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Ignition mechanism of flammable dust and dust mixtures: An insight through thermogravimetric/differential scanning calorimetry analysis

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Abstract

Understanding flame propagation mechanism and thermal behavior of flammable dusts is of crucial importance, since they strongly affect the flammability and explosion parameters. In a previous work, we found that the volatile point of anthraquinone/nicotinic acid mixtures can be lower than the one of the pure dusts, suggesting a synergistic effect. In this work, thermogravimetric and differential scanning calorimetry analyses of anthraquinone/niacin mixtures were carried out both in open and closed cup, to explain the observed synergistic behavior. FTIR analysis on solid residue and evolved gaseous species showed that the mixtures change compositions during the thermal treatment, without undergoing any chemical transformation. The thermal behavior of dust mixtures reveals the presence of a eutectic point, resulting in a volatiles production at lower temperature and accelerating the flame propagation.

KEYWORDS

dust flammability, process safety, synergistic behavior, TG/DSC analysis

1 | INTRODUCTION

Dust ignition and flame propagation are key issues in the study of industrial dust safety.[1] Powder products, in the form of dust mixtures, are ubiquitous in food, pharmaceutical, wood, polymer, pigment, and dyes industrial production. Prevention and mitigation of accidents potentially resulting from their explosions require the knowledge of flammability and explosion parameters. The understanding of flame propagation mechanism is particularly important, since it strongly affects these parameters. In the literature, the flammability behavior of dusts is defined by the minimum ignition temperature (MIT) and the layer ignition temperature (LIT). These values are generally combined to obtain the maximum allowable surface temperature.

Recently, we measured the temperature at which volatiles are produced from several dusts and dust mixtures generating a flammable vapor mixture, and defined this parameter as volatile point (VP),

which is similar to liquids flash point.[2] We also assessed that VP is much lower than both MIT ad LIT and that it is worth using this value to set out the maximum temperature to avoid ignition. Among available dusts, niacin (also known as nicotinic acid) and anthraquinone were chosen, since they are widely employed in pharmaceutical industries. Furthermore, preliminary studies evidenced a peculiar flammability behavior of anthraquinone/niacin mixtures. Notably, we found that the VP of anthraquinone/niacin mixtures may be lower than the values of the pure dusts (198.5°C for niacin and 194.8°C for anthraquinone), suggesting the presence of a synergistic effect.

VP, LIT, and MIT dramatically affect flame propagation. To initiate flame propagation, the dust has to be heated up to the ignition temperature. In this phase, several competitive phenomena may occur (pyrolysis, melting/boiling, sublimation), with consequent volatiles production and ignition.[3-8] Therefore, the flame propagation mechanism significantly depends on the dust heating process and consequent transformations.

As a consequence, assessing dust behavior on heating is a key issue for characterizing and quantifying the response to flame propagation and ignition phenomena.

Simultaneous thermogravimetric and differential scanning calorimetry (TG/DSC) analysis has been already proposed in the literature to investigate the thermal behavior of some metallic dusts in order to derive information on their flammability/explosion reactivity.[9-11]

Notably, Chen et al. studied the effect of heating rates on TG profiles of aluminum nanopowders prepared by laser heating evaporation to assess the dust reactivity.[9] Jiang et al. related the thermal behavior of superfine polystyrene powders to their explosion characteristics. The TG/DSC results allowed the evaluation of the effect of the dust size on the intrinsic kinetics of the dust combustion.[11]

In this work, our aim is to analyse the thermal behavior of dusts and dust mixtures to gain insight into their physicochemical transformation before ignition and flame propagation. To this end, we performed simultaneous TG/DSC analysis on niacin, anthraquinone and their mixtures. We also carried out FTIR analysis on both bare substances and their mixtures before and after the thermal treatment as well as on evolved gaseous species to study the thermal evolution of the systems.

The investigation of the thermal behavior of pure dusts and their mixtures was crucial to unveil the reasons for the observed synergistic behavior.

2 | MATERIALS AND METHODS

Details on niacin and anthraquinone dusts are given in our previous paper.[2] Briefly, samples (analytical grade reagents) were made by mixtures of niacin (i.e., nicotinic acid) (CAS number: 59-67-6) and anthraquinone (CAS number: 84-65-1) provided by Sigma Aldrich.

The thermal behavior of dusts was assessed by using a TG/DSC TA Instrument Q600SDT. TG and DSC profiles have been recorded simultaneously. Tests were performed both in open platinum crucible and in closed aluminum pan, the latter to investigate the overall process and preventing/reducing the sublimation process.

Briefly, for open cup tests, 3–6 mg sample was placed in the crucible and was heated up to 400°C, with heating rate β = 2.0, 5.0, and 10.0°C/min, to investigate the effect of the heating rate on the position of the peaks. Measurements were performed in both N_2 and airflow (100 ml/min) to assess the influence of different atmospheres. For closed cup tests, a thin layer of sample was put on the bottom of an aluminum pan in order to leave a free space for volatiles. The cup was fitted with a coverlid with a hole in the top to allow pressure to escape. Then, the material was heated up to 400°C with heating rate of 5.0°C/min in nitrogen flow (100 ml/min).

