniques were used to characterise the optimised composite, including SEM, FTIR and electronic densimetry. These techniques provided insight into the morphological, chemical and density properties of the elaborated energetic composite. The thermal properties were assessed by TGA and DSC, which provided a comprehensive understanding of the thermal stability and degradation behavior. In addition, isoconversion kinetic methods were used to predict the kinetic triplet associated with the decomposition process, including activation energy, pre-exponential factor and the most appropriate reaction model. This approach aims to provide a thorough understanding of how AP affects not only the physical and chemical properties, but also the thermal behavior of M3CN/DEGDN composite, thereby contributing to the development of advanced energetic formulations with improved performance characteristics.

2. Experimental and methods

2.1. Materials

Ammonium perchlorate with a mean diameter of 200 μm was acquired from Prolabo and utilized without further purification. M3CN and DEGDN were synthesized by our research group at EMLab, following the procedures outlined in our previous publications [28,30]. All chemicals were utilized without additional purification.

2.2. Optimisation and preparation of the energetic composite AP@M3CN/DEGDN

The optimization of the AP@M3CN/DEGDN energetic mixture was performed using NASA-CEA2 software, adjusting the mass proportions of the ingredients to maximize the specific impulse (I_{sp}), a critical parameter for enhancing rocket efficiency. The NASA-CEA2 calculations were conducted under controlled conditions, including an initial chamber pressure of 7 MPa, a nozzle expansion ratio (A_e/A_t) of 10,

an estimated combustion temperature of 3800 K, and an initial reactant temperature of 298 K. These parameters were carefully selected to ensure accurate modeling of the combustion process and to optimize the propellant formulation's thermodynamic and performance characteristics [31]. The optimum proportion obtained from the ternary diagram in Fig. 1(c) for the AP@M3CN/DEGDN formulation is (40:20:40) wt.%. The preparation procedure of the energetic mixture is shown in Fig. 1(a). It consists of a progressive dissolution of the nitro-modified polymer in an acetone solution. Then, DEGDN is incorporated while stirring the mixture. Finally, the oxidizer is added in small quantities to the M3CN/DEGDN matrix, with continuous mixing for 30 mins. This method ensures optimal homogeneity of the mixture, essential to maximize the energetic performance of the composite [32]. Fig. 1(b) illustrates an initial evaluation of the hydrogen bonding interactions in the system. Specifically, it highlights the interaction between the negatively charged nitro group of DEGDN or M3CN and the positively charged hydrogen atom of AP, as well as the interaction between the negatively charged oxygen atom of the oxidizer and the hydrogen atom of the carbamate group within the modified nitrated cellulosic matrix. These interactions play a crucial role in determining the structural and energetic properties of the composite material.

2.3. Measurements

The optimal formulation of the AP@M3CN/DEGDN composite, as well as the M3CN/DEGDN matrix, was determined using NASA-CEA2 software to maximize the specific impulse while ensuring the formulation's feasibility in terms of the maximum acceptable percentage for a modified double-base composite. FTIR analysis using Perkin Elmer Spectrum Two instrument, with 32 scans conducted at a resolution of 4 cm^{-1} were recorded in transmittance mode over a wavenumber range of 4000–400 cm^{-1} to highlight the impact of adding AP on the chemical structure of M3CN/DEGDN. The morphological features were examined using an FEI Helios G3 UC scanning electron microscope (SEM), operating at a working distance of approximately 12 mm and an accelerating voltage of 12.5 kV. The thermal behavior of the composites was analyzed using differential scanning calorimetry (DSC, Perkin Elmer DSC8000) at various heating rates of 5 $^{\circ}\text{C}/\text{min}$, 10 $^{\circ}\text{C}/\text{min}$, 15 $^{\circ}\text{C}/\text{min}$, and 20 $^{\circ}\text{C}/\text{min}$ and thermogravimetry (TGA, TGA8000) from room temperature to 500 $^{\circ}\text{C}$ under a nitrogen purge at a flow rate of 50 mL/min . The combustion energies released by the elaborated energetic composites were measured using a Parr 6200 bomb calorimeter under constant volume conditions. The measurements were conducted in a high-purity oxygen (O_2) atmosphere at a pressure of 30 bar, ensuring complete oxidation of the samples and accurate quantification of energy release. Standard experimental protocols were meticulously followed to ensure the reproducibility and reliability of the obtained data. For a more profound understanding of the thermal stability and reactivity of the prepared energetic composites, the thermokinetic parameters, including activation energy (E_a), pre-exponential factor ($\log(A)$), and integral reaction model $g(\alpha)$, were determined using isoconversional kinetic approaches. Following the guidelines of the International Confederation for Thermal Analysis and Calorimetry (ICTAC), non-isothermal DSC data were analyzed for both M3CN/DEGDN and AP@M3CN/DEGDN composites. The linear isoconversion methods used included Trache-Abdelaziz-Siwani (TAS) [33], iterative Kissinger-Akahira-Sunose (it-KAS) [34], iterative Flynn-Wall-Ozawa (it-FWO) [35], and the non-linear Vyazovkin combined with compensation effect (VYA/CE) [36]. These methods allowed the assessment of how the kinetic triplet varies with the degree of reaction conversion (α). The conversion rate was calculated using Eq. (1), which indicates that temperature is the single variable affecting the reaction rate [7,37].

