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# Influence of water on the thermal stability of nitrocellulose

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## Abstract

Thermal analysis of nitrocellulose (NC) containing water was carried out using an accelerating rate calorimeter (ARC) under the Heat-Wait-Search mode. The results were compared with those of our previous study conducted under isothermal conditions using a heat-flux calorimeter (C80). In the ARC results, the heat-release temperature ( $T_{ARC}$ ) of NC with 2.0-2.5 wt% water was observed at 105°C, whereas that of dry NC was 150-155°C. In the case of NC with more than 5.0 wt% water,  $T_{ARC}$  stayed constant at approximately 130°C. The water amount of 2.0-2.5 wt%, at which the lowest  $T_{ARC}$  was observed, corresponded to the saturated vapor amount at 105°C. From this observation, it was concluded that NC was most destabilized when all the additive water vaporized and is saturated as vapor in the sample vessel. This tendency agrees well with the C80 results under isothermal conditions at 120°C. On the other hand, in the C80 results at 80°C under isothermal conditions, NC was most destabilized when more water was added than the saturated vapor amount, unlike in the ARC results. The reason for this difference was assumed to be that at low temperatures (around 80°C or less), the additive water did not vaporize completely, even when only the saturated vapor amount in the vessel was added to NC.

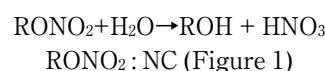
**Keywords** : nitrocellulose, mixing hazard, spontaneous ignition, accelerating rate calorimeter (ARC)

## 1. Introduction

Nitrocellulose (NC, Figure 1) is widely used in various industrial fields in applications such as lacquers, films, celluloid products, and explosives. However, NC has a tendency to cause spontaneous ignition, and many accidents have been reported in the past<sup>1)-5)</sup>.

The spontaneous ignition mechanism of NC has been investigated in some previous studies. Generally, it is

known that spontaneous ignition occurs through the acceleration of NC degradation. The initial degradation process results from the following hydrolysis<sup>6)</sup> :



The hydrolysis is thought to be caused by water adsorbing on NC or by water in the atmosphere. The

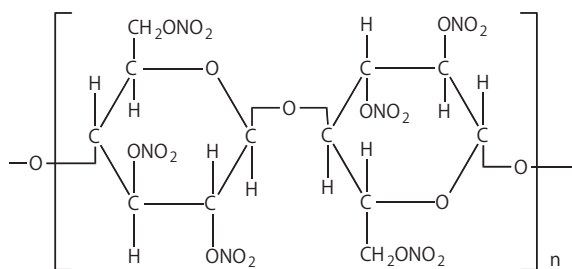


Figure 1 Chemical structure of NC.

hydrolysis is autocatalytically accelerated by the nitric acid generated. In addition, the sulfuric acid used in the synthesis process affects the stability of NC<sup>(7)–(9)</sup>. Therefore, if not adequately removed in the washing process, such acids will further accelerate the hydrolysis<sup>(6)</sup>. Then, the nitric acid generated from the hydrolysis and thermal dissociation of the O-NO<sub>2</sub> bond release NO<sub>2</sub>, and NC gradually degrades through the reaction between NC and NO<sub>2</sub>. It may be that more complicated reactions involving radical species or other reactive substances are conducive to the degradation of NC<sup>(7), (10)–(12)</sup>, but it is commonly understood that water contributes to the degradation and stability of NC. In addition, we reported in our previous study that the thermal stability of NC is degraded by water<sup>(13)</sup>.

On the other hand, it is also known that NC containing excessive amounts of water is more stable than dry NC. For example, the UN recommendation states that NC containing 25 wt% water is exempt from application as an explosive material. Thus, it is expected that there is an inflection point in the relationship between NC stability and water content. However, the influence of water on the thermal stability has hardly been evaluated quantitatively in previous studies.

In the present study, for the investigation of the influence of water on the thermal stability of NC, thermal analysis of NC containing various amounts of water was carried out using an accelerating rate calorimeter (ARC), and the results were compared with the thermal behavior observed with the heat-flux calorimeter (C80) in our previous study<sup>(14)</sup>.

