

Thermal decomposition behavior and mechanical sensitivity of 6-azido-6-deoxy curdlan

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Received : July 6, 2012 Accepted : April 23, 2013

Abstract

For the evaluation of the explosion hazard of 6-azido-6-deoxy curdlan (AC), its thermal decomposition behavior and mechanical sensitivity were investigated. In differential scanning calorimetry (DSC) at a heating rate of 10 K·min⁻¹, the onset temperature (T_{DSC}) of the exothermic peak of AC was observed at 200°C, and its heat amount (Q_{DSC}) was 1.55 kJ·g⁻¹. On the basis of results such as the differences in the IR spectra before and after heating, it is suggested that AC released heat by oxidation at low temperatures prior to the main decomposition step. In the mechanical sensitivity test according to JISK4810, AC was categorized as Class 5 in terms of drop-hammer sensitivity and Class 7 in terms of friction sensitivity. In the friction sensitivity test, a flash was emitted at the instant when AC experienced frictional force. For the evaluation of the mixing hazards, the thermal behaviors of AC with metals (iron, copper, aluminum, and ferric oxide), oxidizers (ammonium nitrate (AN) and ammonium perchlorate (AP)), and H₂SO₄ and NaOH aqueous solutions were investigated using DSC. The results showed that T_{DSC} of AC decreased with H₂SO₄ and NaOH aqueous solutions, and Q_{DSC} of AC with AN and AP increased in comparison with that of AC alone.

Keywords : organic azides, self-reactive substances, mixing hazard, DSC, sensitivity test

1. Introduction

In the presence of a Cu⁺ catalyst, organic azides undergo Huisgen cycloaddition reaction with terminal alkynes that have a triple bond between carbon atoms at the molecule ends, and thus form triazoles¹⁾. Some of the authors previously synthesized various curdlan derivatives with triazole rings at their 6-position, by carrying out the reaction between 6-azido-6-deoxy curdlan (AC, Figure 1) and terminal alkynes bearing various functional groups²⁻⁴⁾. AC was synthesized from hydroxyl curdlan, one of the natural polymers, by regioselective substitution of the azide group for the hydroxyl group at the 6-position. Thus, structurally controlled curdlan derivatives that have triazole rings with different kinds of functional groups can be obtained via the Huisgen cycloaddition reaction.

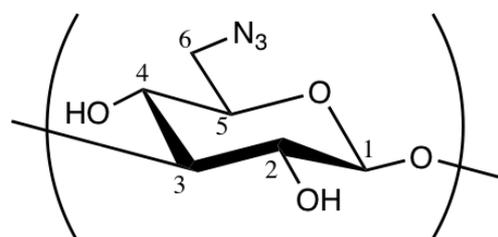


Figure 1 Chemical structure of AC.

Curdlan derivatives are expected to be used in the field of pharmaceuticals or as research reagents, because polysaccharides such as curdlan have various physiological activities and a characteristic three-dimensional structure. In addition, their synthesis technique has the advantage of low production costs,

because the curdlan used as the starting material is inexpensive.

However, it is generally known that organic azides such as AC are sensitive to heat and mechanical impact, and decompose explosively upon contact with strong acids or metals^{5,6}. For example, Mizuno *et al.* reported that phenyl azides had high mechanical sensitivity, and decomposed rapidly at approximately 100°C with heat and pressure release⁷.

Therefore, it is necessary to evaluate the explosion hazards of AC and related chemical processes. As a fundamental study, in this work, we used thermal analyses to investigate the thermal decomposition behaviors of AC and of mixtures of AC with various additives. In addition, the drop-hammer sensitivity and friction sensitivity of AC were evaluated.

2. Experimental

2.1 Materials

The AC used as the experimental sample was synthesized in our laboratory in accordance with the procedure described in a previous study³. The synthesized AC was identified using ¹³C NMR (AL300, JOEL Ltd.). Nitrocellulose (NC, N = 10.6%, Asahi Kasei Chemicals Corp.), which is an energetic polysaccharide similar to AC, was used as a comparative sample. The additives used for the investigation of mixing hazards were copper powder, aluminum, ferric oxide, iron, ammonium nitrate (AN), ammonium perchlorate (AP), water, and H₂SO₄ and NaOH aqueous solutions. These materials (other than water) were purchased from Wako Pure Chemical Industries, Ltd. The water used was Milli-Q water prepared in our laboratory by using MQ Academic (EMD Millipore Corp.).

