

Effect of heating rate on the thermal behavior of nitrocellulose

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Abstract In the previous study, it was observed that the stability of nitrocellulose (NC) cannot be determined by thermal analyses such as differential scanning calorimetry (DSC) at heating rates of 1–10 K/min. This was because the thermal curves of NC samples with different stabilities could not be distinguished from one another. In this study, we explain why such thermal analyses cannot be used to evaluate the thermal stability of NC and identify the conditions under which thermal analyses can be used for this purpose. We investigated the effect of heating rate on the thermal behavior of pure NC and NC stabilized with diphenylamine (DPA) or akarditeII (AKII), which is a conventional stabilizer, by using the heat flux calorimeter (C80). At high heating rates (0.2–0.3 K/min), only single exothermic peak was observed in the thermal curves of both pure NC and NC/DPA and the thermal curve of pure NC was practically similar to that of NC/DPA. At low heating rate (0.02 K/min), two exothermic peaks were observed for both pure NC and NC/DPA. The heat amount of the first peak depended on the partial pressure of O₂ in the atmosphere. The first peak in the thermal curve of NC/DPA was slightly suppressed as compared to that of pure NC. These results indicate that the stability of NC probably

depends on the first exothermic peak that represents oxidation of NC by atmospheric O₂. From this, on the thermal analyses at high heating rates, thermal curves of pure NC and NC/DPA could not be distinguished from one another. This is because the decomposition of NC itself occurs in the second exothermic peak before the oxidation of NC by atmospheric O₂ in the first peak, which is attributed to the stability of NC. The results of the thermal analyses under isothermal conditions at 393 K in an O₂ atmosphere revealed that the induction period of NC/DPA and NC/AKII was longer than that of pure NC. From these results, it is speculated that the stability of NC can be evaluated by thermal analyses carried out under O₂-rich conditions at low heating rates.

Keywords Nitric acid ester · Self-ignition · Spontaneous ignition · Thermal stability

Introduction

Nitrocellulose (NC) is widely used as an ingredient in propellants, explosives, fireworks, and gas generators, although it is capable of igniting spontaneously [1, 2]. The tendency of NC to undergo spontaneous ignition has been the cause of serious accidents in the recent years [3].

The mechanism underlying the spontaneous ignition of NC has been investigated extensively. It is widely known that the spontaneous ignition of NC is due to its reaction with NO₂ released by bond scissions, and the hydrolysis of O–NO₂ bond [1, 2]. Recently, we proposed that NO₂ contributes to the initiation process of the spontaneous ignition of NC, and that atmospheric O₂ favors the heat release [4–6]. In order to prevent the spontaneous ignition of NC, stabilizers such as diphenylamine (DPA) and

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akarditeII (AKII) are used in industries. It has been reported that the stabilizer reacts easily with NO_2 generated by bond scission in NC to produce nitro and nitroso derivatives, thereby terminating the exothermic reaction [1, 2, 7, 8]. Moreover, it has been reported that DPA reacts with the other radical species such as alkoxy or peroxy radical as well [9, 10].

The ABEL heat test [11], which is used to estimate the amount of NO_2 in smokeless powders, is a mandatory stability test in Japan. Although this test is simple and extremely useful for the determination of the stability of NC, it has certain disadvantages [12]. For example, since this test is based on visual inspection, results may vary with the analyst. Moreover, the ABEL heat test cannot be used to evaluate the stability of NC under certain conditions [13]. Hence, we concluded that it is preferable to evaluate the stability of NC by NO_2 measurements and other methods such as thermal analyses. However, previous studies [14, 15] have reported that common thermal analyses such as temperature differential scanning calorimetry (DSC) at heating rates of 1–10 K/min cannot be used to evaluate the stability of NC because the thermal curves of NC samples with different stabilities are indistinguishable from one another.

The purpose of this study is to identify the reason for the failure of thermal analyses to evaluate the thermal stability of NC; further, the conditions under which thermal analyses can be used to estimate the stability of NC are presented herein. For this purpose, we assumed that the heating rate at elevated temperatures contributes to the phenomenon. On the basis of this assumption, we investigated the effect of heating rate on the thermal behavior of NC samples with different stabilities.