## 2. Experimental

### 2.1 Materials

NC (N% = 10.9) provided by Asahi Kasei Chemicals Corp. was used as the experimental sample. The NC was dried under vacuum at ambient temperature for more than three days. The dry NC (100 mg) was put in a spherical sample vessel (material: Hastelloy C; capacity: 2.4 mL) used for the ARC measurements, and a given amount of deionized water (Milli-Q water) was added to the dry NC in the vessel.

### 2.2 Procedure

The reaction vessel containing the NC prepared as described in Section 2.1 was attached to the ARC assembly (Arthur D. Little, Inc., ARC2000). A thermocouple was attached to the bottom outer surface of the reaction vessel. Then, the thermal behavior of the NC

containing water under pseudo-adiabatic conditions was observed in the Heat-Wait-Search mode (temperature detection sensitivity: 0.02 K·min<sup>-1</sup>; waiting and searching time: 30 min; temperature step: 5K)<sup>(15)</sup>.

In this measurement, the sample vessel was heated in 5K increments. At each temperature step, the temperature was maintained for approximately 30 min, and the sample vessel was monitored for any temperature change. If the temperature change by the self-heating reaction did not exceed 0.02 K·min<sup>-1</sup>, the sample was heated to the next temperature step. This temperature control was repeated until a temperature change of up to 0.02 K·min<sup>-1</sup> was detected. Upon detection of heat exceeding 0.02 K·min<sup>-1</sup>, the system automatically switched to “exothermic mode”; the external temperature was controlled to the same temperature as the sample vessel, allowing the temperature of the sample to be observed under pseudo-adiabatic conditions. In this study, the temperature at which heat release of more than 0.02 K·min<sup>-1</sup> is observed is defined as  $T_{ARC}$ , and is used as the index of NC stability.

## 3. Results and discussion

### 3.1 Relationship between $T_{ARC}$ and additive water amount

As an example of the ARC measurement, the thermal behaviors of NC alone and NC with 2.5 wt% water are shown in Figure 2.  $T_{ARC}$  of NC with 2.5 wt% water was observed at approximately 105°C, while that of dry NC was 150–155°C. Figure 3 shows the relationship between  $T_{ARC}$  and the additive water amount.  $T_{ARC}$  of NC with water was lower than that of dry NC. In addition, it can be seen that NC containing 2.0–2.5 wt% water showed the lowest  $T_{ARC}$ . In the case of more than 3.0–5.0 wt% water,  $T_{ARC}$  increased and stayed constant at approximately 130°C.

Next, to investigate why NC had such an inflection point on the plot of  $T_{ARC}$  against additive water amount, we investigated the relationship between  $T_{ARC}$  and the phase state of the additive water in the vessel. In the present