$$\frac{d\alpha}{dT} = \frac{A_a}{\beta} e^{\left(\frac{-E_a}{RT}\right)} f(\alpha) \quad (1)$$

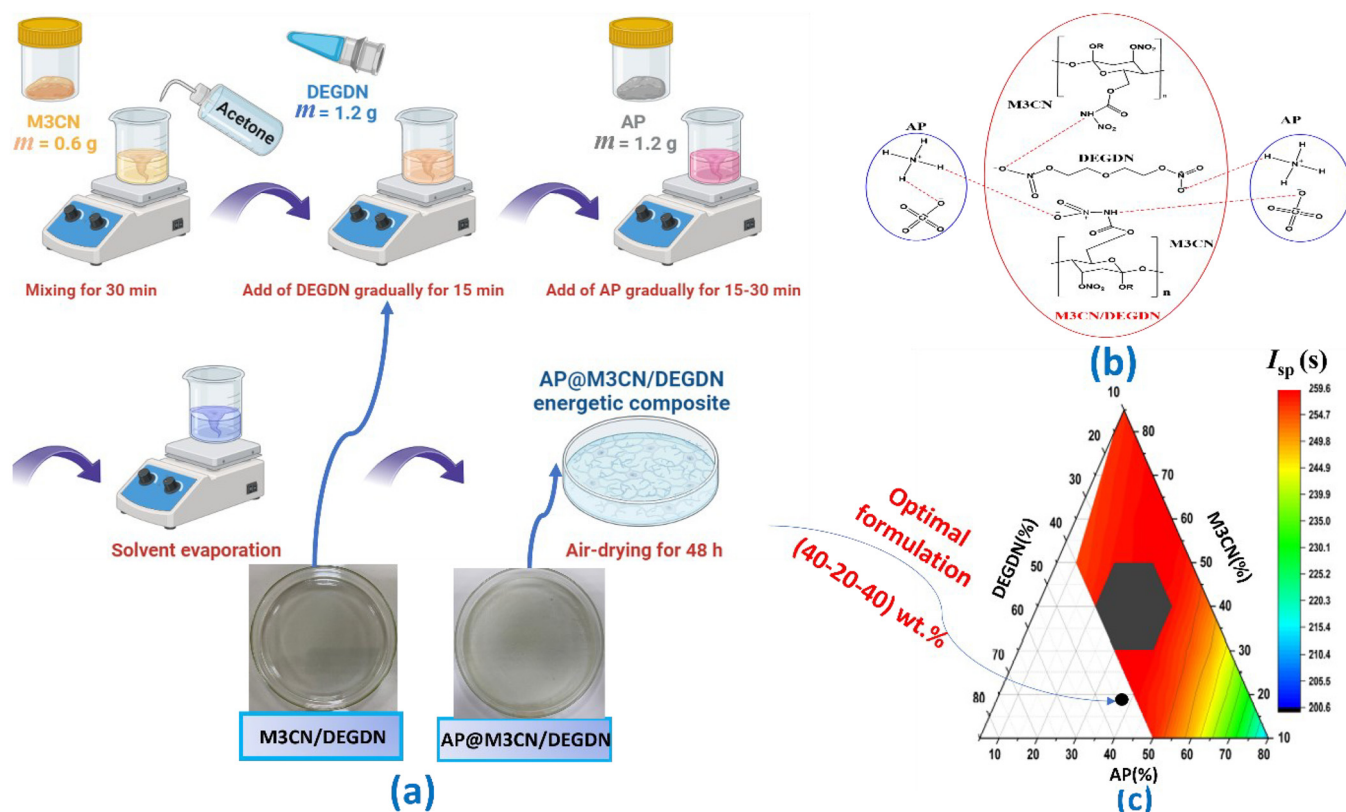


Fig. 1. (a) Illustration of the synthetic procedure for the preparation of AP@M3CN/DEGDN and M3CN/DEGDN composites as well as digital images of the elaborated energetic composites. (b) Molecular structure of the energetic formulation. (c) Evolution of the specific impulse as a function of the mass fractions of the ingredients in AP@M3CN-DEGDN formulations.

where t refers to time, T to temperature, α to the extent of conversion, and $f(\alpha)$ to the reaction mechanism. A_a represents the pre-exponential factor in s^{-1} .

Eq. (2) shows the independence between the Arrhenius parameters and the reaction model [38].

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A_a}{\beta} \int_{T_0}^T e^{-E_a/RT} dT \quad (2)$$

$g(\alpha)$ term presents the reaction model. E_a is the activation energy in kJ/mol, and R is the universal gas constant in J/(mol·K).

DSC curves may be exploited to determine the conversion values, which have a maximum value of $\alpha = 1$.

