Thermal decomposition behavior of nitrocellulose/ acid mixtures in sealed and open systems

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Abstract

In order to investigate the influence of the type of sample container on the thermal behavior of nitrocellulose (NC) mixed with an acid solution (H_2SO_4, HNO_3, or HCl), differential scanning calorimetry and heat flux calorimetry were carried out for NC/acid mixtures in sealed and open containers. The results revealed no significant difference in the thermal behavior of NC/HCl under the sealed and open conditions; the stability (evaluated from the decomposition temperature under controlled ramp heating conditions and the induction time to exothermic decomposition under isothermal conditions) of this system was the same as that of NC alone. In contrast, the thermal behavior of the NC/H_2SO_4 and NC/HNO_3 mixtures varied depending on the conditions used. Specifically, the thermal stability of NC/H_2SO_4 was lower in the open system than in the sealed system, whereas NC/HNO_3 showed the opposite behavior. The phenomenon observed in NC/H_2SO_4 is thought to be attributed to an increase in the concentration of H_2SO_4 under open conditions due to evaporation of the solvent (water) from the H_2SO_4 solution and the low volatility of H_2SO_4. In contrast, in the case of more volatile HNO_3, it was suggested that water and HNO_3 both evaporated to the outside of the system upon heating in an open container, which led to high stability under open conditions. These results may also indicate that the thermal decomposition of NC/HNO_3 under the sealed conditions was caused by the reaction between NC and gaseous HNO_3.

Keywords: nitrocellulose, nitric acid ester, spontaneous ignition, thermal stability, calorimetry

1. Introduction

Nitrocellulose (NC) is an industrially important material that is used as a feedstock for lacquers, celluloid products, and explosives. However, NC is a hazardous material that is prone to spontaneous ignition, even at room temperature (in the summer), due to the heat accumulated as a result of decomposition. Notably, numerous accidental explosions during storage have been reported[1)−9)]. Generally, NC decomposition is triggered by reaction with water and acids such as H_2SO_4 and HNO_3 remaining from the synthesis process or released during storage[10)], and several studies on the thermal stability of NC/water and NC/acid mixtures have been published[11)−16)].

However, the reactivity of NC with acids is still under debate. For example, Osada[11)] and Demougin et al.[12),13)] suggested that H_2SO_4 accelerates the decomposition of NC, whereas HNO_3 exhibits limited reactivity toward NC. These results seem to contradict the generally accepted mechanism for NC decomposition (i.e., autocatalytic decomposition by HNO_3 released from NC[10)]). On the other hand, Nakamura et al.[14)] reported that the thermal stability of NC in the presence of an acid mixture decreases with increasing HNO_3 content, suggesting that HNO_3 plays an active role in the decomposition of NC. Hence, the acid responsible for NC decomposition has not yet been unambiguously identified.
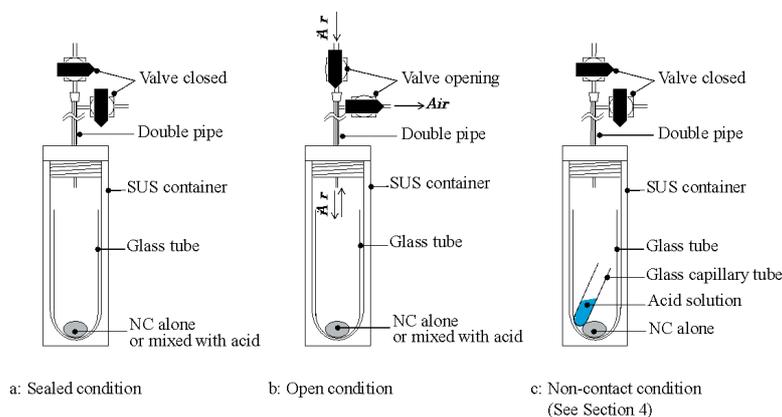
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a: Sealed condition   b: Open condition   c: Non-contact condition
(See Section 4)

Figure 1   Schematic diagram of the C80 container under different conditions.