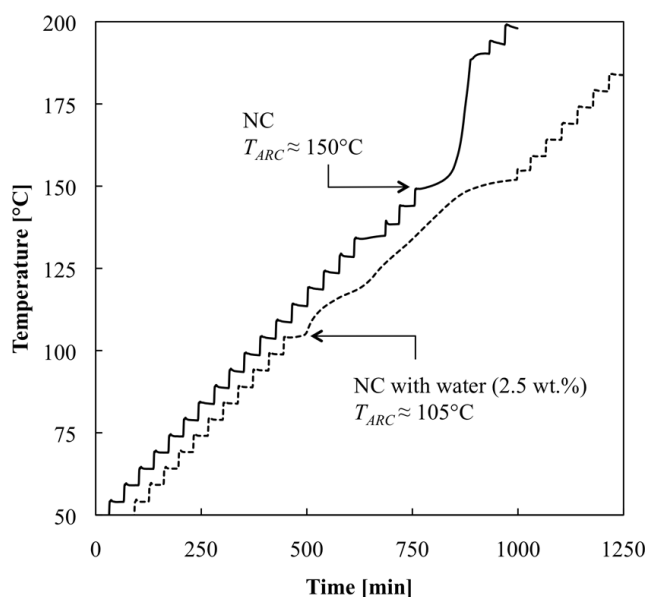
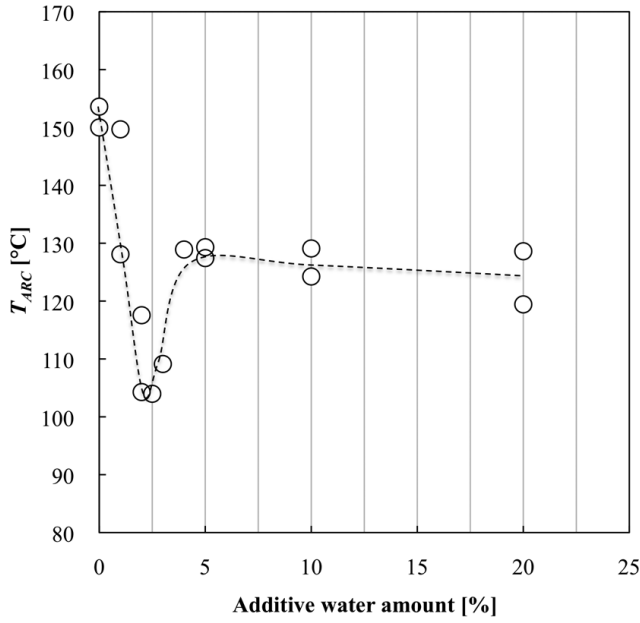
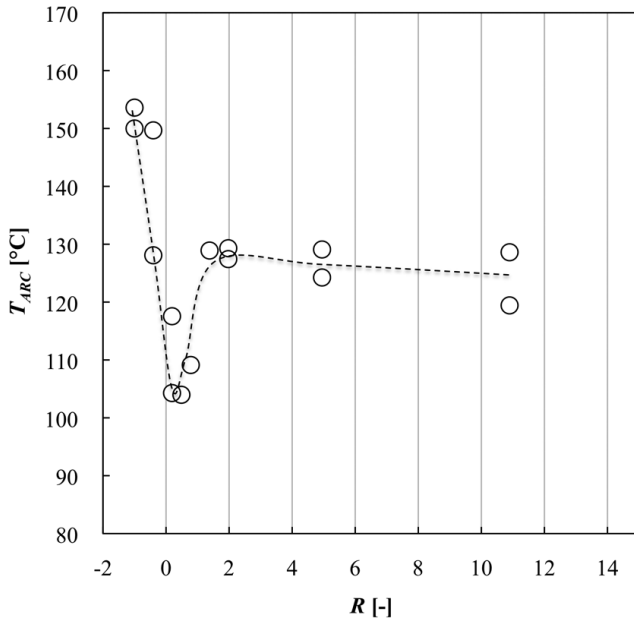


Figure 2 Thermal behavior of NC and its mixture with water.



**Figure 3** Change in  $T_{ARC}$  of NC as a function of additive water amount in NC.



**Figure 4** Change in  $T_{ARC}$  of NC as a function of  $R$  value.

study, as a parameter of the phase state of the additive water,  $R$  is defined by the following equation :

$$R = \frac{W_{H_2O}/V - \rho_A}{\rho_A} \quad (1)$$

where  $W_{H_2O}$  is the additive water amount,  $V$  is the vessel volume (approximately 2.4 mL), and  $\rho_A$  is the amount of saturated water vapor per unit volume.  $R$  shows the ratio of liquid water and the vapor amount in the system, because  $W_{H_2O}/V - \rho_A$  and  $\rho_A$  in Equation (1) correspond to the liquid water and vapor amount, respectively.

Figure 4 indicates the change in  $T_{ARC}$  as a function of  $R$ , which was calculated from  $\rho_A$  at 105°C, that is, the lowest  $T_{ARC}$ .  $T_{ARC}$  showed a minimum value at  $R \approx 0$ . The value  $R = 0$  implies that the additive water vaporizes completely and is saturated as vapor in the system. Under such

conditions, NC will react with water vapor and be most destabilized. Conversely, when an excessive amount of water is added to NC, it is considered that the liquid water increases  $T_{ARC}$  slightly through absorption of the reaction heat. For instance, in the case of NC with 5.0 wt% water, it was calculated that 3.3 mg of water from an added amount of 5.0 mg remained in NC as liquid. The concept of the relationship between  $R$  and NC stability is illustrated in Figure 5 (A).