Experimental

NC in 2-propanol (nitrogen content: 12 mass%; Sigma-Aldrich Corp.) was dried under vacuum at room temperature for 3–4 days. Particles with diameters of 75–106 μm were separated by sieving and again dried under the same conditions for 1–2 days. The NC powder thus obtained was used as the experimental sample. NC/DPA (Sigma-Aldrich Corp.) and NC/AKII (provided by NOF Corp.) were also used. Those additives were used after crushing its particles.

We used 50 mg of pure NC and 50 mg of NC mixed with 1 mg of the stabilizer for the thermal analysis; the samples were placed in a 4-cm³ steel ampoule. The air in the ampoule was removed under vacuum and replaced by dry air or O_2 (Suzuki Shokan Corp., Ltd.). This process was repeated 4–5 times in order to ensure complete replacement of atmospheric air. The sample was then stored in a C80 calorimeter (Setaram Instrumentation) for simultaneous

investigation of the thermal and pressure behaviors of the sample.

Results and discussion

Thermal behavior at high heating rates

The thermal behaviors of pure NC and NC/DPA (2 mass%) were investigated at a heating rate of 0.3 K/min in dry air; the measured heat release temperatures of the samples (436 and 439 K, respectively) did not differ significantly. Moreover, the shapes of the thermal curves obtained for both these samples were very similar, as shown in Fig. 1a. In addition, the pressure behaviors of both NC and NC/DPA were nearly identical, as shown in Fig. 1b. As

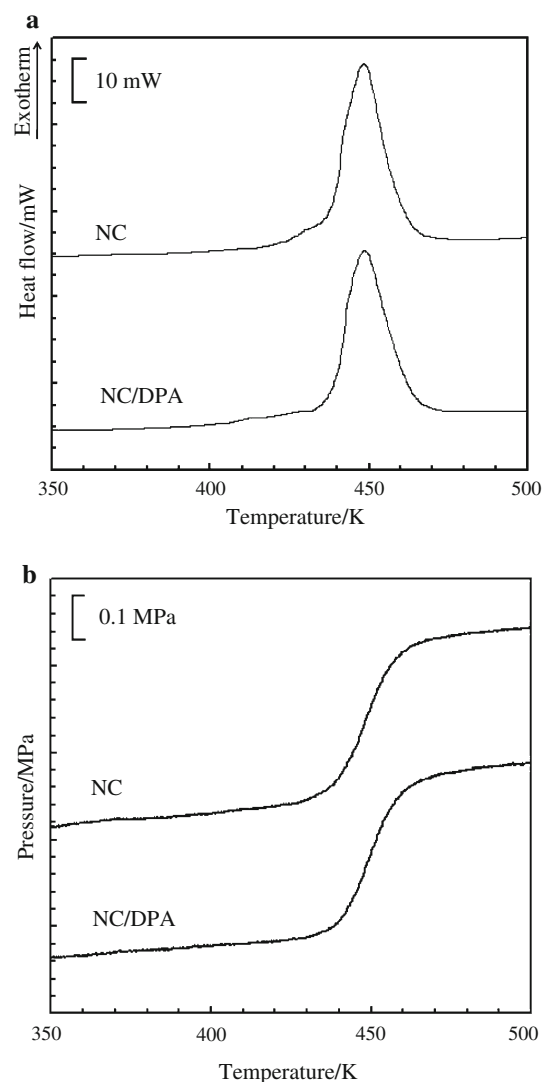


Fig. 1 Thermal and pressure curves of pure NC and NC/DPA (2 mass%) at heating rates <0.3 K/min in air. **a** Thermal curve, **b** pressure curve

mentioned above, Nakamura et al. [14, 15] observed the thermal behaviors of NC and aged NC by DSC at a heating rate of 1–10 K/min and found that the heat release temperatures and the shapes of the thermal curves were almost identical for these samples. The thermal behavior of NC mixed with a destabilizer such as HNO₃ was identical to that of pure NC. Our results were consistent with Nakamura's results, i.e., there was no notable difference in the heat release temperatures of NC samples with different stabilities. Therefore, it could be speculated that a simple comparison of the thermal or pressure behaviors is not sufficient to evaluate the stability of NC unless NC is significantly destabilized in the presence of H₂SO₄ or water.

