Thermal Stability Evaluation of Chemical Processes: Application of the Friedman Method for Estimating TMR

Sumitomo Chemical Co., Ltd.
Production & Safety Fundamental Technology Center
Ryotaro ITOH

To design and develop appropriate operating conditions and the safety system of a chemical production process, it is important to obtain accurate reaction kinetics of the thermal decomposition of the materials dealt with in the process. Thermal analyses using an ARC (Accelerating Rate Calorimeter) have been used to acquire the decomposition kinetics of chemical substances. However, thermal analysis using an ARC is inappropriate in some cases, such as when the latent heat of melting affects the exothermic heat flow or when the heat generation behavior exceeds the adiabatic control limit of the device. In this paper, several examples of applying the Friedman method (model-free kinetic analysis) using sealed cell DSC and C80 data in chemical process which solves several difficulties of reaction kinetics measurement and analysis are introduced.

Introduction

When incidents occur in chemical processes, they can lead to extensive human and material damage. In order to prevent chemical incidents and limit damage, it is important to assess the hazards of substances dealt with in chemical processes in advance, and to implement appropriate operating conditions, operating procedures, and safety measures.

Thermal stability evaluations are necessary to assess the risk of runaway reactions and subsequent incidents that can develop in chemical processes. There are many types of calorimeters used for thermal stability evaluation, and it is necessary to select the appropriate instruments according to the characteristics of the substance to be evaluated, handling conditions, and evaluation purpose, and to consider safety measures comprehensively. **Table 1** shows typical test instruments and their characteristics[1]. Based on the characteristics of various calorimeters, we have conventionally used sealed-cell differential scanning calorimetry (SC-DSC), which is an easy and safe instrument for quantitative evaluation of the endothermic and exothermic behavior of chemical substances on the order of milligrams, and accelerating rate calorimeter (ARC), which can obtain the exothermic behavior of substances on the

Table 1 Characteristics of calorimeter

Method	Temperature range (°C)	Sensitivity	Temperature control			Measurement item		
			Dynamic	Isothermal	Adiabatic	Heat of decomposition	Sample temperature	Pressure
DSC	−100 to 700	○	○	△		○	○	
DTA	RT to 1500	○	○	△			○	
C80	RT to 300	◎	○	○		○	○	○
MS80	RT to 200	◎		○		○	○	○
TAM III	4 to 150	◎	○	○		○	○	○
ARC	RT to 400	○		○	○	△	○	○
Dewar	RT to 250	◎			○		○	

RT: Room temperature, ◎: Excellent, ○: Good, △: Average
Created using data from cited reference[1]

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order of grams under pseudoadiabatic conditions[2]. The reaction rate is analyzed for the measured data obtained by ARC, and the process control temperature is determined based on the time to maximum rate under adiabatic conditions (TMR) and the adiabatic decomposition temperature in 24 hours (ADT24)[2].

In this paper, we focus on the Friedman method[3], which can analyze reaction rates without assuming a reaction model, and introduce a kinetic analysis for thermal decomposition reactions considering the phase state of substances with actual examples. We also present a thermal stability evaluation flowchart that incorporates kinetic analysis using the Friedman method.

Kinetic analysis from thermal analysis data

1. Kinetic analysis method assuming reaction model

The reaction rate of thermal decomposition reactions generally shows Arrhenius-type temperature dependence, and the reaction rate constant k can be generally expressed by Equation (1)[4], where A is the pre-exponential factor, E_a is the apparent activation energy, R is the gas constant, and T is the absolute temperature:

$$k=A\exp\left(-\frac{E_a}{RT}\right) \qquad (1)$$

Assuming that the reaction rate can be expressed as a function of thermal conversion α and temperature only, the rate equation becomes the following equation (2), where t is the time and $f(\alpha)$ is the reaction model:

$$\frac{d\alpha}{dt}=A\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \qquad (2)$$

In a kinetic analysis method that assumes a reaction model, a reasonable reaction scheme (independent, parallel, sequential or other reaction) and reaction model $f(\alpha)$ (the nth order, autocatalytic, or other reaction) are assumed from thermal analysis data such as ARC, and kinetic parameters are determined.