We speculated that the inconsistency of the previous results was due to the dependence of the reactivity of NC with acids on the test conditions such as the heating conditions, sample container volume, sample scale, and amount and concentration of the acid solution. Based on this assumption, we previously investigated the influence of the heating conditions on the acid-induced decomposition of NC via thermal analysis of NC/acid mixtures at a heating rate of $0.2-5\,^{\circ}\mathrm{C\cdot min^{-1}}$ and at a constant temperature of $70\,^{\circ}\mathrm{C}$[15]. The results showed that both HNO_3 and H_2SO_4 promoted the decomposition of NC. Moreover, the decomposition of NC by HNO_3 was strongly dependent on the heating rate: at high heating rates (> 3 $^{\circ}\mathrm{C\cdot min^{-1}}$), the decomposition temperature and the thermogram of NC/HNO_3 were almost identical to those of NC alone, whereas the decomposition temperature significantly decreased at low heating rates ($< 1\,^{\circ}\mathrm{C\cdot min^{-1}}$). Thus, the differences in the results obtained in the thermal analysis of the NC/acid mixtures were found to be linked to the heating conditions. Moreover, it was suggested that the thermal behavior of NC/acid mixtures was influenced by the vaporization or liquid-gas equilibrium of the acid solution added to NC, suggesting that the reaction between NC and the acid could be affected by the type of sample container (the difference between sealed and open containers) and the size of the sample container.

In light of these considerations, in this study, we investigate the thermal behavior of NC/acid mixtures in sealed and open containers by differential scanning calorimetry (DSC) and heat flux calorimetry (C80); these techniques have been widely used as hazard evaluation methods[17),18)].

2. Experimental
2.1 Materials
NC (N%=12.5), provided by NOF Corp., was dried under vacuum at ambient temperature for more than three days. H_2SO_4 (95.0 mass%), HNO_3 (60 mass%), and HCl (37 mass%) solutions purchased from Wako Pure Chemical Industries Ltd. were added to dry NC after dilution.

2.2 DSC measurements
The respective dilute acid solutions (2.5 mg, 2.3 mol·L^{-1}) were added to dry NC (10 mg) in a glass tube, and the mixtures were thoroughly stirred using a bamboo skewer. An aliquot of each sample (0.2 mg) was placed in a cylindrical DSC cell purchased from Hitachi High-Technologies Corp. (material: SUS; capacity: $15\mu\mathrm{L}$). The same cell, originally manufactured as a sealed container, was also used as an open system by not using the sealing cap. To evaluate the thermal behavior of the NC/acid mixtures, DSC measurements were conducted in both sealed and open systems, using a DSC3100 instrument (Mac Science Corp.); measurements were performed at a heating rate of $0.2-5\,^{\circ}\mathrm{C\cdot min^{-1}}$ within the temperature range of $20-280\,^{\circ}\mathrm{C}$. The same experiments were carried out for pure NC as a control.

2.3 C80 measurements
Dry NC (35 mg) was placed in a glass container, and the respective acid solutions (4.7 mg, 6.6 mol·L^{-1}) were added. The samples were thoroughly mixed as described above and inserted into a cylindrical container purchased from Rigaku Corp. (material: SUS; capacity: ~4 mL). This container was equipped with a conduit and valves on the upper side of the lid and could be used sealed (Figure 1a) or open (Figure 1b) by closing or opening the valves. Heat flux calorimetry was performed under both conditions by using a C80 calorimeter (Setaram Instrumentation) at a constant temperature of $70\,^{\circ}\mathrm{C}$.

3. Results
3.1 DSC measurements
The DSC thermograms of NC alone and the NC/acid mixtures, acquired at a heating rate of $1\,^{\circ}\mathrm{C\cdot min^{-1}}$ under sealed and open conditions, are shown in Figures 2 and 3, respectively. Under sealed conditions (Figure 2), the maximum peak temperatures (T_p) of NC/H_2SO_4 and NC/HNO_3 were lower than those of NC alone and NC/HCl, indicating that H_2SO_4 and HNO_3 promoted the exothermic decomposition of NC.