In the case of DSC data, the conversion α which have a maximum value of $\alpha = 1$ is defined as the fraction of the current heat change ΔH to the total reaction enthalpy ΔH_{total} [30,39].

$$\alpha = \frac{\int_{t_0}^t (dH/dt) dt}{\int_{t_0}^{t_f} (dH/dt) dt} = \frac{\Delta H}{\Delta H_{total}} \quad (3)$$

3. Results and discussion

3.1. Morphological and structural results

The energetic AP@M3CN/DEGDN composite was developed to assess the impact of the AP oxidizer on the microstructure and morphology of the double-base M3CN/DEGDN matrix. This analysis was conducted using SEM and FTIR, as illustrated in Fig. 2. As can be seen from

Fig. 2(a), the double-base film without AP exhibits a smooth and uniform surface due to efficient dissolution and excellent mixing compatibility between the modified cellulosic chains and the energetic plasticizer in M3CN/DEGDN, resulting in a dense matrix. The sheet structure, likely due to DEGDN, shows some cavities from solvent evaporation and a few M3CN aggregates from strong intermolecular interactions. The introduction of AP microparticles into M3CN/DEGDN, as shown in Fig. 2(b), alters the initial smooth surface structure. These microparticles are either uniformly integrated into the matrix or present in surface layers, similar to conventional propellants. This effective dispersion enhances interfacial contact between the ingredients, thereby improving the thermal and energetic performance of the composite, as will be demonstrated in the subsequent sections. In addition, to evaluate the performance of energetic materials, density is a critical parameter that must be accurately measured. Recent trends indicate that higher densities correlate with improved energy performance and higher burn rates. In this study, we performed ten analyses per sample using an Accupyc 1340 II densimeter to determine the average density and standard deviation of various formulations. The addition of AP into the M3CN/DEGDN film has significantly increased its density to $1.6385 \pm 0.004 \text{ g/cm}^3$, as compared to the M3CN/DEGDN formulation alone, which had a density of $1.4860 \pm 0.001 \text{ g/cm}^3$. It is expected that with this increase in density, the performance characteristics of the developed AP@M3CN/DEGDN composite will also improve. Besides, the experimental densities agreed with their theoretical values, which are 1.6790 g/cm^3 for AP@M3CN/DEGDN and 1.4950 g/cm^3 for M3CN/DEGDN. Such observations mean that the open porosity of the prepared energetic composites is minimal, showing high loading capacity for the M3CN/DEGDN formulation. These results are in good agreement with

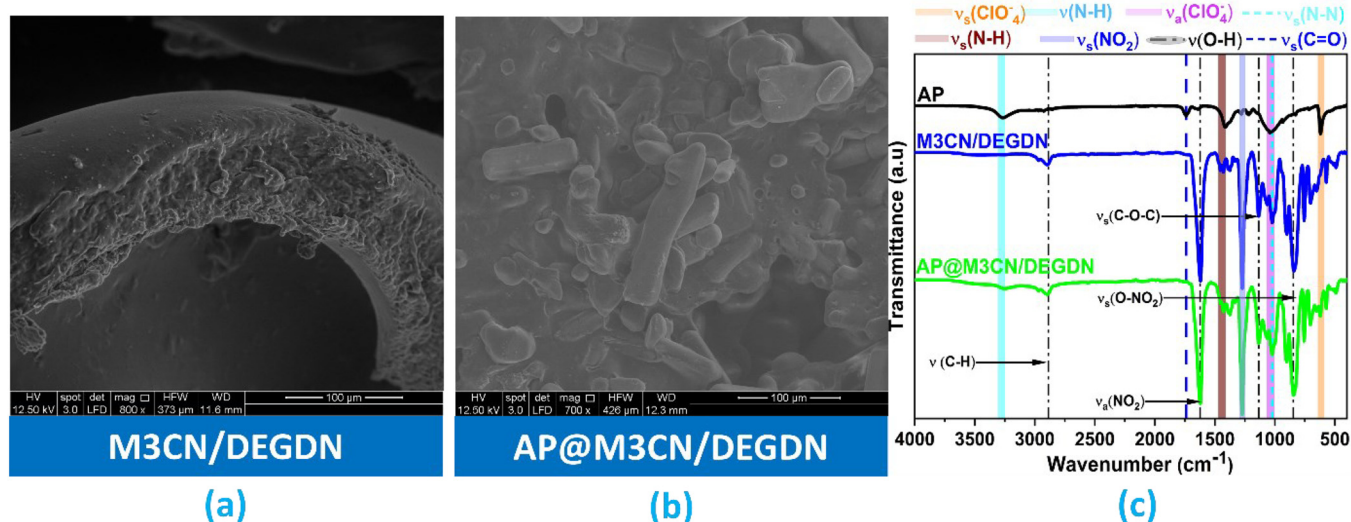


Fig. 2. (a) and (b) SEM micrographs of the investigated energetic composites. (c) FTIR spectra of AP, M3CN/DEGDN and their composite.

the observations of SEM and further, confirm the benefit of using AP oxidizer as an additive in double base propellant for advanced applications. On the other hand, FTIR measurements were conducted to analyze the molecular structure of M3CN/DEGDN and AP@M3CN/DEGDN composite films, as shown in Fig. 2(c). Both formulations exhibit absorption peaks in the ranges of 2855–2935 cm⁻¹, 1620 cm⁻¹, 1270 cm⁻¹, 1132 cm⁻¹, and 840 cm⁻¹. These bands correspond to the stretching vibrations of -C-H_n groups, asymmetric vibrations of the N-O bond in -O-NO₂, symmetric stretching of -NO₂, stretching vibrations of C-O-C bonds, and twisting vibrations of O-NO₂ found in M3CN and DEGDN samples [40–43]. Additionally, a broad peak between 3300 cm⁻¹ and 3500 cm⁻¹ is attributed to -OH group stretching vibrations. After the addition of AP, new peaks were observed, including the stretching vibrations at 620 cm⁻¹ and 1040 cm⁻¹, corresponding to ClO₄⁻, as well as the bending and stretching vibration peaks at 3260 cm⁻¹, attributed to N-H bonds [27,44].