We mainly employ two methods of kinetic analysis assuming a reaction model[2]. In the first method, after assuming an appropriate reaction model based on the relationship between temperature and temperature rise rate obtained from ARC measurement data, the kinetic parameters are determined by regression approximation, and a ϕ correction is conducted using the Huff method[5), 6]. This method determines the temperature rise rate and TMR under adiabatic conditions from the

obtained correction results. In the second method, a more complex reaction model is assumed for the temperature vs. time plots obtained from ARC measurements, and the kinetic parameters are determined by regression analysis using nonlinear optimization methods such as the modified Newton-Gauss or tensor method. A tool to assist in this analysis is ARKS FK, a component of the software TSS-ARKS developed by CISP Ltd. For a more detailed understanding of TSS-ARKS, please refer to the information in the references[1), 2]. The goodness of the kinetic analysis assuming these reaction models depends largely on the validity of the model chosen.

2. Kinetic analysis method that does not assume a reaction model (model-free)

An example of a kinetic analysis method that does not assume a reaction model is the isoconversional method[7]. There are two types of isoconversional methods: integral and differential. This section describes the kinetic analysis by the Friedman method, a differential isoconversional method.

When the pre-exponential factor A and the apparent activation energy E_a are the functions $A(\alpha)$ and $E(\alpha)$, both of which depend on the thermal conversion α, the reaction rate equation is represented by the following equation (3):

$$\frac{d\alpha}{dt}=A(\alpha)\cdot\exp\left(-\frac{E(\alpha)}{RT}\right)f(\alpha) \qquad (3)$$

Taking the logarithm of both sides results in equation (4) below:

$$\ln\left(\frac{d\alpha}{dt}\right)=-\frac{E(\alpha)}{RT}+\ln\left(A(\alpha)\cdot f(\alpha)\right) \qquad (4)$$

By extracting the relationship between temperature T and thermal conversion α from the thermal analysis data obtained by isothermal measurement and/or dynamic measurement under multiple conditions and applying it to equation (4), $E(\alpha)$ and $\ln(A(\alpha)\cdot f(\alpha))$ at each thermal conversion α are obtained. As an example, **Fig. 1** shows the relationship between $1/T$ and $\ln(d\alpha/dt)$ obtained based on SC-DSC data measured under multiple heating rate measurement conditions for 20 wt% di-*tert*-butyl peroxide/80 wt% toluene (hereinafter 20 wt% DTBP/toluene).

A linear approximation of the $1/T$ and $\ln(d\alpha/dt)$ plots at the same α yields a straight line with slope $-E(\alpha)/R$. This plot is called the Friedman plot. Specifically, an

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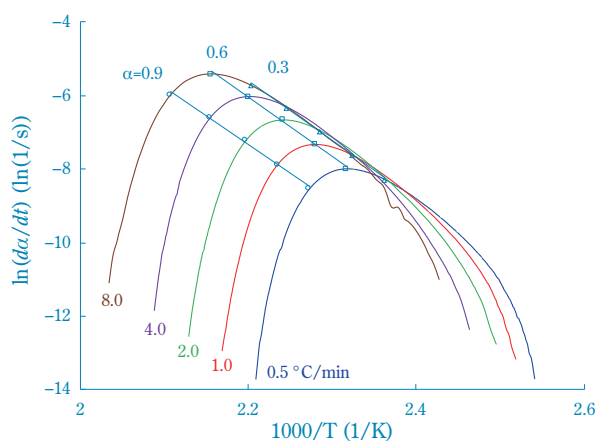
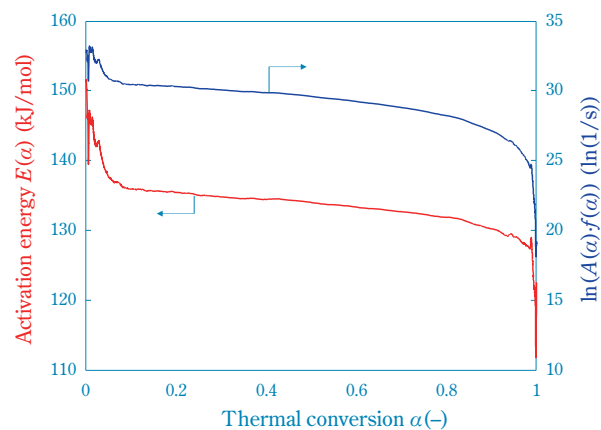**Fig. 1** Friedman plot (20 wt%DTBP/Toluene)