In the open container (Figure 3), the intensity of the exothermic peak decreased for all samples, compared with the results obtained under sealed conditions. This was attributed to heat loss from the system. In addition, for the NC/HNO_3 mixture, the T_p was almost the same as that of NC alone, whereas a lower T_p was observed in the sealed system, suggesting differences in the thermal behavior

depending on the conditions used. The thermal behavior of NC/H_2SO_4 in the two systems also differed, where a lower T_p was observed under open conditions. On the other hand, for NC/HCl, no change in the T_p was observed for the open versus closed system, indicating that HCl exhibited no reactivity toward NC.

DSC measurements were conducted at different heating rates, and kinetic analysis was performed by applying the Kissinger method[19]. From the slope of the Kissinger plot (ln (heating rate (β)/T_p^2) versus $1/T_p$) shown in Figure 4, under sealed conditions, NC/HNO_3 had the lowest activation energy (E_a) of the evaluated systems, whereas in the open system, the E_a was similar to that of NC alone. Thus, the difference between the sealed and open conditions of the sample container significantly influenced the reactivity of the NC/HNO_3 mixture. Moreover, for NC /H_2SO_4, at all heating rates, the T_p shifted to lower values for the open system compared to that of the sealed systems, although large variations in the plots of the data acquired at a low heating rate (0.2 °C·min^{-1}) were

observed. For NC/HCl, no significant difference in the E_a was observed for the sealed versus open conditions.

3.2 C80 measurements

The thermal behavior of NC alone and the NC/acid mixtures at a constant temperature of 70 °C was measured using a C80 calorimeter under sealed and open conditions, and the obtained thermograms are shown in Figures 5 and 6. Under sealed conditions (Figures 5(a) and 6(a)), an exothermic peak was observed for NC/H_2SO_4 and NC/HNO_3, with the induction time (t_p) of 6 h and 10 h indicating the maximum intensity, respectively. For NC alone and NC/HCl (not shown), no exothermic peak was observed for at least 70 h.

Under open conditions (Figures 5b and 6b), reaction of the NC/H_2SO_4 mixture resulted in heat release before the temperature reached 70 °C, which indicated that the decomposition of NC/H_2SO_4 was accelerated compared to the case under sealed conditions. For NC/HNO_3, no exothermic peak was observed, similar to the case of NC
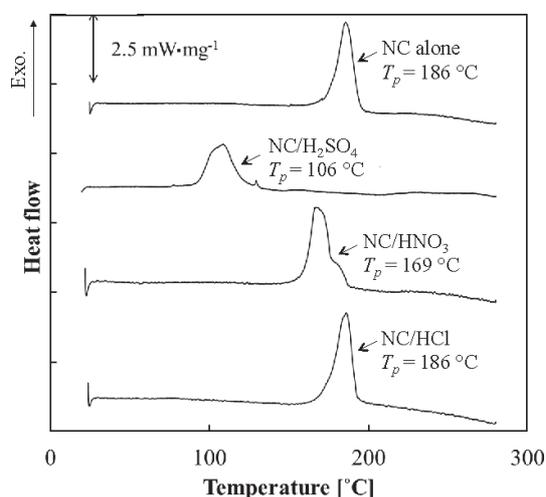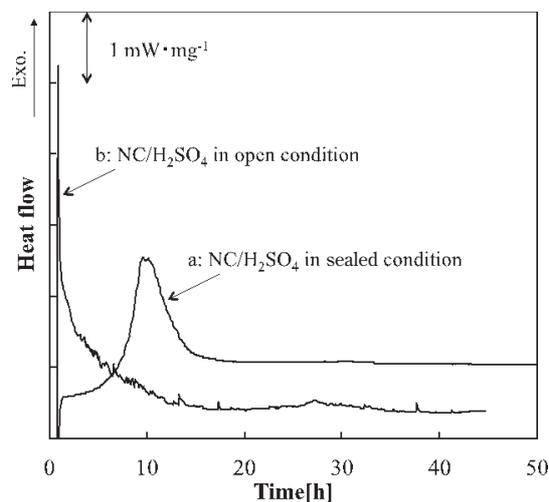