2.2 Thermal analyses

Differential scanning calorimetry (DSC) was conducted for AC and AC with the additives, using a DSC3100 instrument (Mac Science Corp.). In DSC, 15-μL sealed vessels (Seiko Instruments Inc.) were used as sample containers. The measurements were carried out under heating rates of 5, 10, 15, and 20 K·min⁻¹. Prior to the experiments, calibration was performed using standard substances (indium, tin, lead, and zinc).

In addition, thermal analysis using a C80 calorimeter (SETARAM Instrumentation) was performed at a heating rate of 0.2 K·min⁻¹. For this measurement, a gas circulation vessel (approximately 4 mL, RIGAKU Corp.) was used as the sample container for the investigation of the influence of atmospheric gases on the thermal decomposition behavior of AC.

2.3 FT-IR spectroscopy

The changes in the FT-IR spectra of AC before and after heating were observed with a Spectrum One instrument (PerkinElmer, Inc.) using the KBr method. The heated AC was prepared by heating at 10 K·min⁻¹ using a thermogravimetric differential thermal analyzer (TG/DTA) (TGDTA220, Seiko Instruments Inc.).

2.4 Mechanical sensitivity test

The drop-hammer sensitivity and friction sensitivity were investigated using the test apparatus complying with Testing Methods of Explosives (JISK4810, 5.2.1 and 5.2.3). These sensitivities were evaluated by measuring the drop height and friction load corresponding to the 1/6 explosion point in accordance with JISK4810.

3. Results and discussion

3.1 Thermal behavior and mechanical sensitivity of AC

3.1.1 Thermal behavior

When the thermal behavior of AC (1 mg, particle diameter < 100 μm) was measured using DSC at a heating rate of 10 K·min⁻¹, two exothermic peaks were observed around 180 and 230°C, as shown in Figure 2. The onset temperature (T_{DSC}) of the larger second peak was observed at 200°C, and total heat amount (Q_{DSC}) was 1.55 kJ·g⁻¹ (Table 1). Comparison with NC indicated that T_{DSC} of AC was almost the same as that of NC (200°C), whereas Q_{DSC} of AC was lower than that of NC (2.98 kJ·g⁻¹).

Using the obtained T_{DSC} and Q_{DSC} data, the potential of the explosion propagation (EP) was evaluated in accordance with the method proposed by Yoshida *et al.*^{8,9}. In this method, the boundary of explosion propagation is expressed by Equation 1:

$$\log(Q_{DSC}) = 0.38\log(T_{DSC} - 25) + 1.67 \quad (1)$$

Rearranging Equation 1 allows EP to be defined as shown in Equation 2:

$$EP = \log(Q_{DSC}) - 0.38\log(T_{DSC} - 25) - 1.67 \quad (2)$$

The units of Q_{DSC} and T_{DSC} are cal·g⁻¹ and °C, respectively. If a material has $EP \geq 0$, it has the potential to cause explosion propagation. In the case of AC, the EP value was +0.047, as summarized in Table 1. This result indicates that AC may have explosion potential, whereas the EP value of AC is close to the boundary ($EP=0$).

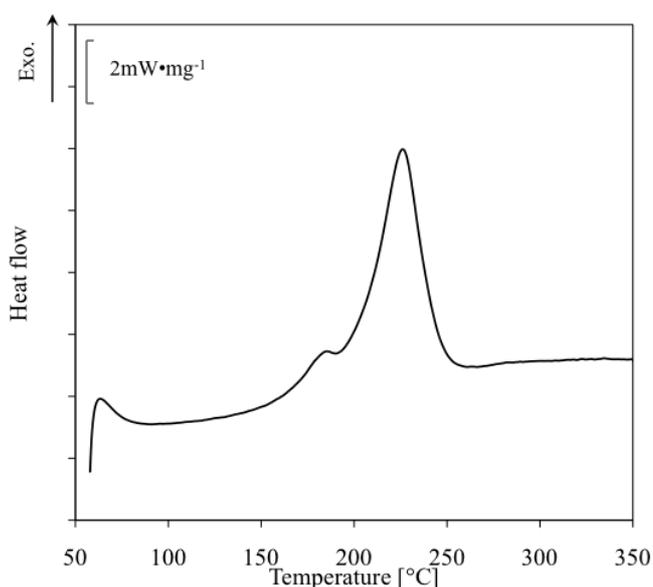


Figure 2 Thermal behavior of AC (particle size < 100 μm), measured by DSC at a heating rate of 10 K·min⁻¹.