### 3.2 Comparison with 120°C isothermal experiment

In our previous study<sup>14)</sup>, the thermal behavior of NC (50 mg) containing water was investigated under isothermal conditions at 80°C and 120°C using the heat-flux calorimeter (C80, SETARAM Instrumentation). In this study, NC stability was evaluated in terms of the induction period ( $t_{C80}$ ), which is the time elapsed before heat release from the beginning of storage. In this section, we compare the ARC results observed in the present study with the C80 results at 120°C.

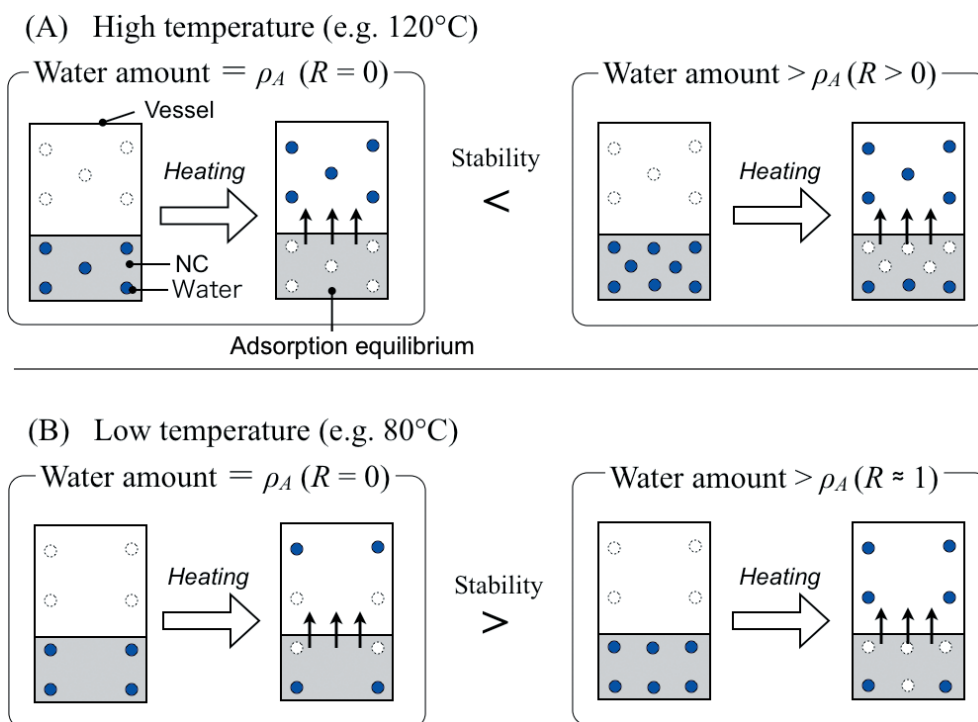
Figure 6 shows the relationship between  $t_{C80}$  and additive water content in conjunction with the ARC results (Figure 3). In this figure, the water contents at which  $T_{ARC}$  and  $t_{C80}$  show their minimum values are different; the water content at the lowest  $T_{ARC}$  is 2.0–2.5 wt%, whereas that at the lowest  $t_{C80}$  is 10 wt% for 120°C isothermal storage. Therefore, it can be said that the NC stability is not determined by the additive water content.

As the reason for this difference, it is considered that the phase state of the additive water is different for the ARC and C80 measurements because the vessel capacities (ARC: 2.4 mL; C80: 4 mL) and sample amounts (ARC: 100 mg; C80: 50 mg) are different. Therefore,  $T_{ARC}$  and  $t_{C80}$  were plotted again as a function of  $R$ , as shown in Figure 7. In this figure, both  $T_{ARC}$  and  $t_{C80}$  show minimum values at approximately  $R \approx 0$ . This result supports the assumption that the NC stability decreases most when most of the additive water vaporizes and is saturated as vapor in the system, as described in Section 3.1.