Solid mixtures were prepared by intimately mixing, through grinding, the suitable amount of substances. Pure compounds were niacin (CAS number: 59-67-6) and anthraquinone (CAS number: 84-65-1) provided by Sigma Aldrich.

FTIR spectroscopy analysis was carried out using a Nicolet 5700 FTIR Thermo Fisher Scientific apparatus. FTIR analysis on solid samples was carried out in transmission mode in the range 400–4,000 cm^{-1} using KBr disks prepared by mixing 2 mg of powdered sample and 200 mg of KBr. FTIR spectra were recorded on pure dusts and on the mixtures before, during and after the TG/DSC test to evaluate the chemical/physical transformations.

In order to assess the nature of thermal phenomena recorded by TG/DSC analysis, simultaneous FTIR/TG analysis on evolved gaseous species was carried out through Thermo Scientific TG-IR Module. This was mechanically connected to TG/DSC TA Instrument Q600SDT through a glass-lined stainless-steel transfer line, which was kept at constant temperature (220°C) to avoid any sample condensation. Gaseous samples were detected in a 10 cm pathlength nickel-plated aluminum flow cell (cell volume 22 ml) and through a DTGS detector.

3 | TG/DSC RESULTS

3.1 | Pure dusts

In the following, the results of TG/DSC analysis for niacin and anthraquinone are reported. Measurements were performed in both N_2 and airflow. Three values of the heating rate (β = 2.0; 5.0; and 10.0°C/min) were used to highlight the effect of the temperature increase rate on the position of the peaks.

3.2 | TG/DSC of niacin

We used both N_2 and air purging gas flow to assess the role of the gas nature on the thermal evolution of the investigated systems. Figure S1 shows that no significant differences were recorded between DSC curves obtained in N_2 and air, thus ruling out any possible oxidative processes.

In order assess the effect of the heating rate (β) on the peaks position, TG/DSC profiles were recorded at different heating rates (Figure S2). The peak temperature shifts to higher temperatures with a faster heating rate. Therefore, low heating rates are more suitable for phase change materials scanning during DSC measurements, ensuring thermodynamic equilibrium within the sample.

Figure 1a shows the recorded TG curve and its derivative (dW/dt) for niacin measured under nitrogen flow at β = 2.0°C/min. The corresponding DSC profile is shown in Figure 1b.

Weight loss starts at 150°C (T_{onset}) and, in the corresponding DSC curve, two endothermic peaks are found. In both cases, the peaks occur simultaneously to the weight loss.

A first small peak is found at 180°C, caused by a solid–solid transition already reported in literature.[12] The second peak is observed at 205°C (T_{peak}) and concurrently, the weight loss rapidly drops top zero. These findings suggest that the complete consumption of the niacin sample has occurred after the second endothermic peak. The simultaneous presence of the endothermic peak and of the weight loss suggests that sublimation is preferentially occurring, rather than melting followed by boiling.

Comparing VP (198.5°C), as measured in a previous study,[2] we found that it is higher than the weight loss onset temperature (T_{onset}) and lower than DSC peak temperature (T_{peak}):

$$T_{onset} < VP < T_{peak}$$

Menon et al. performed TG/DSC analysis of niacin at atmospheric conditions under N_2 flow and heating rate 10.0°C/min. They found two peaks in the DTA curve and addressed these peaks to a sublimation and evaporation phenomena, in the range 220–236°C.[13] In the literature, different results were obtained for the niacin sample. The most relevant among them are summarized in Table 1, in terms of temperature range and proposed process accounting for thermal effect.
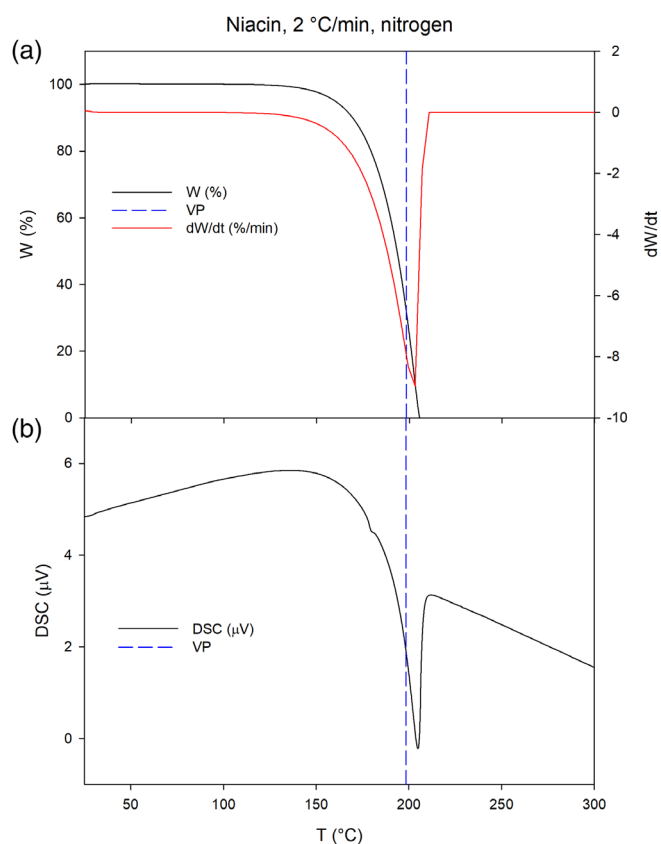
As reported in Table 1, some authors found direct sublimation while others found fusion and then evaporation.[13-16]