Fig. 2 Kinetic parameters (20 wt%DTBP/Toluene)

approximate straight line is derived from a plot of $1/T$ and $\ln(d\alpha/dt)$ at each heating rate for the thermal conversion α = 0.9 in **Fig. 1**, and $E(0.9)$ is obtained from the slope of the line and $\ln(A(0.9) \cdot f(0.9))$ from the intercept. Similarly, by obtaining a linear relationship from the Friedman plot at each thermal conversion, the relationship between the thermal conversion α and $E(\alpha)$ and $\ln(A(\alpha) \cdot f(\alpha))$ can be obtained. The relationship between $E(\alpha)$ and $\ln(A(\alpha) \cdot f(\alpha))$ at each thermal conversion is shown in **Fig. 2**.

From the heat of the reaction Q, the heat capacity C_p of the sample, and the kinetic parameters obtained in **Fig. 2**, the relationship between the thermal conversion α and the temperature rise rate at any initial temperature is obtained by the following equation (5). This relationship allows the prediction of exothermic behavior under adiabatic conditions.

$$\frac{dT}{dt} = \frac{Q}{C_p} \cdot \frac{d\alpha}{dt} = \frac{Q}{C_p} \cdot A(\alpha) \cdot \exp\left(-\frac{E(\alpha)}{RT}\right) f(\alpha) \qquad (5)$$

AKTS-THERMOKINETICS Software & THERMAL SAFETY Software (AKTS), a kinetic analysis software developed by AKTS AG, is a tool that supports kinetic analysis using the Friedman method[8]. The two criteria for judging the goodness of the kinetic parameters of this method recommended by AKTS AG are as follows[9]:

(1) The average value of the correlation coefficient between the Friedman plot and its approximate straight line over the entire inversion rate range (hereafter, the average correlation coefficient R) is −0.990 or less.

(2) The standard deviation of the heat of reaction obtained under all measurement conditions does not exceed 10% of the mean value.

The Friedman method can be applied to the evaluation of kinetic parameters for multi-step reactions where the reaction mechanism is not known or where analysis is difficult with a kinetic analysis method that assumes a reaction model[7),10)]. The advantage of this method is that it does not need to consider the problematic points presented in kinetic analysis methods that assume a reaction model (*i.e.*, goodness of the kinetic analysis is determined by the validity of the assumed model).

Background for introducing the Friedman method

Since ARC can simultaneously measure exothermic and pressure behavior under adiabatic conditions, it is considered a useful device for evaluating the thermal stability of chemical processes. However, for some substances, decomposition reactions with intense exothermic heating that exceeds the heating capacity of the adiabatic control heater of the ARC are observed, and exothermal reactions can continue in temperature ranges above the upper limit of the measurement temperature. In such cases, the quality of the ARC measurement data is low and reliable kinetic parameters cannot be determined. In some cases, reducing the amount of sample may provide measurable conditions, but the smaller amount of sample may also result in larger corrections and errors[2]. In addition, since ARC measures exothermic behavior by adiabatic tracking, if a melting point exists in the middle of the temperature rise, the effect of heat of melting (endothermic) may be observed in the exothermic behavior. It is also difficult to analyze reaction rates taking this effect into account.

On the other hand, even for substances that are difficult to measure with ARC, reliable exothermic behavior may be obtained using SC-DSC or Calve calorimeter C80 with finely tuned measurement conditions. Therefore, we thought that for substances that are difficult to measure by ARC or substances for which reaction model selection is difficult, appropriate thermal stability evaluation could be realized by analyzing reaction rates using the Friedman method based on thermal analysis data obtained from SC-DSC and C80.

Application of the Friedman method[11]

In order to properly implement the Friedman method in practice, it is necessary to ensure that the analysis method, assuming a reaction model, is consistent with the Friedman method with respect to the decomposition reactions of the substances that can be measured and analyzed. After ensuring the consistency, we studied the selection method of appropriate calorimeters depending on the substance and reaction behavior, using the compounds handled in our company.