### 3.3 Comparison with 80°C isothermal experiment

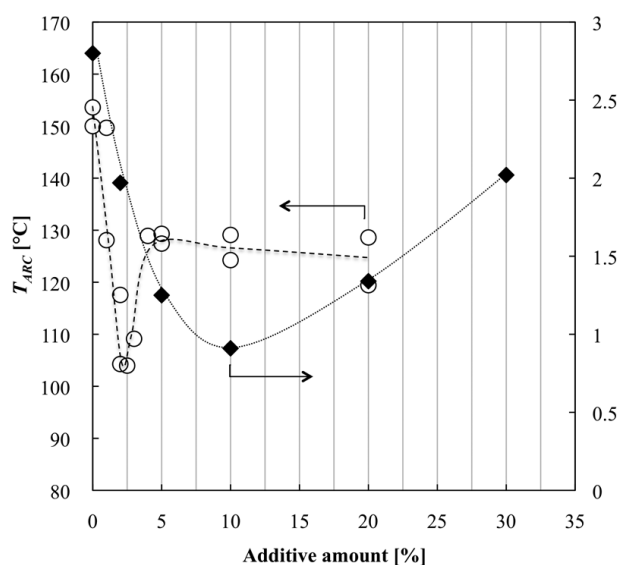
We compared the ARC results with the C80 results<sup>14)</sup> at 80°C. As shown in Figure 8, the water amounts at which  $T_{ARC}$  and  $t_{C80}$  indicate their minimum values are comparatively close; the water content at the lowest  $T_{ARC}$  is 2.0–2.5 wt%, whereas that at the lowest  $t_{C80}$  is 4.8 wt% for 80°C isothermal storage. On the other hand, unlike the ARC results, the plots of  $t_{C80}$  versus  $R$  have larger deviations from  $R = 0$ ; the minimum value of  $t_{C80}$  at 80°C occurs at  $R \approx 1$  (Figure 9).

Regarding this phenomenon, we assumed that the difference in  $R$  values at the minimum  $T_{ARC}$  and  $t_{C80}$  values resulted from the difference between the vaporization behaviors because of the temperature. At low temperatures (such as the 80°C isothermal condition), as shown in Figure 5 (B), a part of the additive water is thought to absorb in the NC in the liquid state, even if the same amount of water as saturated vapor amount is added. In other words, the water vapor is not saturated in

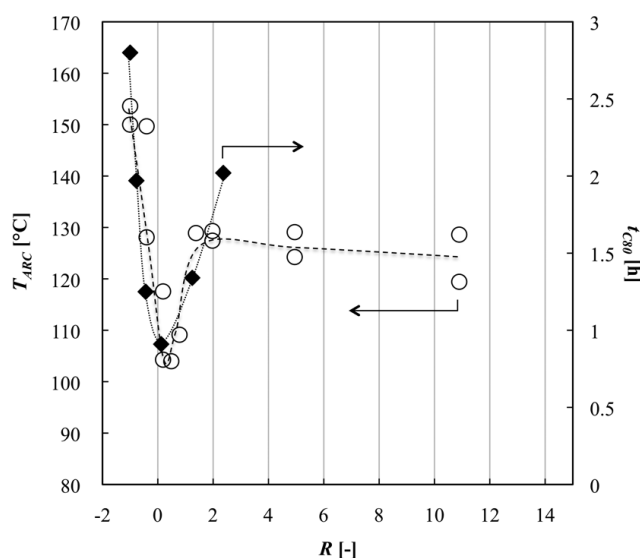


**Figure 5** Conceptual figure showing the relationship between the vaporization behavior of additive water and NC stability, based on the results of the present study<sup>†</sup>.

<sup>†</sup>In this figure, white circles in the gas phase denote saturated water amount (capacity). For instance, if all white circles in the gas phase change to blue circles, it implies that water was saturated in the gas phase.



**Figure 6** Change in  $T_{ARC}$  and  $t_{C80}(120^\circ\text{C})$  as a function of additive water amount in NC.



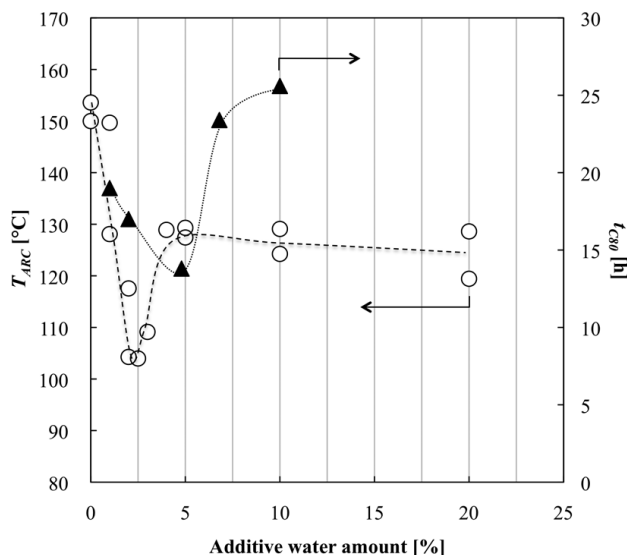
**Figure 7** Change in  $T_{ARC}$  and  $t_{C80}(120^\circ\text{C})$  as a function of  $R$  value.