Table 1 DSC results of AC and NC.

Sample	T_{DSC}^* [°C]	Q_{DSC}^* [kJ·g ⁻¹]	EP^*	E_a [kJ·mol ⁻¹]	
				Kissinger	Ozawa
AC	200	1.55	+0.047	87	91
NC	200	2.98	+0.331	127	128

* At 10 K·min⁻¹

DSC was carried out under various heating rates to calculate the activation energy (E_a). In this study, E_a was determined using Kissinger (Equation 3) and Ozawa equations (Equation 4)¹⁰:

$$\ln\left(\frac{\phi}{T_p^2}\right) = \ln\left(\frac{AR}{T_p}\right) - \frac{E_a}{RT_p} \quad (3)$$

$$\log\phi = \log\frac{AE_a}{g(\alpha)} - 2.315 - 0.4567\frac{E_a}{RT_p} \quad (4)$$

where ϕ is the heating rate, T_p is the temperature at the exothermic peak, A is the frequency factor, and R is the gas constant. The calculated E_a values for AC and NC are summarized in Table 1. E_a of AC is lower than that of NC, which indicates that AC is thermally unstable and may decompose in a comparatively low-temperature region.

3.1.2 Effect of particle diameter

For the investigation of the influence of the particle diameter on the thermal behavior of AC, DSC was carried out for AC (1 mg) with different particle sizes (< 100µm, 100 - 212µm, and > 212µm). The results indicate that the thermal hazard is independent of particle size, because no changes in T_{DSC} and Q_{DSC} were observed, as summarized in Table 2. On the other hand, as shown in Figure 3, the shape of the first peak around 180°C changed slightly with particle size, that is, the heat amount of the first peak increased with decreasing particle size. This observation indicated that the first peak results from atmospheric

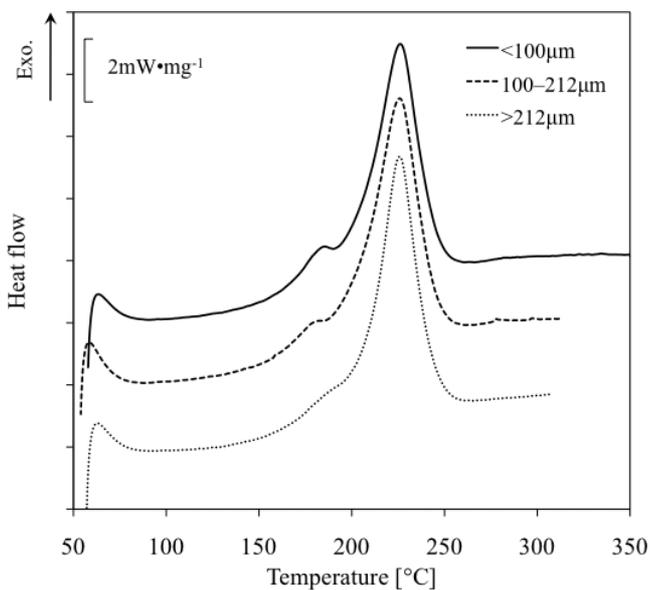


Figure 3 Thermal behaviors of AC with different particle sizes, measured by DSC at a heating rate of 10 K·min⁻¹.

Table 2 DSC results of AC with different particle sizes.

Particle size [µm]	T_{DSC}^* [°C]	Q_{DSC}^* [kJ·g ⁻¹]	EP^*
<100	200	1.55	+0.047
100-212	197	1.61	+0.066
>212	205	1.50	+0.028

* At 10 K·min⁻¹

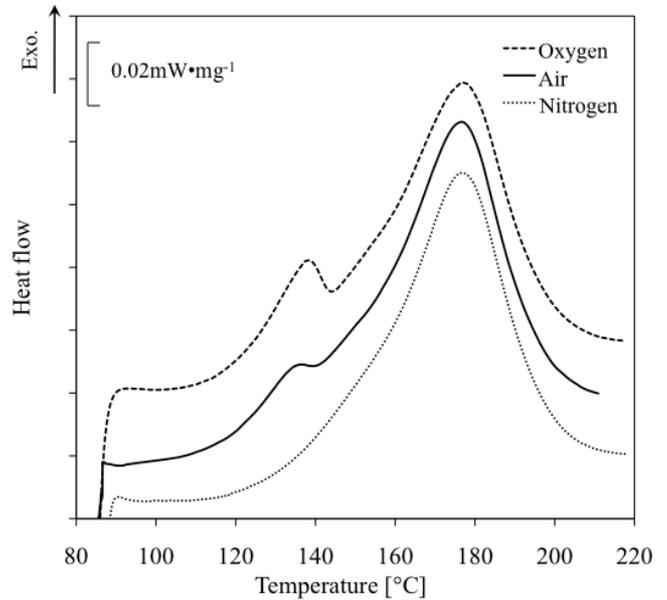


Figure 4 Thermal behavior of AC (particle size < 100µm) in different types of atmospheres, measured with C80 apparatus at a heating rate of 0.2 K·min⁻¹.