In particular, Wang et al. observed a sharply endothermic peak corresponding to the melting of the sample at 237°C. On increasing the temperature, they found another peak temperature at 307°C. They ascribed this peak to evaporation and thermal decomposition of the sample.[15]

In our case, since both measured DSC peaks occur with weight loss in TG curve, they cannot be only ascribed to melting processes.

To assess the presence of sample melting, niacin was heated up to the weight loss onset temperature and then cooled down (Figure S3). During the cooling phase, DSC profile shows an exothermic broad peak, related to the solidification process.

In order to elucidate the nature of the weight loss, FTIR analysis was carried on the produced gaseous phase during the weight loss in TG/DSC apparatus (Figure S4). Recorded FTIR spectrum matches with that of pure niacin, thus confirming that changes in TG/DSC profiles are due to physical phenomena of sublimation and melting/evaporation, occurring in the same temperature range.

3.3 | TG/DSC of anthraquinone

Similar tests were carried out on anthraquinone. Analogously, no differences were appreciated between TG/DSC curves of anthraquinone recorded under N_2 and airflow, respectively (Figure S5). TG/DSC measurements, at different heating rates (β = 2.0; 5.0; and 10.0°C/min) in N_2 flow (Figure S6), showed that the peak temperature shifts to higher temperatures, when increasing the heating rate. TG and DSC curves, as function of temperature measured in nitrogen flow at β = 2.0°C/min, are reported in Figure 2a,b, respectively. The weight loss onset temperature is T_{onset} = 176°C. The main peak is observed at 240°C, which corresponds to the complete consumption of the sample (the weight approaches zero). As in the case of the niacin sample, the VP (194.8°C) falls between the onset temperature and the peak temperature of the weight change.

Contrary to niacin, in this case only one main peak is observed. From the literature, it is found that anthraquinone melting point is equal to 286°C.[17] However, in some cases, at this temperature sublimation was also observed. In the material safety sheet, the boiling point is reported to be equal to 379–381°C.
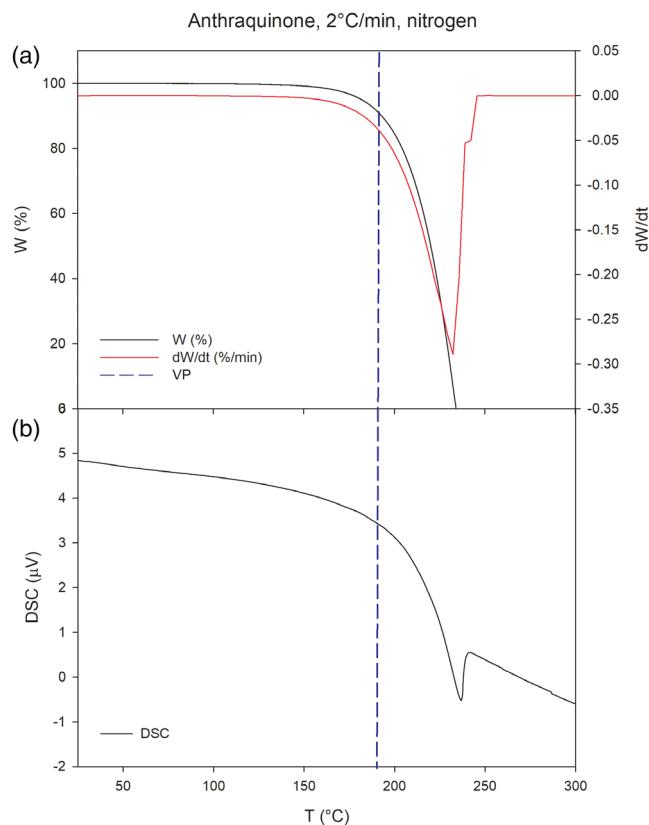

FIGURE 1 Thermogravimetric/differential scanning calorimetry (TG/DSC) results: weight loss (%) and weight derivative (dW/dt) (a) and DSC (b) as function of temperature; niacin, nitrogen flow, β = 2.0°C/min [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 1 Data on TG/DSC results, comparison with the literature values for niacin

°C/min	Flow	Temperature range of thermal phenomena T (°C)	Mechanism phenomenon	Reference
10	N_2	220–236	Dual sublimation and evaporation phase	Menon et al.[13]
2	He	235.2 + 0.2	Sublimation	Volkova et al.[14]
10	N_2	237–307	Fusion-evaporation/decomposition	Wang et al.[15]
		237	Fusion	Allan et al.[16]

Abbreviations: DSC, differential scanning calorimetry; TG, thermogravimetric.