Figure 2 DSC thermograms of NC alone and NC/acid mixtures, acquired at a heating rate of 1 °C·min^{-1} under sealed conditions.
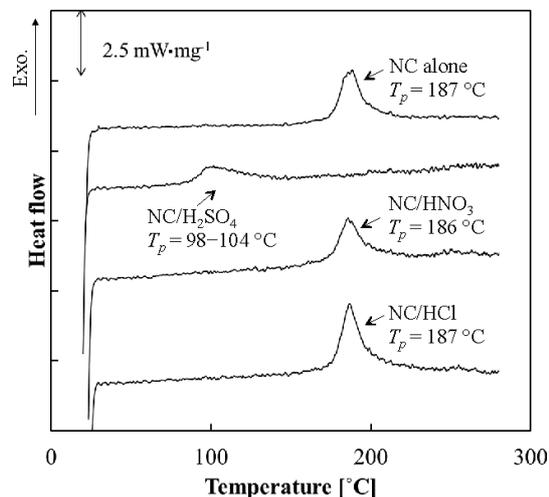

Figure 3 DSC thermograms of NC alone and NC/acid mixtures, acquired at a heating rate of 1 °C·min^{-1} under open conditions.
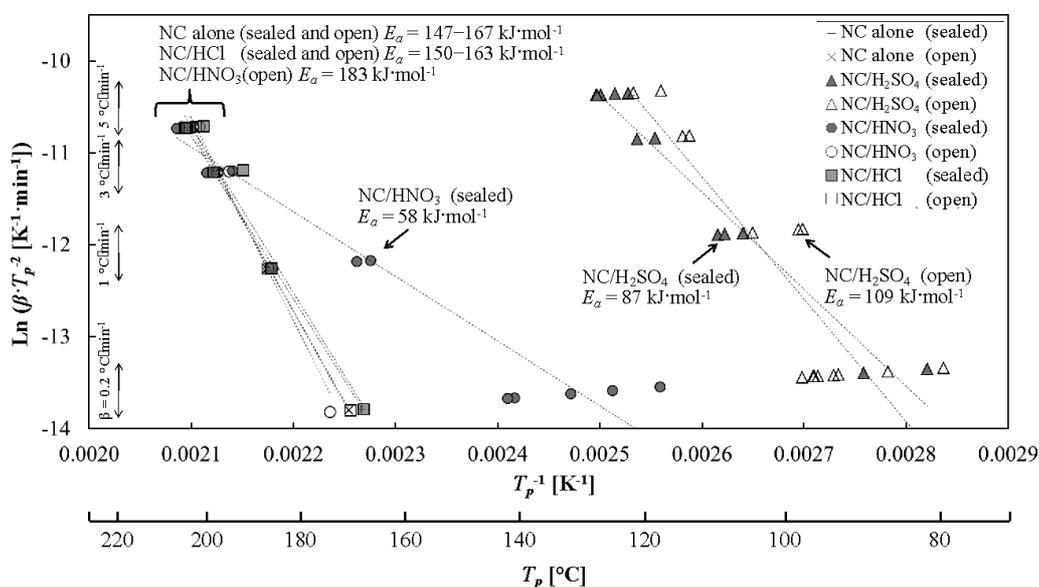
Figure 4 Kissinger plots of NC alone and NC/acid mixtures based on DSC results, obtained under open and sealed conditions.

Figure 5 Thermograms of the NC/H₂SO₄ mixture, measured with a C80 calorimeter at a constant temperature of 70 °C under (a) sealed and (b) open conditions.
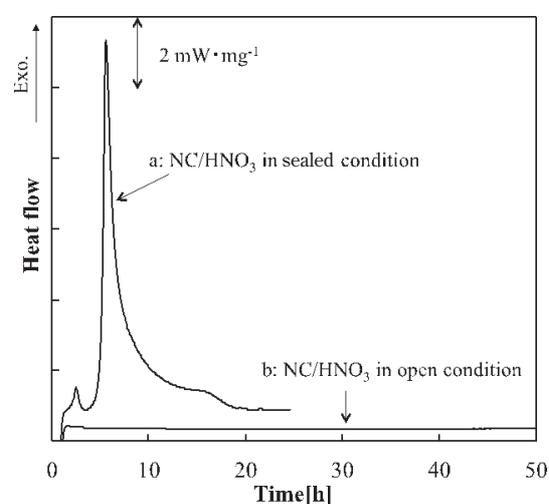
Figure 6 Thermograms of the NC/HNO₃ mixture, measured with a C80 calorimeter at a constant temperature of 70 °C under (a) sealed and (b) open conditions.