oxidation, which is affected by the contact area between oxygen and the sample.

3.1.3 Effect of reaction atmosphere

As described in section 3.1.2, AC may suffer facile oxidation. Thus, for the investigation of the influence of oxidation, the thermal behavior of AC (50 mg, particle diameter < 100µm) was observed in nitrogen, air, and oxygen atmospheres using a heat-flux calorimeter (C80).

The thermal behavior of AC in the air atmosphere showed two exothermic peaks similar to the DSC results, as shown in Figure 4. The heat amount of the first exothermic peak observed at the lower temperature (approximately 130°C) increased with increasing oxygen content in the atmospheric gas. In addition, no exothermic peak was observed around this temperature in the nitrogen atmosphere. From these results, the first exothermic peaks around 130°C observed in the air and oxygen atmospheres are thought to result from oxidation by atmospheric oxygen.

In a previous study on NC¹¹), similar thermal behavior was observed. In the case of NC, the heat release by oxidation was observed at approximately 150°C, whereas that of AC was observed around 130°C. From this comparison, it can be said that AC can undergo atmospheric oxidation relatively easily. In addition, the possibility exists that atmospheric oxidation contributes to the thermal decomposition and the low E_a of AC.

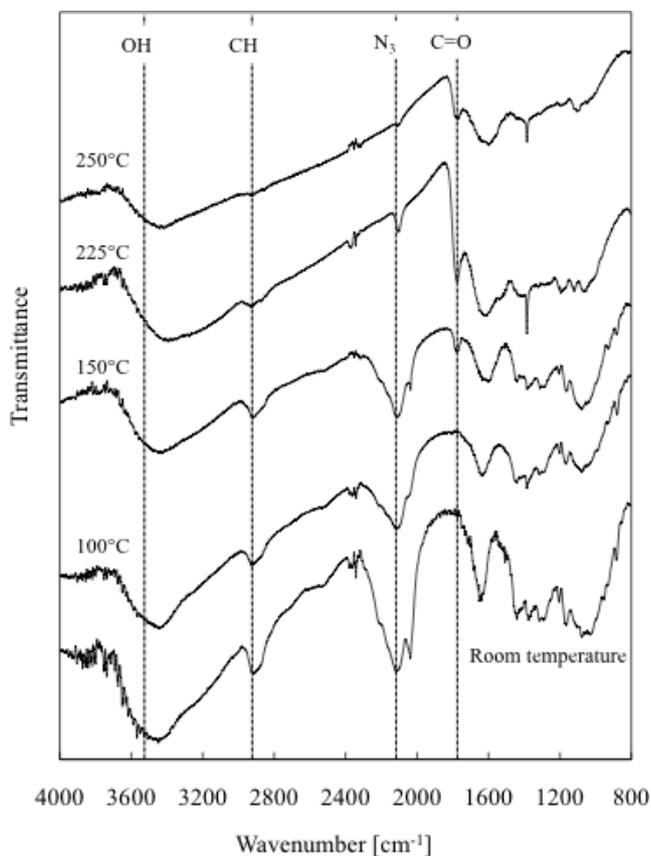


Figure 5 FT-IR spectra of AC and heated AC.

3.1.4 Structural changes upon thermal decomposition

The heated AC (particle diameter < 100 μm) was prepared by heating at 10 $\text{K}\cdot\text{min}^{-1}$ using TG/DTA, and the FT-IR spectra of the AC were observed before and after heating (Figure 5).

With reference to previous studies^{12,13}, the peaks observed in the spectrum of AC before heating were attributed to the OH stretching vibration (3000–3800 cm^{-1}), CH stretching vibration (2900 cm^{-1}), and N_3 asymmetric stretching vibration (2100 cm^{-1}).