Activation energy

A comparison of the activation energies of pure NC and NC/DPA (2 mass%) revealed a characteristic difference between the two samples. The heating rate was varied from 0.02 to 0.3 K/min. Friedman's formula (Eq. 1) was used to plot the value of $\ln(dx/dt)$ at the isoconversional point on each thermal curve as a function of $1/T$, as shown in Fig. 2a–d. The slopes in each figure correspond to the activation energies of pure NC and NC/DPA.

$$\ln\left(\frac{dx}{dt}\right) = \ln[Af(x)] - \frac{E_a}{RT} \quad (1)$$

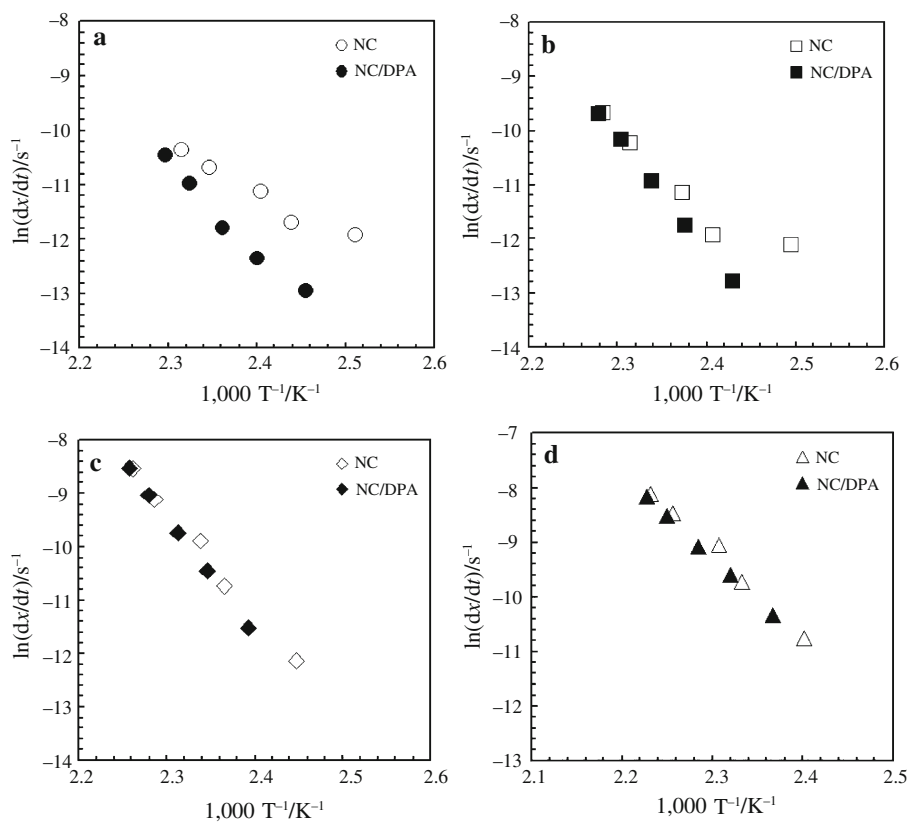
(x : Conversion)

Figure 2a shows the plots of $\ln(dx/dt)$ against $1/T$ at the isoconversional point 0.07; in this case, the activation energy of pure NC is lower than that of NC/DPA. The difference in the activation energies is particularly apparent at lower heating rates. Figure 2b shows the plots of $\ln(dx/dt)$ against $1/T$ at the isoconversional point 0.1; in this case, the plot for NC/DPA is linear, while that obtained for pure NC is not. This is because the plot for pure NC is inflected at 0.02 K/min. Figure 2c, d show the plots of $\ln(dx/dt)$ against $1/T$ beyond the isoconversional point 0.2; the plots for both pure NC and NC/DPA are linear, and their activation energies are approximately identical. By observing the activation energies of pure NC and NC/DPA at low heating rates at the beginning of the reaction, we can conclude that NC/DPA is more stable than pure NC.