Figure 7 Relationship between T_{ARC} and H⁺ abundance in 100 mg of NC[21], measured with ARC in heat−wait−search mode.
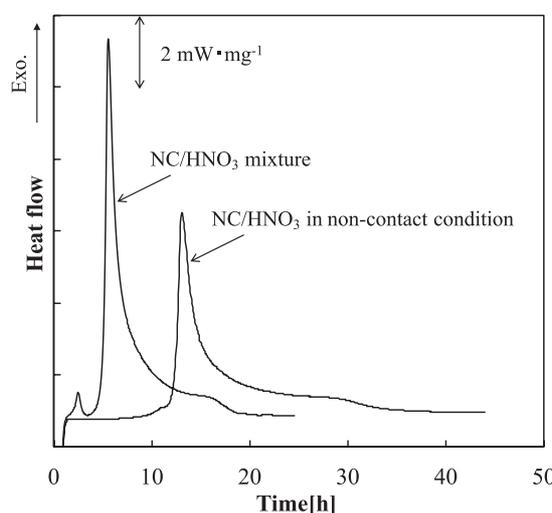
Figure 8 Thermogram of NC/HNO₃, measured with a C80 calorimeter at a constant temperature of 70 °C in non-contact condition.
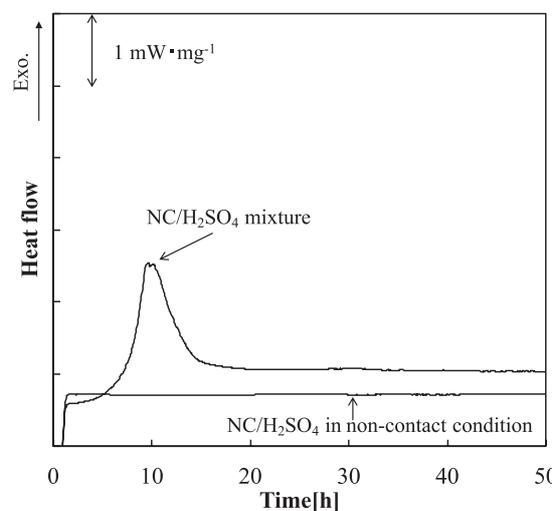
Figure 9 Thermogram of NC/H₂SO₄, measured with a C80 calorimeter at a constant temperature of 70 °C in non-contact condition.
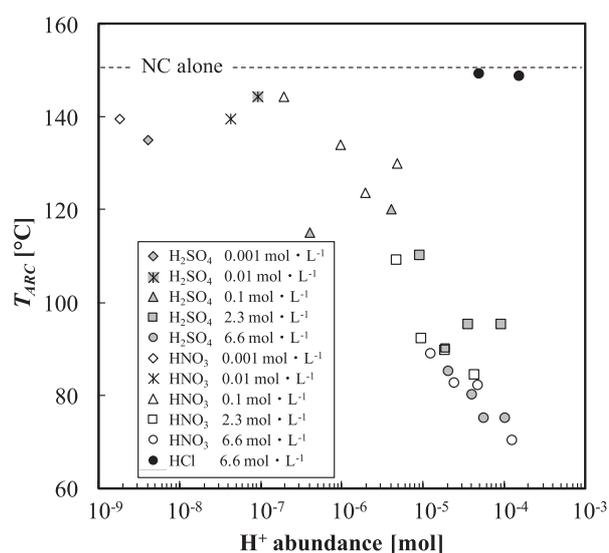
alone, although in the sealed container, heat release due to the reaction was observed within 6 h. The NC/HCl mixture showed no exothermic reaction in the open system, similar to the corresponding system under sealed conditions and NC alone.

Combined with the DSC results, these data demonstrate that the thermal stability of NC/H₂SO₄ decreased in the open system, whereas the opposite tendency was observed for NC/HNO₃. Moreover, HCl did not react with NC regardless of the conditions used (open or sealed).