A peak at 1700 cm^{-1} , which is considered to be due to the carbonyl group, appeared upon heating at 150°C. On the other hand, the peaks attributed to the N_3 , CH, and OH groups decreased with increasing heating temperature. These peaks were hardly observed at all for AC heated to 225–250°C. On the basis of these results, it is suggested that AC is oxidized at low temperatures, and then desorption of the azide group and decomposition of the curdlan skeleton occur. The spectroscopic changes are in good agreement with the results of the thermal analyses.

3.1.5 Mechanical sensitivity

The drop-hammer sensitivity and friction sensitivity were evaluated in accordance with the Testing Methods of Explosives (JISK4810, 5.2.1 and 5.2.3).

In the drop-hammer sensitivity test at a drop height of 20 cm, black residue on the cylindrical skids between which the sample was placed was observed in one out of six test repetitions (Table 3). On the other hand, with a lower drop height of 15 cm, no obvious explosion or

Table 3 Results of drop-hammer sensitivity test.

Drop height [cm]	1st	2nd	3rd	4th	5th	6th
30	○	-	-	-	-	-
25	×	×	○	○	-	-
20	×	×	×	○	×	×
15	×	×	×	×	×	×

○ : Explosion or decomposition

Table 4 Results of friction sensitivity test.

Friction load [kgf]	1st	2nd	3rd	4th	5th	6th
36	×	○	×	×	×	×
16	×	×	×	×	×	×

○ : Explosion or decomposition

decomposition was observed in the six test repetitions. From these results, the 1/6 explosion point for drop-hammer sensitivity was evaluated as 20 cm, which means that AC is categorized as Class 5 according to JISK4810, 5.2.1.

In the friction sensitivity test with a friction load of 36 kgf, a clearer explosion was observed: a flash was emitted at the instant when AC experienced frictional force in one out of six test repetitions (Table 4). With a lower friction load (16 kgf), such an explosion was not observed in six test repetitions. In accordance with JISK4810, 5.2.3, the friction sensitivity of AC was categorized as Class 7.

As described above, the sensitivities of AC were categorized as Class 5 for the drop-hammer sensitivity and Class 7 for the friction sensitivity. With reference to previous data¹⁴, these results are found to be on the same level as black powder.

3.2 Thermal behaviors of AC with additives

For the evaluation of the mixing hazards of AC (particle diameter < 100 μm), the thermal behaviors of mixtures of AC with metals, oxidizers, water, and acid/base aqueous solutions were investigated using DSC at a heating rate of 10 $\text{K}\cdot\text{min}^{-1}$. The results (T_{DSC} , Q_{DSC} , and EP) are summarized in Table 5.

3.2.1 Thermal behaviors of AC with metals

AC (1 mg) and copper powder, aluminum, ferric oxide, and iron (0.2 mg of each) were put in the 15- μL vessels for DSC measurements. After sealing, the vessels were shaken to mix the AC and the additives. Thereafter, DSC measurements of the mixture were conducted.

The results showed that AC reacted with copper because the shape of the exothermic peak changed in comparison with that of AC alone (Figure 6). Some kinds of azide compounds are known to react with copper⁵, and a similar tendency is seen in the case of AC. However, we considered that the potential of the explosion hazard of AC with copper was almost the same as that of AC alone, because there was hardly any difference between the T_{DSC} and Q_{DSC} values of AC with and without copper.

Table 5 DSC results of AC and mixtures of AC with additives

Sample	T_{DSC}^* [°C]	Q_{DSC}^* [kJ·g ⁻¹]	EP^*
AC alone	200	1.55	+0.047
AC/Al	203	1.38	-0.006
AC/Fe	198	1.50	+0.034
AC/Cu	168	1.34	+0.017
AC/Fe ₂ O ₃	203	1.43	+0.009
AC/AN	209	2.59	+0.261
AC/AP	207	0.64	-0.344
	318**	3.73***	+0.343
AC/Water	211	0.58	-0.390
AC/1.1 N H ₂ SO ₄	190	0.44	-0.490
AC/4.6 N H ₂ SO ₄	197	0.41	-0.528
AC/13.1 N H ₂ SO ₄	118	0.91	-0.080
AC/1.1 N NaOH	204	0.46	-0.485
AC/4.6 N NaOH	****	****	****
AC/13.1 N NaOH	113	0.40	-0.428

* At 10 K·min⁻¹

** T_{DSC} of the third peak (see Figure 7a)

*** Total Q_{DSC} of the second and third peaks (see Figure 7a)

**** Cannot be calculated because of the broad peak (see Figure 8b)

In the cases of aluminum, ferric oxide, and iron, no change in the thermal behavior was observed, so these metals have a low reactivity with AC.