3.2. TGA/DTG results

The TGA/DTG experiments of the prepared energetic composites were conducted at $\beta = 10$ °C/min to investigate the thermal decomposition and mass loss. As illustrated in Fig. 3(a), the composite M3CN/DEGDN exhibited two distinct mass loss events at 124.2 °C and 197.4 °C, corresponding to mass losses of 43.5% and 47.5%, respectively. The first event is attributed to the moisture evaporation and the partial volatilization of the plasticizer, while the second one is attributed to the decomposition of the nitric ester groups within the double base M3CN/DEGDN matrix [41,45]. This decomposition process releases nitrogen oxides (N_xO_y) and carbon dioxide (CO₂), consistent with findings from previous studies employing hyphenated TGA-FTIR on analogous nitrate esters-based composites [46]. It can be also revealed from Fig. 3(b) that AP@M3CN/DEGDN composite presents distinct stages of mass loss occurring at maximum peak temperatures of 116.1 °C, 182.5 °C, 206.5 °C, and 277.8 °C, corresponding to mass losses of 26.5%, 29%, 18.5%, and 26%, respectively. The first stage corresponds to the volatilization of DEGDN, while the second stage reflects the decomposition of nitrate ester groups within the NC/DEGDN matrix. The third stage represents the low-temperature decomposition (LTD), and the fourth stage involves the high-temperature decomposition (HTD) of ammonium perchlorate, leading to the release of gaseous products such as H₂O, O₂, Cl₂, and N₂O. These findings are consistent with previous reports, which highlights the sequential thermal degrada-

tion behavior of the system [34,47]. It is noteworthy that upon reaching 500 °C, both M3CN/DEGDN and AP@M3CN/DEGDN composites exhibit a significant mass loss of approximately 90% of their initial weight. Beyond this temperature, no further thermal events or mass loss were recorded up to 800 °C; consequently, data collected beyond 500 °C have been excluded from this study.

3.3. DSC findings

To further elucidate the impact of AP on the thermal decomposition reactivity and energy output of the M3CN/DEGDN energetic double-base, a thermal study was conducted at varying heating rates, complemented by calorimetric tests. As illustrated in Fig. 3(c), which corresponds to the double-base M3CN/DEGDN system, a single exothermic decomposition peak is observed at 193.2 °C at a heating rate of 10 °C/min. This peak indicates a single-step decomposition process primarily associated with the cleavage of nitrate ester and nitrocarbamate functional groups. In contrast, the modified double-base AP@M3CN/DEGDN composite, as shown in Fig. 3(d), exhibits a more complex thermal decomposition profile characterized by three distinct exothermic peaks. The first peak at 182.5 °C corresponds to the decomposition of nitric ester and nitrocarbamate groups. The second and third exothermic peaks, observed at 257.3 °C and 339.6 °C, are associated with the LTD and high-temperature HTD decomposition processes, respectively. Furthermore, a minor endothermic peak is detected at approximately 237 °C, signifying the allotropic transition of ammonium perchlorate from its orthorhombic to cubic phase [48]. Due to the limitations of DSC and the small mass of energetic materials used in the analysis, the initial DTG peak is not detectable in the DSC measurements. Additionally, the thermal decomposition parameters of the investigated energetic composites, including the T_{onset} , peak temperature T_{peak} , and reaction enthalpy (ΔH), were analyzed using DSC measurements processed with Pyris software. The resulting data are summarized in Table 1. The analysis reveals a significant shift in decomposition temperatures and a reduction in peak widths for the AP@M3CN/DEGDN composite compared to the baseline M3CN/DEGDN. This behavior is primarily attributed to the catalytic effect of AP on the decomposition of the M3CN/DEGDN matrix, driven by the presence of chlorine ions in the oxidizer, which enhance the overall reactivity of the system [49]. The observed decrease in peak intensity for each decomposition event can be linked to gas confinement resulting from intimate contact between components and reduced heat transfer distances. In contrast, the total heat