FIGURE 2 Thermogravimetric/differential scanning calorimetry (TG/DSC) results: weight loss (%) and weight derivative (*dW/dt*) (a) and DSC (b) as function of temperature; anthraquinone, nitrogen flow, β = 2.0°C/min [Color figure can be viewed at wileyonlinelibrary.com]
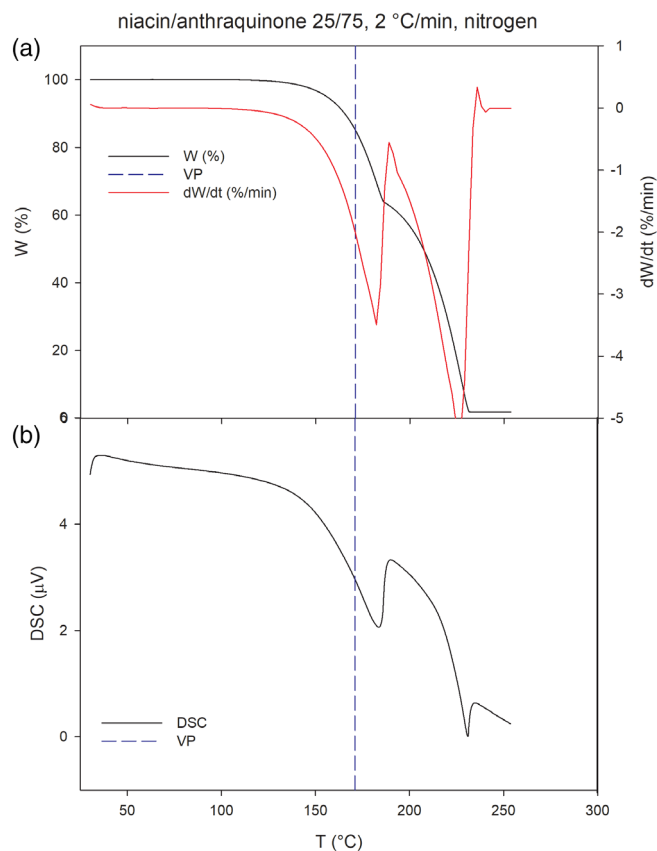

FIGURE 3 Thermogravimetric/differential scanning calorimetry (TG/DSC) results: weight loss (%) and weight derivative (*dW/dt*) (a) and DSC (b) as function of temperature; anthraquinone/niacin (75/25), N_2 flow, β = 2.0°C/min [Color figure can be viewed at wileyonlinelibrary.com]

It is worth noting that the triple point of anthraquinone is equal to 284°C.[18] As a consequence, the phase transition significantly depends on the temperature/pressure values.

3.4 | Dust mixtures

TG/DSC tests on different anthraquinone/niacin mixtures, with niacin content of 25, 50, and 75 wt%, were carried out to investigate the lower observed VP, compared to pure species.

Figure 3 shows TG and weight derivative curves (Figure 3a), and DSC profile (Figure 3b), for a mixture containing 75–25% (wt/wt) anthraquinone/niacin recorded at β = 2.0°C/min, in N_2 flow.

DSC profile shows the presence of two endothermic peaks, which correspond to a weight loss in TG analysis. Peak temperatures for the investigated composition are reported in Table 2. As in the case of pure dusts, the VP (170°C) lies between the onset temperature (145°C) and the peak temperature in *dW/dt* and DSC curve.

Figures S7 and S8 show TG and weight derivative curves, as well as DSC profiles, of 50–50% and 25–75% anthraquinone/niacin mixtures, respectively, recorded at β = 2.0°C/min, in N_2 flow. Measured peak temperatures for the investigated compositions are reported in

Table 2. It is worth noting that the weight loss relative to the first DSC peak corresponds to niacin weight % in each mixture, as driven from Table 2.

The first peak can be ascribed to the niacin phase transition and it shifts towards lower temperatures when adding anthraquinone. Similarly, the second DSC peak, correspondent to anthraquinone phase change, shifts to lower temperatures, when adding niacin. We may then conclude that the mixtures present a lower transition point than pure dusts.

This result agrees with the results on flammability and in particular on the VP results.[2] Notably, it was assessed the mixture niacin/anthraquinone (25/75) had a significantly lower VP (170°C) than pure niacin (198.5°C) and pure anthraquinone (194.8°C).

4 | FTIR SPECTRA

To better understand the nature of the transformations resulting in thermal effects and weight loss during TG/DSC analysis, FTIR spectroscopy was carried out on solid samples before and after the thermal treatment in TG/DSC apparatus up to the first DSC peak, to

check any presence of chemical species due to the decomposition of niacin and/or anthraquinone.