3.2.2 Thermal behaviors of AC with oxidizers

AC (0.25 mg)/AP (0.25 mg) and AC (0.25 mg)/AN (0.25 mg) mixtures were prepared by the procedure described in section 3.2.1. Then, the thermal behaviors of AC/AP and AC/AN were observed using DSC.

With regards to the thermal behavior of AC/AP, three exothermic peaks were observed around 225, 300, and 330°C (Figure 7a). Comparison with the thermal behavior

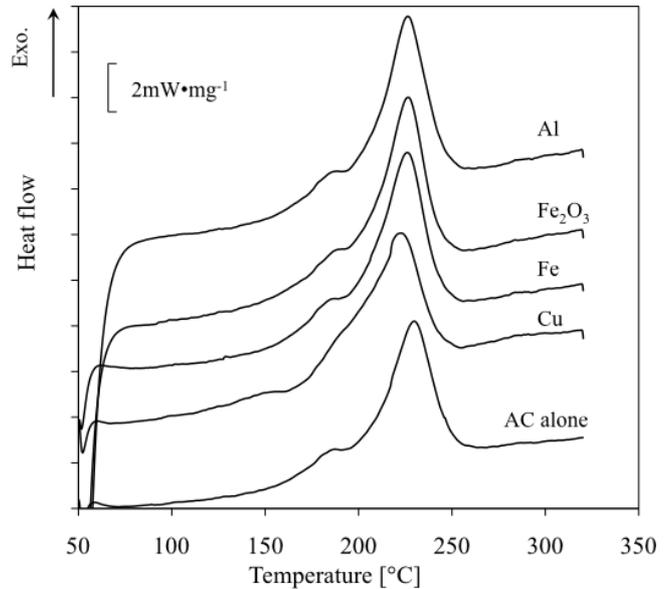


Figure 6 Thermal behaviors of AC (particle size <100µm) with metals, measured by DSC at a heating rate of 10 K·min⁻¹.

of AC alone shows that the first exothermic peak at 225°C observed in AC/AP is due to the decomposition of AC alone. The second and third peaks around 300 and 330°C possibly result from the reaction between the pyrolysis residues of AC and AP. The total heat amount of AC/AP was 3.7 kJ·g⁻¹, and a high EP value was obtained for AC/AP. The height of the exothermic peak at 180°C observed for AC alone, possibly due to oxidation with atmospheric oxygen, was more than that of the peak in the case of AC/AP. However, this comparison may be inadequate because AP has an endothermic peak around 180°C due to crystal structure transformation and this endothermic peak overlaps with the exothermic one.

In the case of AC/AN, a sharp exothermic peak was observed, and its T_{DSC} of 209°C was similar to that of AC alone (Figure 7b). The Q_{DSC} and EP values of AC/AN

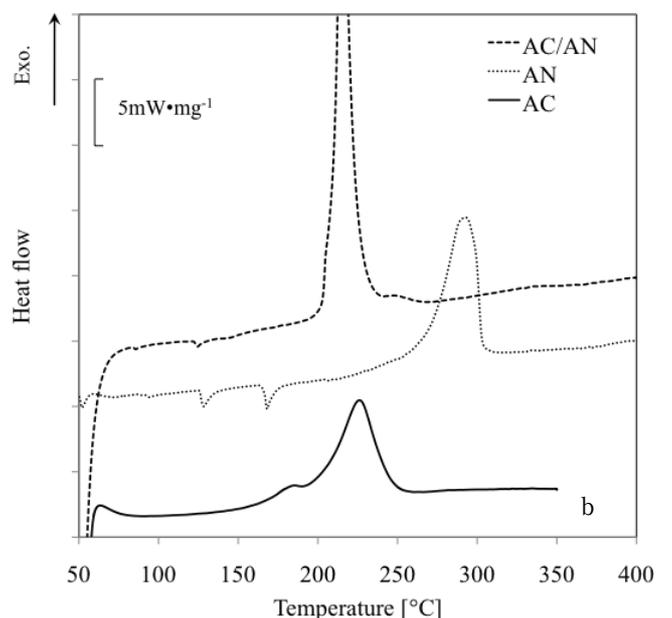
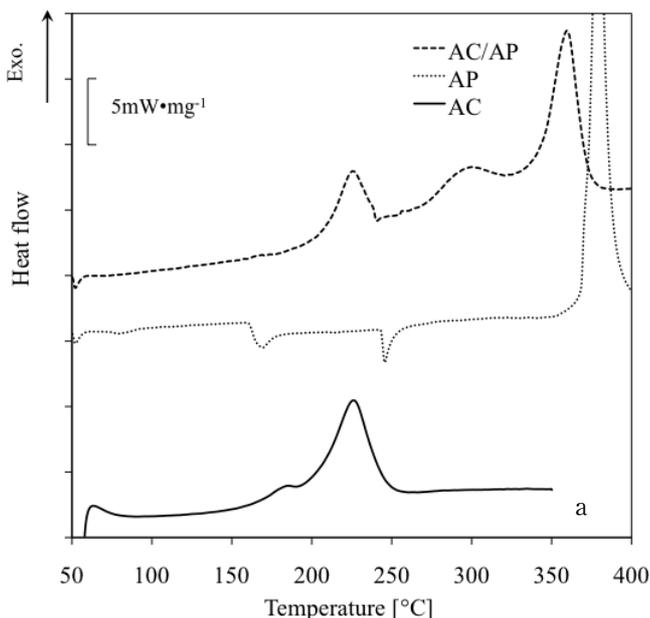