Thermal behavior at low heating rates

The difference in the activation energies of pure NC and NC/DPA at the initial stages of the reaction at low heating rates is due to the small amount of heat released before the main heat release. As shown in Fig. 3, two exothermic

Fig. 2 $\ln(dx/dt)$ at isoconversional points on each thermal curve as a function of $1/T$. **a** Conversion 0.07, **b** conversion 0.1, **c** conversion 0.2, and **d** conversion 0.5. DPA content: 2 mass%



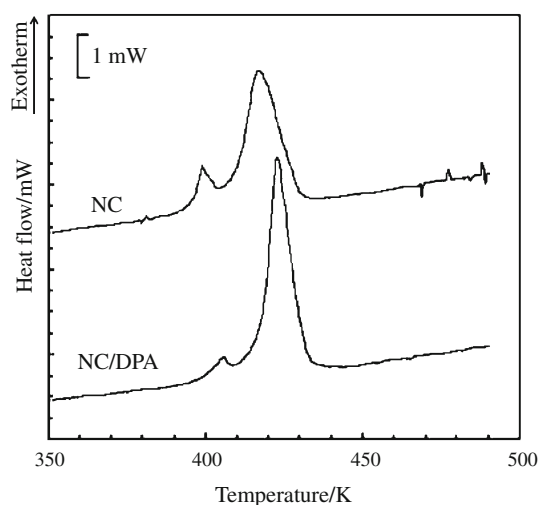


Fig. 3 Thermal curves of pure NC and NC/DPA (2 mass%) at heating rate $<0.02\text{ K/min}$ in air

peaks are observed at 0.02 K/min ; however, the first peak diminishes at higher heating rates. The ratio of the heat released in the first peak to that released in the second stage increases with a decrease in the heating rate. This tendency is more apparent in the case of pure NC than in the case of NC/DPA. This implies the difference in the activation energies of pure NC and NC/DPA, as shown in Fig. 2a, results from the reaction amount of the first peak.

By studying the thermal curves at 0.02 K/min (Fig. 3), we speculate the reactions that correspond to each of the two exothermic peaks. In an earlier study [4–6], we investigated the heat release mechanism in NC and found that the amount of heat released in the first step depends on

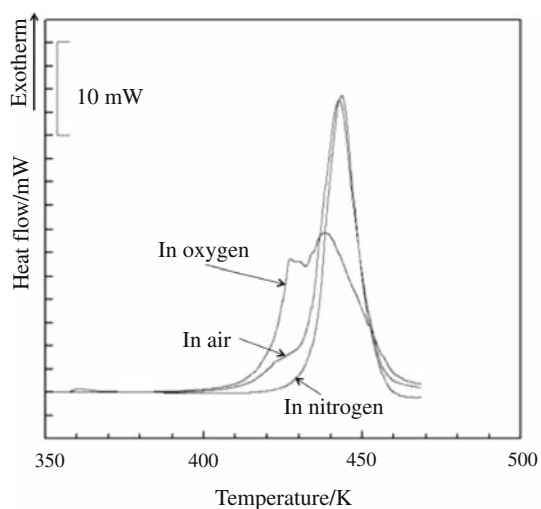


Fig. 4 Effect of storage atmosphere on the thermal curve of pure NC [4]

the presence of atmospheric O_2 . As shown in Fig. 4, the amount of heat corresponding to the first peak increases with the partial pressure of O_2 in the atmosphere, and this behavior is not observed in a N_2 atmosphere. From these results, we concluded that the first heat release results from oxidation of NC by atmospheric O_2 . We also concluded that the second heat release is the result of a reaction with intramolecular O_2 because this heat release is observed in a N_2 atmosphere as well. No difference in the thermal behaviors of pure NC and NC/DPA could be detected in the thermal analyses conducted at high heating rates, probably because the decomposition of NC itself (attributed to the second peak) occurs before the oxidation of NC by atmospheric O_2 , which corresponds to the first peak. Hence, similar exothermic peaks were obtained in the thermal curves of pure NC and NC/DPA at high heating rates.

Next, we study the thermal curves in order to evaluate the stability of NC. The stability of NC depends on the first heat release because its amount was influenced by the initial amount of stabilizer that means the stability of NC. In considering the use as a stability evaluation method, however, the difference between pure NC and NC/DPA is also small. In addition, the pressure curves of pure NC and NC/DPA exhibit nearly identical behavior. In this study, we assume that when measurements are carried out at a high O_2 partial pressure under isothermal conditions, the amount of heat released in the first step will increase, and differences in the thermal and pressure behaviors of pure NC and NC/DPA will be apparent.