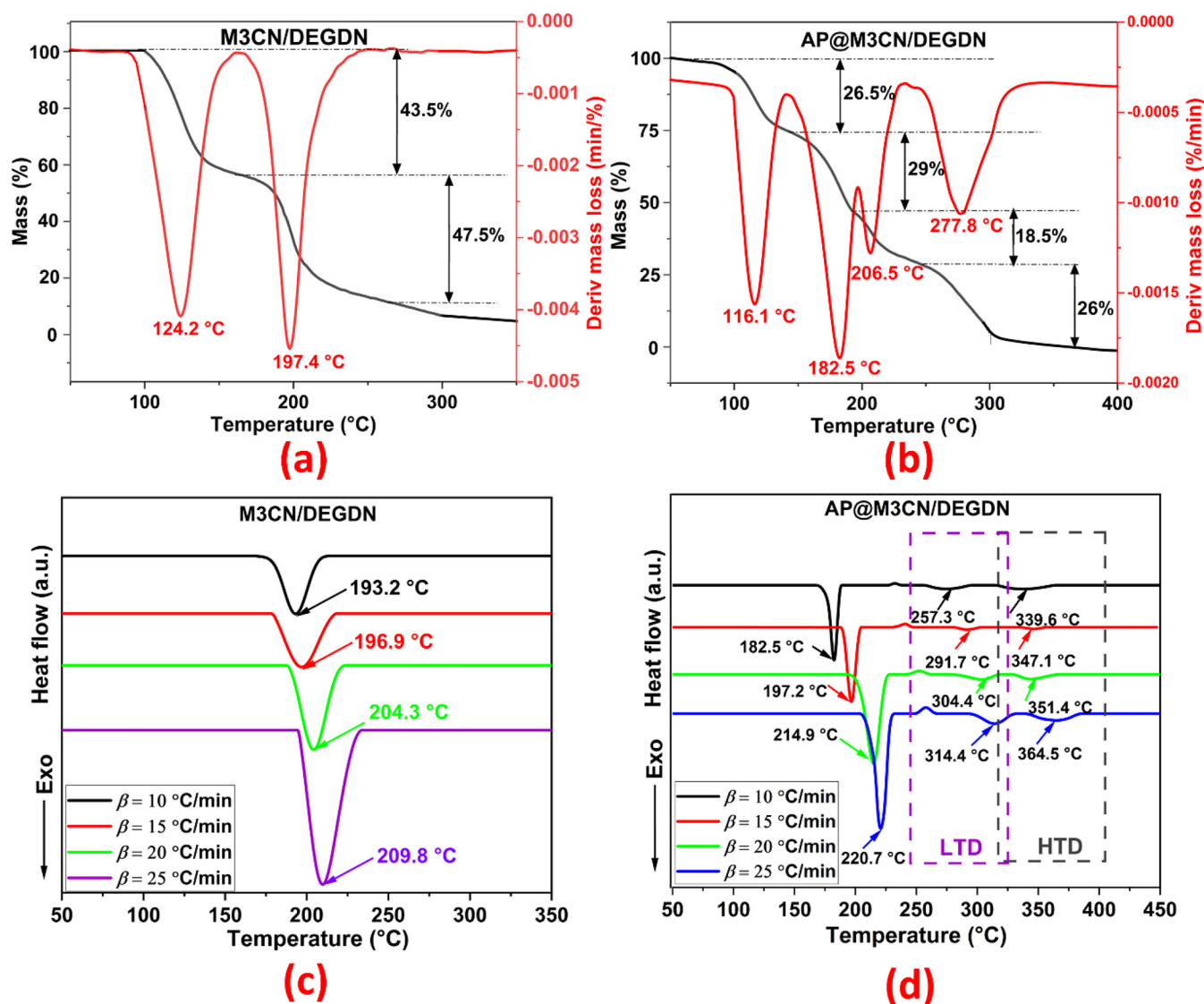


Fig. 3. (a)-(b) TGA/DTG thermograms of the elaborated energetic formulations at $\beta = 10$ °C/min. (c)-(d) DSC thermograms of M3CN/DEGDN and AP@M3CN/DEGDN composites at different heating rates.

release during the decomposition of the AP@M3CN/DEGDN composite (2245.3 J/g) is notably higher than that of the baseline M3CN/DEGDN formulation (1903.2 J/g). Moreover, it is clear from Fig. 4 that the combustion heat of the AP@M3CN/DEGDN composite surpasses that of the M3CN/DEGDN composite by 2632.57 J/g, clearly demonstrating that the incorporation of ammonium perchlorate significantly enhances the energetic performance of the composite.

3.4. Determination of the kinetic parameters

The thermal behavior and decomposition mechanisms of energetic materials, particularly nitrate ester-based composites, require comprehensive investigation due to their susceptibility to hazardous thermal runaway reactions. This phenomenon requires careful treatment of the critical parameters that influence thermal stability. Therefore, the decomposition temperatures obtained from the DSC and TGA data in the previous section (Table 1) should not be relied upon alone to assess the complexity of thermal stability in these prepared energetic formulations (M3CN/DEGDN and AP@M3CN/DEGDN). Instead, a comprehensive thermokinetic study is essential to complement these results to understand the underlying mechanisms and ensure safe application in

propulsion systems to provide a more accurate assessment of the thermal properties of these materials. In this study, the kinetic parameters for the thermal decomposition of the investigated composites were determined using advanced isoconversional methods, including the Trache-Abdelaziz-Siwani method, iterative Kissinger-Akahira-Sunose method, iterative Flynn-Wall-Ozawa method, and Vyazovkin's non-linear approach integrated with the compensation effect. The results, displayed in Fig. 5, show a strong correlation between the activation energy (E_a) and the pre-exponential factor ($\log(A)$) across all methods, with a relative deviation of < 10%. This consistency confirms the reliability of the calculations, supported by a regression coefficient exceeding 0.9991 for the linear methods. Additionally, the standard deviation of activation energy values remains within the recommended limits set by ICTAC (< 30%) [51,52]. The observed trends in E_a and $\log(A)$ as a function of conversion extent reflect a compensation effect during decomposition [36]. As shown in Fig. 5, the thermokinetic behavior of the M3CN/DEGDN baseline follows a single pathway characterized by its own activation energy and pre-exponential factor. The apparent activation energy is approximately 139.8 kJ/mol, corresponding to the primary homolytic cleavage of the O-NO₂ and N-NO₂ explosophoric groups within the M3CN/DEGDN matrix. As the conversion rate increases, the E_a values increase until they reach $0.02 < \alpha < 0.55$, where they stabilize around

Table 1
Thermal Characteristics of the studied samples derived from DSC analysis at a heating rate of 10 °C/min.