Figure 7 Thermal behaviors of AC (particle size <100µm) with oxidizers, measured by DSC at a heating rate of 10 K·min⁻¹. a: AC/AP, b: AC/AN

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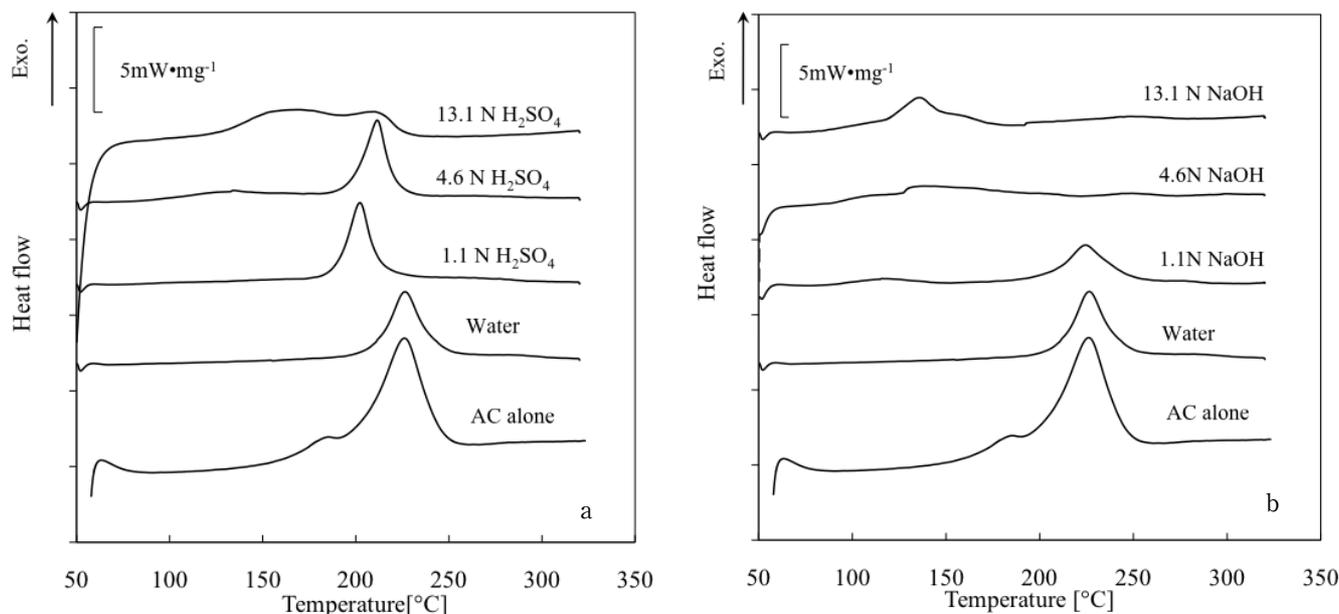


Figure 8 Thermal behaviors of AC (particle size $<100\mu\text{m}$) with acid and base solutions, measured by DSC at a heating rate of $10\text{K}\cdot\text{min}^{-1}$.
a: AC/ H_2SO_4 solution, b: AC/ NaOH solution

were $2.6\text{kJ}\cdot\text{g}^{-1}$ and $+0.261$, respectively, which coincided with those of NC.