Figure 4 shows the FTIR spectra as measured for the anthraquinone–niacin mixture (75/25% wt/wt) plotted together with the spectra of the pure components. All the characteristic peaks of pure dusts (niacin main peaks = 500; 643; 690; 743; 813; 960; 1,034; 1,320; 1,413; 1,600; 1,700; 1,940; 2,440; 2,830; and 3,070 cm^{-1}; anthraquinone main peaks = 630; 700; 810; 940; 1,170; 1,300; 1,580; and 1,680 cm^{-1}) were found in mixture spectra. We then performed FTIR analysis on the same mixture after TG/DSC run up to the end of the first weight loss in TG curve, in order to assess if it is due to a chemical reaction (pyrolysis) or to a physical change (evaporation/sublimation). Recorded FTIR spectra are shown in Figure 5 in comparison with the spectra of pure anthraquinone and pure niacin. Figure 5 shows that niacin is no longer present in the sample since the FTIR spectrum of treated samples, completely matches with that of pure anthraquinone. Similar behavior was also obtained for 50/50 niacin/anthraquinone mixture, as shown in Figure S9. This result allows addressing the first weight loss and DSC peak to physical phenomena, exclusively involving niacin, that undergoes to melting-evaporation or sublimation in that temperature range. Furthermore, it is worth noting that, in the presence of anthraquinone, the niacin phase transformation occurs at a lower temperature than pure niacin.

TABLE 2 DSC peaks temperatures for anthraquinone/niacin mixtures

Mixtures	First DSC peaks temperatures (°C)	Second DSC peaks temperatures (°C)	VP (°C)^2	First weight loss (%)
Anthraquinone/ niacin 75–25%	185	230	170	25
Anthraquinone/ niacin 50–50%	190	225	175	50
Anthraquinone/ niacin 25–75%	198	214	180	75

Abbreviations: DSC, differential scanning calorimetry; VP, volatile point.

5 | TG/DSC IN CLOSED CUP CONFIGURATION

The TG/DSC curves in an open pan show that the samples undergo endothermic transformation involving weight loss. These results suggest that sublimation and/or evaporation superimposed to melting is occurring. We also found that the VP of pure niacin and anthraquinone, as well as their mixture falls in the temperature range where only physical phenomena (sublimation/melting/evaporation) occur. The TG/DSC curves of investigated anthraquinone/niacin mixtures show that phase change occurs at lower temperature, compared to pure compounds. TG/DSC analysis in closed cup configuration was carried out to discriminate between melting and sublimation processes involving niacin and its mixtures.
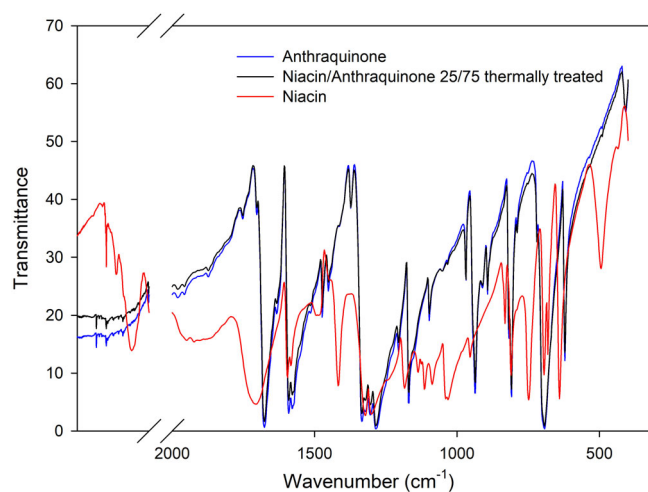

FIGURE 4 FTIR spectra of the anthraquinone–niacin mixture (75/25) in comparison with the pure anthraquinone (a) and pure niacin (b) [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 5 FTIR spectra of the thermal-treated mixture anthraquinone/niacin 75/25 [Color figure can be viewed at wileyonlinelibrary.com]

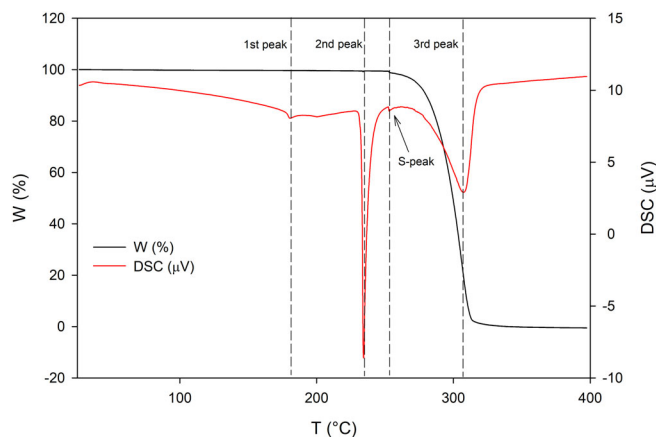**FIGURE 6** Thermogravimetric/differential scanning calorimetry (TG/DSC) niacin, N_2 flow, β = 5.0°C/min; closed cup [Color figure can be viewed at wileyonlinelibrary.com]