the vessel. When the amount of water added to the NC is greater than saturated vapor amount, the water vapor is finally saturated in the system. This assumption can explain the experimental result that the minimum  $t_{C80}$  value is observed when water with  $R$  slightly more than 0 is added to NC. On the other hand, in the case of ARC measurements and isothermal storage at 120°C,  $T_{ARC}$  and  $t_{C80}$  are minimized at  $R \approx 0$ , because the additive water is almost completely vaporized when the additive water amount is the same as the saturated vapor amount, as shown in Figure 5 (A).

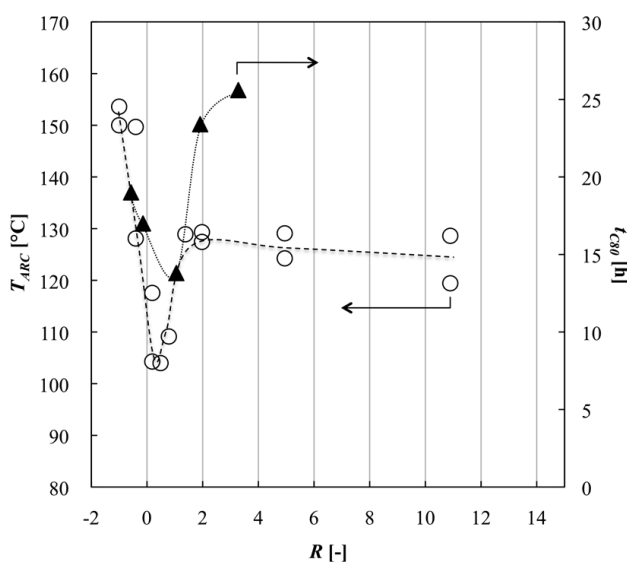
### 3.4 Vaporization behavior of water added to cotton

For the investigation of the vaporization behaviors at different temperatures, a simple experiment was conducted using wet cotton as a simulated sample. In this experiment, screw-top glass tubes (~114 mL) containing dried cotton (6g) with water (2g) or water alone (2g) were stored at 77 or 117°C using a constant-temperature oven. The glass tubes were opened at intervals of approximately 10 min. By measuring the weight of the tubes after heating, the residual water amount was predicted.

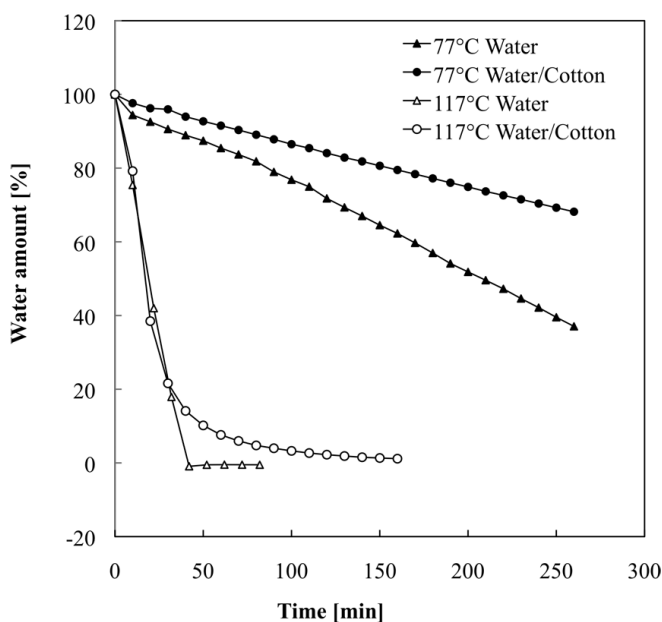
At 117°C, a small amount of residual water was observed after storage for 60 min (Figure 10), regardless of