Sample	1st decomposition stage			LTD stage			HTD stage			Total heat release	
	T_{onset} (°C)	T_{peak} (°C)	ΔH (J/g)	T_{onset} (°C)	T_{peak} (°C)	ΔH (J/g)	T_{onset} (°C)	T_{peak} (°C)	ΔH (J/g)	ΔH_T (J/g)	
M3CN [28]	189.8	196.4	1902.4	/	/	/	/	/	/	1902.4	
AP [50]	/	/	/	318.2	335.4	61.0	408.9	432.9	356.2	417.2	
M3CN/ DEGDN (33.33 – 66.67)	173.5	193.2	1903.2	/	/	/	/	/	/	1903.2	
wt.%											
AP@M3CN/DEGDN (40 - 20 - 40)	170.1	182.5	1594.9	257.3	274.5	291.7	315.9	339.6	358.7	2245.3	
wt.%											

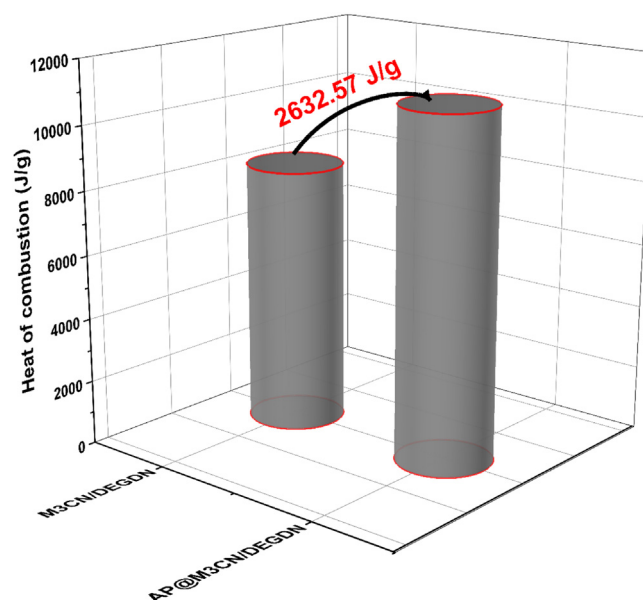


Fig. 4. Combustion energy of the as-prepared energetic composites.

146.5 kJ/mol at $\alpha = 0.6$. This behavior indicates that thermolysis is faster in the initial stages ($\alpha \leq 0.6$) and slower at higher conversions. It can be also revealed from Fig. 5 that the AP@M3CN/DEGDN composite undergoes a three-stage degradation process. The first two stages show moderate changes in the Arrhenius parameters, while the third stage shows a significant increase in the activation energy (E_a) with the degree of conversion (α). During the first decomposition event, E_a decreases from 118 kJ/mol at $\alpha = 0.08$ to its lowest value of 90 kJ/mol at $\alpha = 0.98$. This trend is practically a simple one-step process associated with the homolytic cleavage of nitrate ester groups. Incorporating ammonium perchlorate (AP) into the formulation reduces the activation energy (E_a) of the first decomposition step by approximately 25%, emphasizing its catalytic effect on the thermolysis of nitrate esters. This catalytic influence improves heat and mass transfer within the nitrated ester groups, thereby accelerating their decomposition, as corroborated by the DSC thermal results. Similar findings have been reported in previous studies conducted by Chen et al., Li et al. [48], and Jain et al. [53–55]. Furthermore, the average activation energies for the second and third decomposition steps of AP@M3CN/DEGDN, as presented in Fig. 5 and Table 2, correspond to LTD at $E_a = 111.4$ kJ/mol and HTD at $E_a = 212.4$ kJ/mol. These values are notably lower than those reported for pure AP, highlighting the synergistic catalytic effect between AP and the nitrate esters in the double-base M3CN/DEGDN composite. This observation demonstrates the reciprocal catalytic interactions within the components of the as-prepared energetic composite, enhancing its thermal reactivity and decomposition efficiency.

The theoretical mechanism $g(\alpha)$ was also calculated using the TAS, it-KAS, and it-FWO approaches described in Table 2. Since the nonlinear Vyazovkin method does not allow the direct calculation for the theoretical model, its combination with the VYA/CE compensation effect permitted the calculation of numerical values related to $g(\alpha)$. As shown in Fig. 5 and Table 2, the thermolysis of the M3CN/DEGDN composite follows a G_8 mechanism based on the TAS approach, while the it-KAS and it-FWO models suggest an A_2 random nucleation process. However, upon incorporating AP into the formulation, the decomposition reaction model of the M3CN/DEGDN matrix transitions to a nucleation (power law) mechanism, described as $P_{1/4}$, $P_{1/3}$, and $P_{1/3}$ for TAS, it-KAS, and it-FWO, respectively. This shift indicates that the addition of AP alters the reaction pathway, moving from sigmoidal rate equations or random nucleation with subsequent growth to a class of acceleratory rate equations. This transformation highlights the significant impact of AP on