Thermal behavior under isothermal conditions

On the basis of the abovementioned assumption, we carried out measurements in pure O_2 atmosphere under isothermal conditions. The storage temperature was 393 K ; this temperature is lower than the decomposition temperature of NC. The results are shown in Fig. 5a. The heat released corresponding to the first peak increased for both NC and NC/DPA, and the induction period of the heat release for NC/DPA (2 mass%) was significantly longer than that for pure NC. The induction period is defined as the intersection of the tangent at the maximum inclination point of the heat flow and the baseline. The induction periods for pure NC and NC/DPA were 7 and 27 h, respectively. As seen from Fig. 5b, the pressure behaviors of pure NC and NC/DPA were similar to their corresponding thermal behaviors. The induction period of the pressure change for NC/DPA was longer than that for pure NC. The relatively stability of NC could be determined from the abovementioned measurements carried out in an O_2 atmosphere under isothermal conditions.

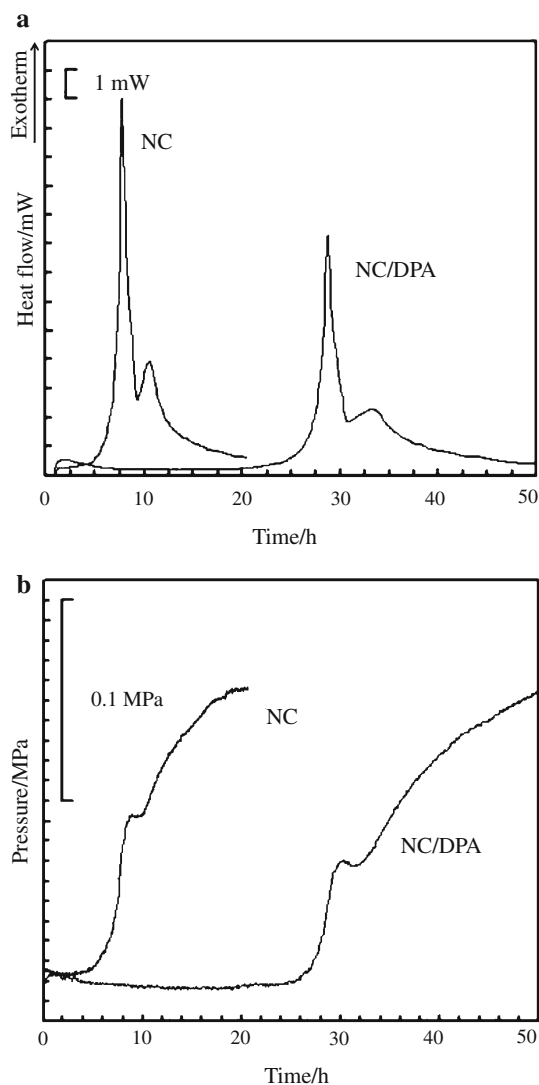


Fig. 5 Thermal and pressure curves of pure NC and NC/DPA (2 mass%) under isothermal conditions at 393 K in an O₂ atmosphere. **a** Thermal curves, **b** pressure curves

Comparison of the results of the thermal analyses with those of ABEL heat test and the effect of the type of stabilizer on the stability of NC

We compared the results of our experiments with those of the ABEL heat test, which the mandatory stability test in

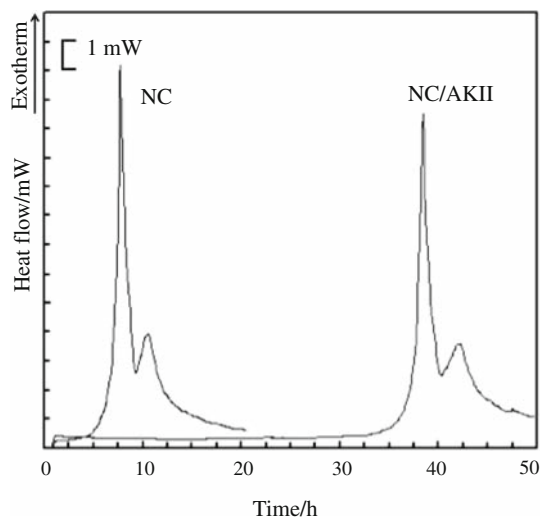


Fig. 6 Thermal curves of pure NC and NC/AKII (2 mass%) under isothermal conditions at 393 K in an O₂ atmosphere