**Figure 8** Change in  $T_{ARC}$  and  $t_{C80}(80^{\circ}\text{C})$  as a function of additive water amount for NC.



**Figure 9** Change in  $T_{ARC}$  and  $t_{C80}(80^{\circ}\text{C})$  as a function of  $R$  value.



**Figure 10** Vaporization behavior of water and water added to cotton.

whether or not cotton was present. However, it was observed that the profiles were not completely consistent with each other; water was difficult to volatilize in the presence of cotton. This tendency was increased at  $77^{\circ}\text{C}$ . Namely, approximately 70% of the water remained in the cotton after 250 min, and in the case of water alone, the residual water after storage for 250 min was 37%. From this, it is concluded that the vaporization behavior differs substantially in accordance with temperature, and water remains for longer when an adsorptive material such as cotton is present. Therefore, we consider that these results support the hypothesis described in Section 3.3 about the difference between the ARC and C80 results under  $80^{\circ}\text{C}$  isothermal conditions.

## 4. Conclusion

For the investigation of the influence of water on the thermal stability of NC, thermal analysis of NC containing water was carried out using ARC under the Heat-Wait-Search mode. The results were compared with the thermal behavior under isothermal conditions observed by C80 in a previous study. The following conclusions can be drawn:

- (1) In ARC measurements,  $T_{ARC}$  of NC with water ( $T_{ARC}=105\text{--}130^{\circ}\text{C}$ ) was lower than that of dry NC ( $T_{ARC}=150\text{--}155^{\circ}\text{C}$ ). NC with 2.0–2.5 wt% water showed the lowest  $T_{ARC}$  ( $105^{\circ}\text{C}$ ). In the case of NC with more than 5 wt% water,  $T_{ARC}$  remained constant at approximately  $130^{\circ}\text{C}$ .
- (2) When the relationship between  $T_{ARC}$  and the  $R$  value Equation (1) was investigated,  $T_{ARC}$  showed its minimum value at  $R \approx 0$ . Since the value  $R = 0$  corresponds to the water amount at which the additive water vaporizes completely and is saturated as water vapor in the system, NC is destabilized most under such conditions. This result agreed well with the C80 results under isothermal conditions at  $120^{\circ}\text{C}$ .
- (3) In the C80 results under the  $80^{\circ}\text{C}$  isothermal condition, the induction time before heat release,  $t_{C80}$ , was minimized at  $R \approx 1$ , unlike in the ARC results. As the reason for this difference, it is considered that at low temperatures, the water vapor is not saturated because some of the additive water exists in the NC in its liquid state, even if the amount of water added to the NC is the same as the saturated vapor amount.

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## ニトロセルロースの熱安定性に及ぼす水の影響

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水分を含有したニトロセルロース (NC) の熱的挙動を加速速度熱量計 (ARC, 加熱–待機–探索モード) を用いて観察し, 既往の研究において, 熱流束型反応熱量計 (C80) により観察した等温貯蔵下における熱的挙動と比較した。ARC 測定結果では, 乾燥 NC の発熱開始温度 ( $T_{ARC}$ ) は, 150–155°C であるのに対して, 2.0–2.5 wt. % の水を含む NC の  $T_{ARC}$  は 105°C, 5wt. % 以上の水を含む NC の  $T_{ARC}$  は, 約 130°C で一定となった。最も  $T_{ARC}$  が低下した水分添加量である 2.0–2.5wt. % は, 発熱開始温度における飽和水蒸気量とほぼ等しいことから, 添加した水のほとんどが水蒸気として系内に飽和し, 水が NC 中に残存しない条件において NC が最も不安定化する可能性がある。この傾向は, 既往の研究で観察した 120°C 等温貯蔵下における実験結果と合致した。一方, 80°C 等温貯蔵下における結果では, 貯蔵温度における飽和水蒸気量よりも過剰な水を添加した際に最も不安定化し, ARC 測定結果とは異なる傾向を示した。この相違の理由として, 温度が低い場合 (80°C 程度あるいはそれ以下) には, 飽和水蒸気量と同量の水を添加しても, 水の一部が NC 中に残存するため系内は水蒸気で飽和せず, それよりも多い水分を加えた際に飽和することが考えられる。

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