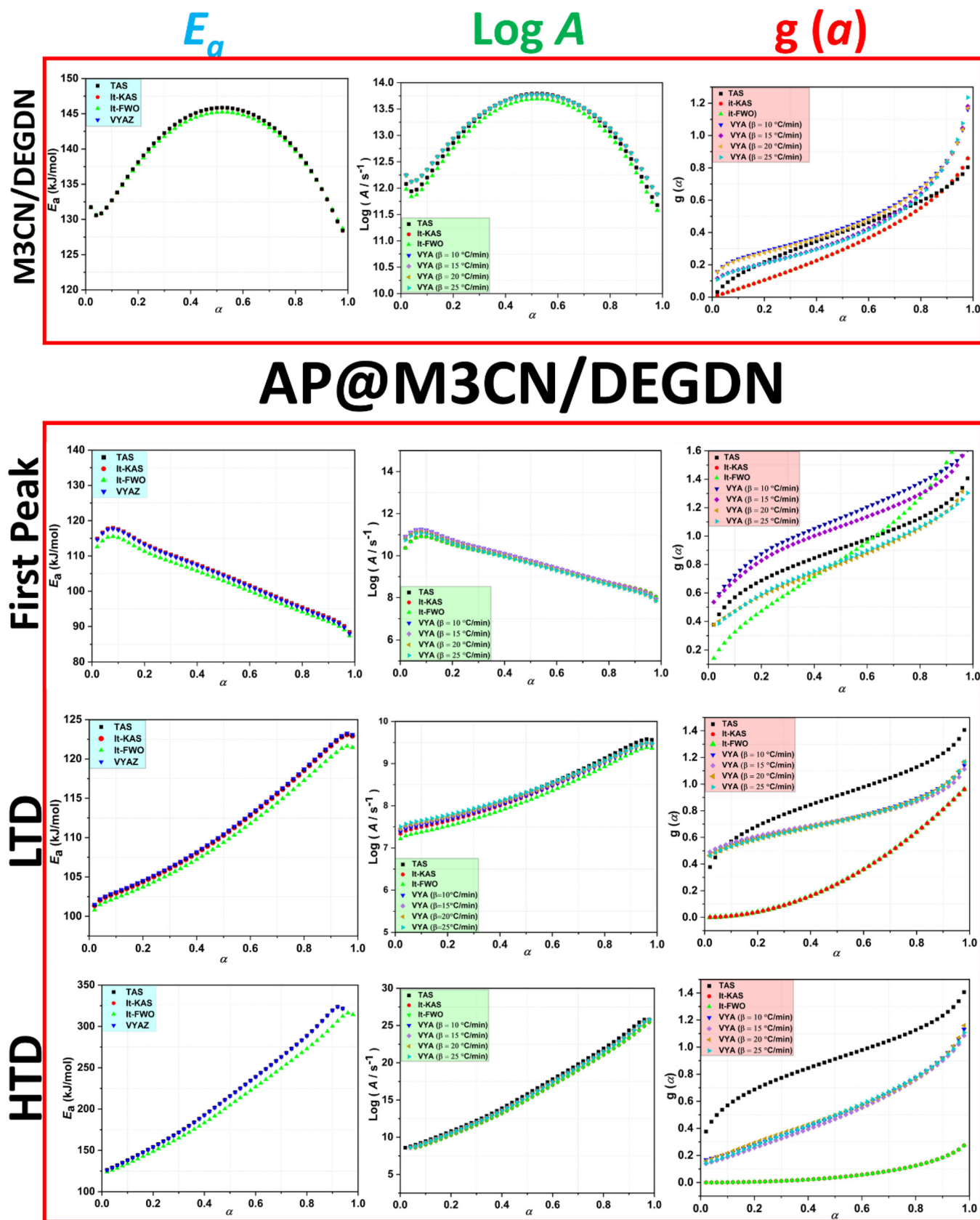


Fig. 5. Variation of the kinetic triplet of M3CN/DEGDN and AP@M3CN/DEGDN as a function of the conversion α .

Table 2

Kinetic parameters for the thermal decomposition of the as-prepared composites.