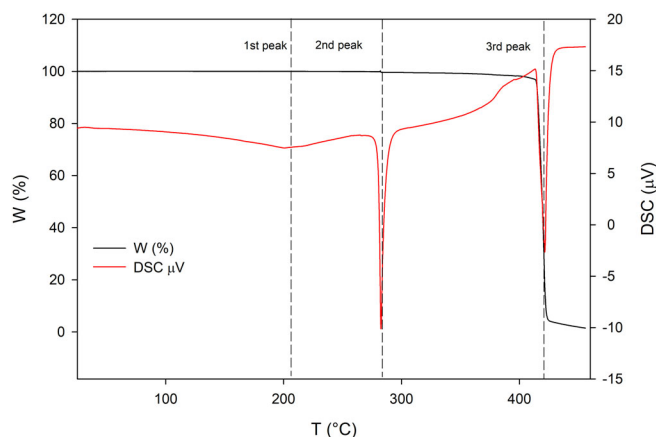**FIGURE 7** Thermogravimetric/differential scanning calorimetry (TG/DSC) anthraquinone, N_2 flow, β = 5.0°C/min; closed cup [Color figure can be viewed at wileyonlinelibrary.com]

Both processes are reported in the literature,[12] but typical range temperatures are not well distinguished. In fact, the nature of phase transitions on heating strictly depends on the partial pressure of the volatile species. In the open cup TG/DSC tests, produced volatiles are rapidly removed from the sample and then, at low partial pressure, sublimation is favored. In closed cup configuration, as detailed in Section 2, the pan was not completely filled with solid and a certain volume was available to host volatiles. This allowed to establish higher vapor pressure and consequently preventing or reducing the sublimation processes. As a result, we could appreciate melting and boiling processes through the evaluation of DSC curves up to the venting of the cup.

Figures 6 and 7 show the TG/DSC curves of pure niacin and pure anthraquinone in closed cup configuration. In the case of niacin, four main peaks are found: the first two peaks, found at 180 and 235°C have no associated weight loss. Accordingly, the first peak can be ascribed to a solid–solid transformation, while the second peak is due to the sample melting.
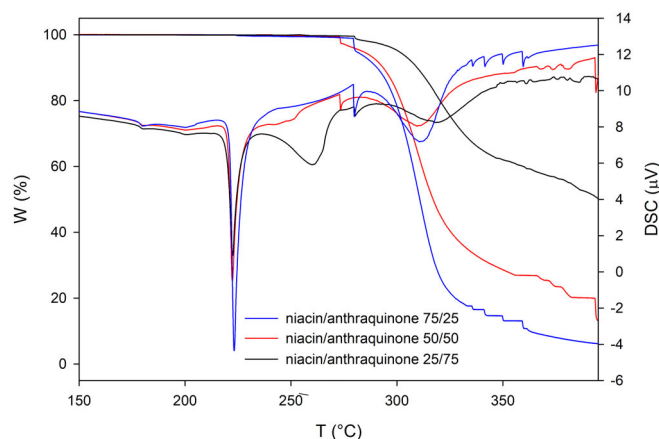

FIGURE 8 Thermogravimetric/differential scanning calorimetry (TG/DSC) anthraquinone/niacin at varying composition, N_2 flow, β = 5.0°C/min, closed cup [Color figure can be viewed at wileyonlinelibrary.com]

After the second peak, a small and sharp peak (S-peak) associated to a sharp weight loss is observed. In closed cup tests, a sharp yet short change in the baseline of both TG and DSC curves was observed (Figures 6, S10, S11, and S12–S14). This effect was named S-peak and was more intense as the content of niacin increased. It does not indicate a real peak, it is not representative of any exothermic/endothermic process, but it can be ascribed to gas venting due to pressure increase as a consequence of evaporation process. The S-peak does not provide any significant information on thermal behavior of investigated substances, therefore it will not be considered in the following. The evaporation/volatilization process terminates at about 310°C (third peak).
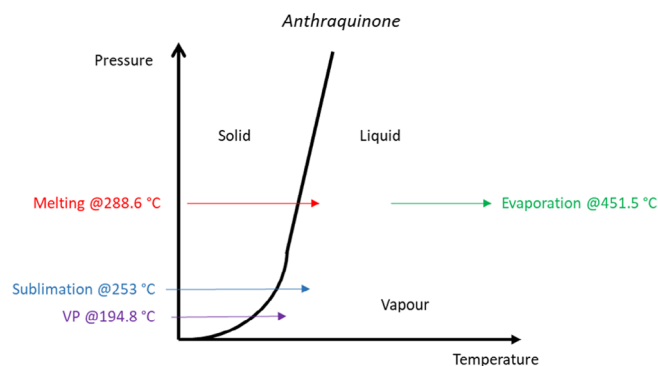
In the case of pure anthraquinone (Figure 7), the S-peak does not appear. Three peaks are observed: the first peak (T = 215°C) due to solid–solid transformation, the second peak (T = 283°C) due to melting, and the third peak (T = 421°C) due to evaporation/volatilization/decomposition processes. Sublimation is prevented by high-pressure values.