From a comparison between AC/AP and AC/AN, it can be said that AN reacts with AC at a lower temperature than AP does. This difference is considered to result from the difference in mixing efficiency. In other words, AC mixes well with AN because AN melts at 170°C , while AC is immiscible with AP because AP does not melt in the observed temperature range.

3.2.3 Thermal behaviors of AC with water and acid/base solutions

By using a syringe, 2mg of either water or H_2SO_4 and NaOH solutions was injected into AC in separate $15\text{-}\mu\text{L}$ vessels. After allowing the AC to stand at room temperature for more than 30min , DSC measurements were conducted.

The results showed that in the case of AC with water, the T_{DSC} value was almost the same as that for AC alone, whereas Q_{DSC} decreased in comparison with that of AC alone (Figure 8a and 8b). From these results, it can be considered that water does not increase the thermal hazard of AC.

In the case of AC mixed with 1.1N and 4.6N H_2SO_4 , the exothermic peak shifted to a lower temperature ($T_{\text{DSC}} \approx 180^\circ\text{C}$) compared with that of AC alone ($T_{\text{DSC}} = 200^\circ\text{C}$), as shown in Figure 8a. In addition, for AC with 13.1N H_2SO_4 , the other exothermic peak was observed around 150°C . Therefore, it is considered that T_{DSC} is shifted to the low-temperature region with increasing acid concentration. Similar behavior was observed in the case of AC with NaOH solution, as shown in Figure 8b. However, the Q_{DSC} values of AC with H_2SO_4 and NaOH solutions decreased in comparison with that of AC alone, because the heat capacities of the solutions were comparatively large. Consequently, the EP values indicated negative values,

whereas the acid or base reacts with AC.

4. Conclusion

In this study, we investigated the thermal decomposition behavior and mechanical sensitivity of AC and mixtures of AC with various additives. From the results, the following conclusions can be drawn:

- (1) The explosion hazard evaluated by Yoshida's method suggested that AC had explosion potential, whereas the EP value of AC was close to the boundary ($EP=0$).
- (2) The DSC results at a heating rate of $10\text{K}\cdot\text{min}^{-1}$ indicated that the thermal stability of AC was comparatively low, because T_{DSC} of AC was almost the same as that of NC. In addition, E_a was lower for AC than for NC. Furthermore, AC released heat through atmospheric oxidation.
- (3) From the mechanical sensitivity test (JISK4810), AC was categorized as Class 5 in terms of the drop-hammer sensitivity and Class 7 in terms of the friction sensitivity. In the friction sensitivity test with a friction load of 36kgf , a flash was emitted at the instant when AC experienced frictional force.
- (4) The DSC investigation of the mixing hazard showed that concentrated acid/base solutions and oxidizers have high reactivity with AC. Therefore, it is necessary to prevent inadvertent contact with these materials when using AC in actual processes.

5. Acknowledgment

We thank Mr. Masahiko Sugimoto and Dr. Masahiko Otsuka of Asahi Kasei Chemicals Corp. for help in the mechanical sensitivity tests.

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6-アジド-6-デオキシカードランの熱分解挙動 および機械的感度

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本研究では、6-アジド-6-デオキシカードラン (AC) の発火・爆発危険性を評価することを目的として、ACの熱分解挙動および機械的感度特性を調査した。昇温加熱下 ($10\text{K} \cdot \text{min}^{-1}$) におけるACの発熱開始温度 (T_{DSC}) は 200°C 、総発熱量 (Q_{DSC}) は $1.55\text{kJ} \cdot \text{g}^{-1}$ であった。加熱前後におけるIRスペクトル変化等の検討から、ACの主たる発熱ピークよりも低温領域で酸化発熱を起こすことが示唆された。また、落つい感度は5級、摩擦感度は7級であり、摩擦感度試験の際には、閃光が観察された。金属 (鉄, 銅, アルミニウムおよび酸化鉄 (III)), 酸化剤 (過塩素酸アンモニウムおよび硝酸アンモニウム), 水酸化ナトリウム水溶液および硫酸水溶液それぞれとACの混合物の熱的挙動をDSCにより観察した結果、高濃度の水酸化ナトリウムあるいは硫酸水溶液と混合した場合、AC単独と比較して、 T_{DSC} が低下した。また、酸化剤との混合物の場合では、 Q_{DSC} が増加した。

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