Sample	Isoconversional method	E_a (kJ/mol)	$\text{Log}(A \text{ (s}^{-1}\text{)})$	$g(\alpha)$	
M3CN/DEGDN	TAS	139.8 ± 14.5	13.2 ± 1.1	$G_8 = [1 - (1 - \alpha)^{1/3}]^{1/2}$	
	it-KAS	136.4 ± 14.4	12.9 ± 1.1	$A_2 = [-\ln(1 - \alpha)]^{1/2}$	
	it-FWO	139.8 ± 14.5	13.0 ± 1.1	$A_2 = [-\ln(1 - \alpha)]^{1/2}$	
	VYA/CE	136.4 ± 14.7	$\beta = 10 \text{ }^\circ\text{C/min}$	13.2 ± 1.0	/
			$\beta = 15 \text{ }^\circ\text{C/min}$	13.0 ± 1.0	/
			$\beta = 20 \text{ }^\circ\text{C/min}$	13.2 ± 1.0	/
$\beta = 25 \text{ }^\circ\text{C/min}$			13.0 ± 1.0	/	
AP@M3CN/DEGDN 1st decomposition stage	TAS	104.5 ± 7.2	9.7 ± 2.1	$P_{1/4} = \alpha^{1/4}$	
	it-KAS	104.5 ± 7.2	9.6 ± 2.1	$P_{1/3} = \alpha^{1/3}$	
	it-FWO	104.7 ± 7.3	9.8 ± 2.1	$P_{1/3} = \alpha^{1/3}$	
	VYA/CE	104.4 ± 7.5	$\beta = 10 \text{ }^\circ\text{C/min}$	9.7 ± 1.3	/
			$\beta = 15 \text{ }^\circ\text{C/min}$	9.6 ± 1.3	/
			$\beta = 20 \text{ }^\circ\text{C/min}$	9.6 ± 1.3	/
$\beta = 25 \text{ }^\circ\text{C/min}$			9.6 ± 1.3	/	
AP@M3CN/DEGDN LTD	TAS	111.4 ± 8.2	8.4 ± 1.9	$P_{1/4} = \alpha^{1/4}$	
	it-KAS	110.9 ± 8.2	8.3 ± 1.9	$P_2 = \alpha^2$	
	it-FWO	111.3 ± 8.2	8.3 ± 1.9	$P_2 = \alpha^2$	
	VYA/CE	111.3 ± 8.3	$\beta = 10 \text{ }^\circ\text{C/min}$	8.3 ± 1.4	/
			$\beta = 15 \text{ }^\circ\text{C/min}$	8.4 ± 1.4	/
			$\beta = 20 \text{ }^\circ\text{C/min}$	8.4 ± 1.4	/
$\beta = 25 \text{ }^\circ\text{C/min}$			8.3 ± 1.4	/	
AP@M3CN/DEGDN HTD	TAS	212.4 ± 19.9	15.1 ± 1.3	$P_{1/4} = \alpha^{1/4}$	
	it-KAS	212.1 ± 20.1	14.7 ± 1.3	$D_1 = \alpha^2$	
	it-FWO	212.5 ± 20.1	15.2 ± 1.3	$D_1 = \alpha^2$	
	VYA/CE	212.2 ± 17.2	$\beta = 10 \text{ }^\circ\text{C/min}$	15.1 ± 1.4	/
			$\beta = 15 \text{ }^\circ\text{C/min}$	15.3 ± 1.4	/
			$\beta = 20 \text{ }^\circ\text{C/min}$	15.4 ± 1.4	/
$\beta = 25 \text{ }^\circ\text{C/min}$			15.6 ± 1.4	/	

the kinetic behavior of the energetic composite [56]. Additionally, the LTD and HTD decomposition steps of AP follow the $P_{1/4}$ power law nucleation mechanism, as indicated by the TAS model. The reciprocal influence of the energetic matrix M3CN/DEGDN is evident, as it not only reduces the decomposition temperatures of AP but also modifies the activation energy and reaction model, shifting from a D_1 deceleratory rate equation to an acceleratory rate equation. This transformation underscores the catalytic effect of M3CN/DEGDN on AP and highlights the synergistic interaction between the energetic matrix and the oxidizer, enhancing the overall thermolysis efficiency of the composite [57]. Overall, the incorporation of AP effectively reduces the activation energy due to its catalytic influence, thereby enhancing the reactivity of the dual biopolymer-AP composite. This improvement highlights the potential of this energetic composite as a highly promising material for propulsion applications.

4. Conclusions

This study explores the development of a novel energetic composite utilizing nitrated microcrystalline cellulose carbamate as the biopolymer matrix, diethylene glycol dinitrate as the plasticizer, and ammonium perchlorate as the oxidizer. The energetic mixtures were prepared using a solvent evaporation process and subsequently characterized through various spectroscopic and thermal techniques. The optimum composition of the AP@M3CN/DEGDN formulation was determined to be (40% AP, 20% M3CN, and 40% DEGDN) wt.%. A theoretical performance calculation was carried out using the NASA-CEA2 software for the above composition, balancing high I_{sp} with a significant percentage of AP oxidizer. The choice of this formulation is a compromise between maximum performance and proper integration of the components. FTIR results demonstrated the chemical structure of the elaborated energetic composites, confirming that all characteristic bands of the double-base M3CN/DEGDN remained intact following the incorporation of ammonium perchlorate without altering its structural integrity. Furthermore, thermal findings revealed a significant reciprocal catalytic interaction

between AP and the M3CN/DEGDN matrix. This synergistic effect was demonstrated by a shift in decomposition temperatures to lower values across all stages of thermolysis for the AP@M3CN/DEGDN composite. Additionally, a notable reduction in activation energy and an approximate 18% increase in the total enthalpy released during degradation further highlight the enhanced energetic performance of the composite. Overall, these findings indicate that the AP@M3CN/DEGDN energetic composite demonstrates favorable thermal properties and enhanced reactivity, making it a promising candidate for the development of advanced energetic formulations.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Djallal Trache is an editorial board member for FirePhysChem and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

CRediT authorship contribution statement

Hani Boukeciat: Writing – original draft, Methodology, Investigation, Data curation, Conceptualization. **Ahmed Fouzi Tarchoun:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Conceptualization. **Amir Abdelaziz:** Writing – review & editing, Software, Formal analysis. **Chemseddine Boustila:** Investigation, Data curation. **Aymen Bouhantala:** Investigation, Data curation. **Thomas M. Klapötke:** Writing – review & editing, Visualization. **Djallal Trache:** Writing – review & editing, Validation, Supervision, Project administration.

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