In the case of 75/25 (Figure S10) and 50/50 (Figure S11) anthraquinone/niacin mixtures, three peaks are present other than the peak related to the solid/solid transformation for each mixture. In this case, melting occurs in two steps through the first and the second peak. The enthalpy related to these two peaks is about 30 kJ/mol, typical value of fusion processes of niacin and anthraquinone.[16,19] Similar to pure niacin, the S-peak can be ascribed to gas venting due to pressure increase as a consequence of evaporation/volatilization process. That occurs at 310°C, producing the third DSC peak.

Figure S12 shows the TG/DSC curves of the 25/75 anthraquinone/niacin mixture. In this case, melting occurs through only one-step. After melting, the S-peak is observed followed by the evaporation step. In Figures S13 and S14, the TG/DSC curves are shown as obtained of the 90/10 anthraquinone/niacin and 10/90 anthraquinone/niacin mixtures, respectively. In the former case, melting occurs through two steps and after melting, the S-peak is not observed. In

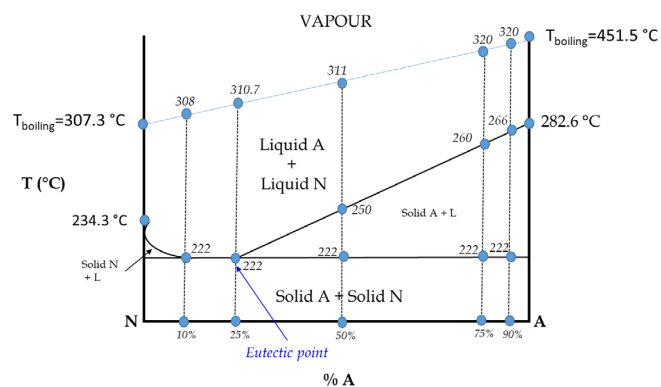**TABLE 3** The peaks temperatures for closed cup tests

Sample	First peak	S-peak	Second peak	Third peak
Niacin	180	265	235	310
Anthraquinone	215	—	283	421
Anthraquinone/niacin 10/90	222	250	—	305
Anthraquinone/niacin 25/75	222	279	—	311
Anthraquinone/niacin 50/50	222	274	250	311
Anthraquinone/niacin 75/25	222	280	260	320
Anthraquinone/niacin 90/10	222	—	266	320
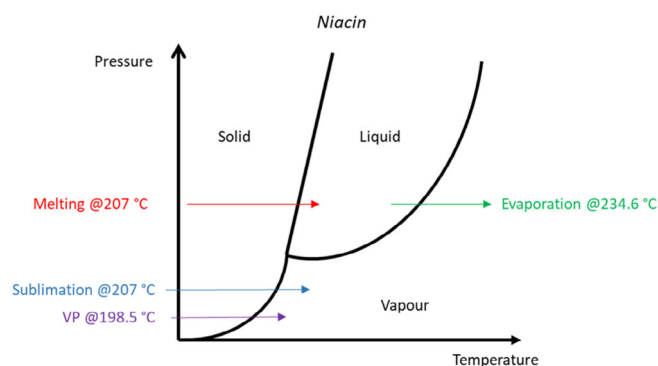
FIGURE 9 State diagram of nicotinic acid (niacin) [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 11 State diagram of mixtures [Color figure can be viewed at wileyonlinelibrary.com]

FIGURE 10 Phase diagram of anthraquinone [Color figure can be viewed at wileyonlinelibrary.com]

the latter, melting occurs through only one-step and the S-peak is observed before a broad peak of evaporation.

The curves correspondent to 75, 50, and 25% of niacin are compared in Figure 8.

It is worth noting that the first peak temperature does not change with the composition of the mixture. Conversely, the second peaks shift at higher temperature, when increasing the anthraquinone content. Table 3 reports the peak temperature of the analyzed samples, in closed cup tests. For pure dusts, the first peak is related to a solid–solid transition, whereas this endothermic effect was almost negligible for mixtures. Surprisingly, the first peak is occurring at the same

temperature for all investigated mixtures (222°C, Figure 8), suggesting that melting occurs always at the same temperature, regardless of the solid composition. To assess that the first peak is due to melting, an anthraquinone/niacin 75/25 sample was heated up to the third peak onset temperature and then cooled down (Figure S15). During the cooling phase, the DSC profile shows an exothermic peak at 222°C, corresponding to the solidification process.

6 | PHASE TRANSFORMATION DIAGRAMS

The performed measurements and the literature data enabled us to identify the possible paths from the solid to the gas state in a phase diagram.