4. Discussion

The observed difference between the thermal behavior of NC/H₂SO₄ and NC/HNO₃ in the sealed and open systems is suggested to be attributed to evaporation of the acid, and assumed as follows.

In NC/H₂SO₄, because the vapor pressure of H₂SO₄ is extremely low (vapor pressure of 95 wt% H₂SO₄ solution : 0.2 Pa at 35 °C[20]), only the water evaporates from the dilute acid when the NC/H₂SO₄ system is heated. Thus, in the open system, the release of water vapor to the outside of the system resulted in a higher H₂SO₄ concentration,

which was presumably responsible for the lower thermal stability of NC/H$_2$SO$_4$ under open conditions. In a previous study[21], the thermal behavior of NC with acid solutions of different concentrations was investigated using an accelerating rate calorimeter (ARC) in the heating-waiting -searching mode (detection sensitivity : 0.02 °C·min^{-1}, waiting and searching time : 20 min, temperature step : 5°C). The results showed that the T_{ARC}, defined as the temperature at which the heat release rate is 0.02 °C·min^{-1} or more, decreased with increasing H$_2$SO$_4$ concentration, as shown in Figure 7. Thus, in the present study, the lower T_p and t_p values of the NC/H$_2$SO$_4$ mixture in the open system could also be attributed to the increased concentration of H$_2$SO$_4$.

On the other hand, when the NC/HNO$_3$ mixture is heated, both water and HNO$_3$ can evaporate because of the high volatility of HNO$_3$ (vapor pressure of pure HNO$_3$: 1.3×10^4 Pa at 34.1°C[22]). Hence, under open conditions, gaseous HNO$_3$ was released to the outside of the system. This can explain the similar thermal stability observed for NC/HNO$_3$ and NC alone in the open system. Conversely, under sealed conditions, gaseous HNO$_3$ or nitrogen oxides derived from HNO$_3$ can exclusively react with NC thus promoting its decomposition.

In order to confirm the reaction between NC and gaseous HNO$_3$, C80 measurements were carried out at a constant temperature of 70 °C by placing NC and the acid (HNO$_3$ or H$_2$SO$_4$, 4.7 mg, 6.6 mol·L^{-1}) in separate containers, as shown in Figure 1(c). Under these conditions (referred to as non-contact condition), the decomposition of NC in the NC/HNO$_3$ system was indicated by heat release after 13 h (Figure 8). On the other hand, no exothermic peak was observed for the non-contact NC/H$_2$SO$_4$ system (Figure 9). The heat released by the non-contact NC/ HNO$_3$ system (1.5 kJ·g^{-1}) corresponded to the heat released from the NC/HNO$_3$ mixture in the sealed system (1.7 kJ·g^{-1}), suggesting that the reaction between NC and gaseous HNO$_3$ actively contributed to the heat released by the NC/HNO$_3$ mixture. Thus, the reactivity of the NC/ HNO$_3$ mixture was significantly affected by the sealability of the sample container.

5. Conclusions

In this study, the thermal behavior of NC/acid mixtures was analyzed by DSC and C80 calorimetry in open and sealed systems. Based on the experimental results, the following conclusions can be drawn :

· The thermal stability of NC/H$_2$SO$_4$ was lower than that of NC alone under both sealed and open conditions. Further, comparison between the sealed and open conditions indicated that the thermal stability of NC/H$_2$SO$_4$ was lower in the open system. This destabilization was considered to be due to H$_2$SO$_4$ because no difference in the stability was observed for NC alone under sealed versus open conditions. This behavior is attributed to an increase in the concentration of H$_2$SO$_4$ under open conditions due to evaporation of the solvent (water) from the dilute acid upon heating.

· For NC/HNO$_3$ under sealed conditions, the thermal stability was lower than that of NC alone, whereas in the open system, the stability was similar to that of NC alone. Upon heating in an open container, HNO$_3$ evaporated to the outside of the system, suggesting that the exothermic decomposition of NC/HNO$_3$ was associated with the reaction between NC and gaseous HNO$_3$.

· A relatively small difference in the thermal stability of NC/HCl was observed under sealed versus open conditions, and the thermal stability was almost the same as that of NC alone. Hence, HCl did not react with NC.

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