Japan. The elongation ratio for the induction period of the first heat release of NC/DPA was correlated with the results of the ABEL heat test. Table 1 lists the values of the induction periods determined from the ABEL heat test conducted in an earlier study [13] and the induction periods of the first heat release for pure NC, NC/DPA (2 mass%), and NC/DPA (3 mass%). From these results, the induction of heat was related to that of the ABEL test.

We investigate the thermal behaviors of NC and NC/AKII (2 mass%) (AKII is a conventional NC stabilizer) under isothermal conditions at 393 K in an O₂ atmosphere. The induction period of NC/AKII is longer than that of pure NC, as shown in Fig. 6. These results indicate that the relative stability of NC can be determined by carrying out measurements under the abovementioned conditions. The results obtained from the ABEL heat test are in good agreement with those obtained in our experiments performed using pure NC and NC/AKII; these results are also listed in Table 1. Kimura et al. suggested that volatility of the stabilizer is conducive to the results of ABEL heat test [16]. From the abovementioned suggestion, we speculate that the stability of NC/AKII has been underestimated. This is because AKII, which has a lower volatility than DPA, is less reactive toward NO₂ in the gas phase than DPA.

Table 1 Comparison of the induction periods obtained in the ABEL heat test and thermal analyses

| Content/mass% | DPA | | AKII | |
|---------------|--------------------|--------------------|--------------------|--------------------|
| | ABEL heat test/min | Thermal analysis/h | ABEL heat test/min | Thermal analysis/h |
| 0 | 8 | 7 | 8 | 7 |
| 2 | 35 | 27 | 10 | 38 |
| 3 | 58 | 48 | 10 | 60 |

ABEL heat test: NC produced by NOF Corp.; Thermal analyses: NC produced by Sigma-Aldrich Corp

Therefore, the stability of NC/AKII needs to be evaluated comprehensively by the ABEL heat test as well as by thermal analyses.

Conclusions

We investigated the effect of heating rate on the thermal behaviors of NC samples with different stabilities for the following reasons: (1) to identify why temperature thermal analyses under cannot be used to evaluate the stability of NC and (2) to identify the conditions under which thermal analyses can be used to estimate the stability of NC. From our experiments, we could draw the following conclusions:

- The thermal behaviors of pure NC and NC/DPA were observed at a heating rate of 0.3 K/min in dry air; the measured heat release temperatures were approximately same for these samples. Moreover, the shapes of the thermal curves and the pressure behaviors obtained for NC and NC/DPA were also practically similar. Therefore, we concluded that the stability of NC cannot be evaluated by simply comparing the thermal or pressure behaviors unless NC is significantly destabilized in the presence of excess H₂SO₄.
- At low heating rates (approximately 0.02 K/min), two exothermic peaks were observed in the thermal curves of NC and NC/DPA. The ratio of the heat released in the first step to that released in the second step increased with a decrease in the heating rate. This tendency was more apparent in the case of pure NC than in the case of NC/DPA. This indicated that the stability of NC depended on the first heat release because its amount was changed by the amount of stabilizer that means the stability of NC. Therefore, we concluded that the stability of NC could be evaluated by studying the first heat release.
- At a high heating rate, no difference could be detected in the thermal behaviors of pure NC and NC/DPA, probably because of the decomposition of NC itself (attributed to the second peak) occurs before the oxidation of NC by atmospheric O₂, which corresponds to the first peak. Hence, similar exothermic peaks were obtained in the thermal curves of pure NC and NC/DPA at high heating rates.
- The measurement was performed in pure O₂ atmosphere under isothermal conditions. The storage temperature was 393 K. The heat released in the first step increased for both pure NC and NC/DPA, and the corresponding

induction period of NC/DPA was significantly longer than that of pure NC. In addition, the induction period for pressure change for NC/DPA was longer than that for pure NC. These measurements carried out in an O₂ atmosphere under isothermal conditions are expected to be useful in determining the relative stability of NC.

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