Two main paths are identified: sublimation and melting/evaporation. Sublimation occurs at low pressure (observed in the TG/DSC tests performed at open cup) whereas the melting/evaporation path occurs at high pressure. By merging all the data obtained in closed cup and open cup tests, we may identify the most crucial paths in the phase diagram.

In Figures 9 and 10, the phase diagrams of pure niacin and anthraquinone are shown.

In both diagrams, it is clear that the VP is due to the direct sublimation of the pure dusts.

In the case of the mixtures, we observed complete melting/evaporation of nicotinic acid, whereas anthraquinone remains partially in
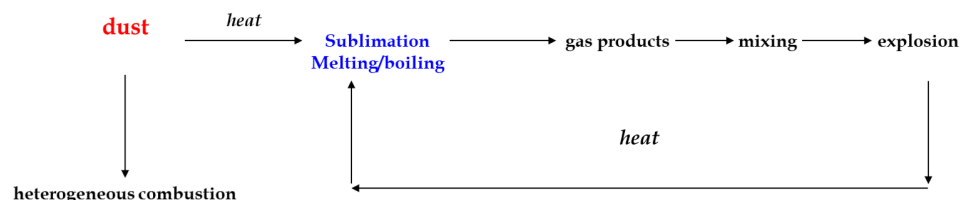
FIGURE 12 Mechanism of flame propagation for niacin, anthraquinone, and their mixtures [Color figure can be viewed at wileyonlinelibrary.com]

the solid phase. Accordingly, we may assume the presence of a eutectic point. Figure 11 shows temperature-concentration phase diagram of the mixture built from DSC data.

7 | DISCUSSION

The presence of a eutectic point justifies lower temperatures at which vapors are formed both by sublimation and by melting/boiling for the investigated solid mixtures. As a result, their VPs are lower than the ones recorded for the pure compounds.

Based on these considerations, the following explosion mechanism can be proposed to investigate pure samples as well as their mixture (Figure 12).

Obtained results contribute to shed light on concurring phenomena leading to volatile formation. In fact, this can be the result of either physical (melting and sublimation/boiling) or chemical processes (pyrolysis). Chemical nature of dusts as well as their storage conditions (pressure and temperature) determines the main volatile formation mechanism.

Notably, in the case of the samples investigated in this work, physical phenomena rather than pyrolysis processes (Figure 12) are responsible for the formation of fuel/air gaseous mixtures inside their flammable region.

Interestingly, TG/DSC measurements suggest that synergy between niacin and anthraquinone, already observed in a recent work,[2] is due to the formation of a eutectic point, thus lowering volatile formation temperature and leading to results very similar to those reported for liquid mixtures.

In that case, it was found that nonideal mixtures with low-boiling azeotrope may have flash points lower than the ones of the pure components. In this case, the intermolecular forces increase the volatility of the mixtures leading to a synergistic behavior.

From these results, we may assert that the flammability behavior of dust mixtures cannot be simply evaluated by measuring the MIT, the LIT, and the VP. A complete scanning of the thermal behavior of dusts and dust mixtures is required in order to gain insight into the mechanisms underlying the physicochemical transformation driving ignition and flame propagation.

8 | CONCLUSIONS

The thermal behavior of the niacin, anthraquinone, and niacin/anthraquinone mixtures has been studied by TG/DSC analysis.

TG/DSC tests were performed at two different conditions: closed and open cup. In the open cup tests, the gas produced are vented away thus reducing the partial pressure of the volatiles formed. A main peak is observed which represents the simultaneous sample melting/evaporation and sublimation.

FTIR analysis show that the sample does not change its chemical nature and that in the case of mixture niacin melts-evaporates/sublimates first and anthraquinone last. It has been found that the mixture may undergo melting-boiling /sublimation at temperature lower than the values of the pure niacin and pure anthraquinone. This result may explain the recent result on the VP of the mixture which was found to be lower than the values of the pure dusts.

In the closed cup tests where sublimation is prevented, we clearly observed melting and evaporation of the sample. However, melting and subsequent boiling also occur in open cup configurations in the same temperature range as sublimation. Competition between these phenomena is strongly influenced by pressure, thus accounting for the great dispersion in experimental data and their interpretation found in previous studies. Melting of the mixtures always occurs at the same temperature (222°C) which is lower than both the pure niacin and pure anthraquinone melting temperature, suggesting the presence of a eutectic point, thus indicating that the mixtures may produce (flammable) volatiles at temperature lower than the pure dusts.

Overall, this study evidences that volatile production can be the result of either physical (melting and sublimation/boiling) or chemical processes (pyrolysis).

In the investigated samples the former are responsible for the formation of fuel/air gaseous mixtures inside their flammable region.

This behavior could be appreciated even in other mixtures; further studies are in progress to address this aspect.

From these results, it may be concluded that in order to characterize the dust as well as mixtures flammability and explosion behavior, a complete thermal scanning is advisable.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.