1. Confirming the consistency of the Friedman method with an analysis method that assumes a reaction model

Using 20 wt% DTBP/toluene[12], which is the standard sample for ARC, the results of ARC measurement data analyzed by ARKS FK (hereafter, ARC/ARKS FK) and SC-DSC measurement data analyzed by AKTS (hereafter, SC-DSC/AKTS) were compared to confirm the consistency of analysis results for the two methods.

(1) ARC/ARKS FK analysis results

The results of the comparison of measured and regression data on the temperature rise curve under adiabatic conditions by applying ARKS FK to the ARC data of 20 wt% DTBP/Toluene are shown in **Fig. 3**, and the kinetic parameters obtained from the regression data

are shown in **Table 2**[11]. **Fig. 3** shows that the regression data obtained by ARKS FK reproduces the ARC data well, and that the activation energy (163.5 kJ/mol) obtained by this analysis method is close to that of the previous study (154.5 to 161.8 kJ/mol)[13]. Therefore, it is considered that the measurement and analysis are highly reliable.

(2) SC-DSC/AKTS analysis results

SC-DSC measurements of 20 wt% DTBP/Toluene were conducted at heating rates of 0.5, 1.0, 2.0, 4.0, and 8.0 °C/min. The measurement results are shown in **Table 3** and **Fig. 4**[11]. The reaction rate was analyzed by AKTS from SC-DSC measurement data. The obtained standard deviation of the heat of decomposition, 12 J/g, did not exceed 10% of the mean heat of decomposition of 298 J/g, and the mean correlation coefficient R was -0.999, which is not more than -0.990, thus the thermal analysis data met the aforementioned suitability criteria. Therefore, it was confirmed that appropriate data were obtained for 20 wt% DTBP/toluene by SC-DSC measurement in the heating rate range of 0.5 to 8.0 °C/min.
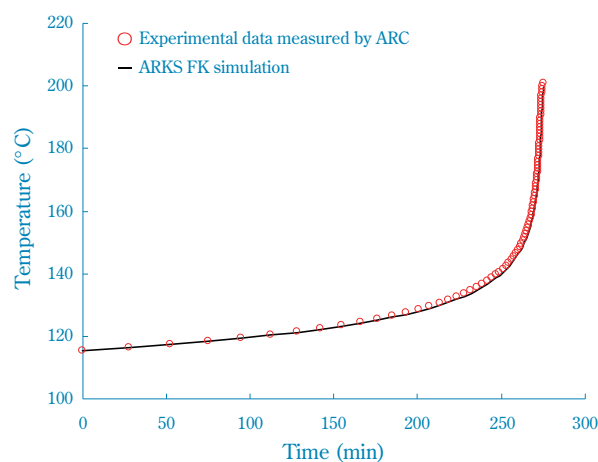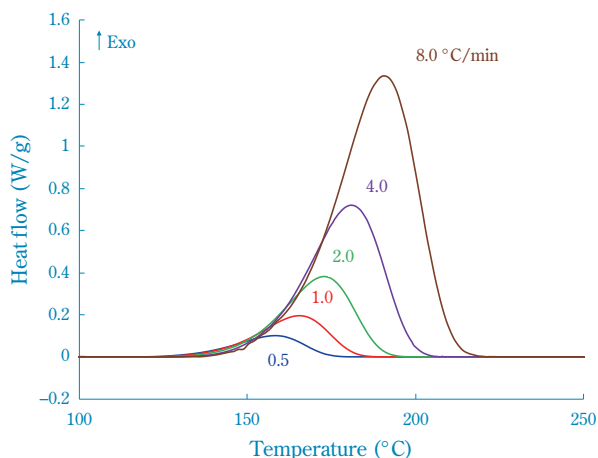

Fig. 3 Comparison of temperature curves between the experimental data measured by ARC and ARKS FK simulation[11]

Table 2 Parameters calculated by ARKS FK (20 wt%DTBP/Toluene)[11]

Parameter	Unit	Value
Reaction rate constant	ln(1/s)	38.7
Activation energy	kJ/mol	163.5
Reaction order	-	1.06
Heat of decomposition	J/g	248.3

Table 3 Measurement conditions and results of SC-DSC (20 wt%DTBP/Toluene)[11]

Sample	Cell	Sample amount (mg)	Heating rate (°C/min)	Heat of decomposition (J/g)
20 wt%DTBP/Toluene	Stainless steel	5.26	0.5	312
		5.06	1.0	304
		4.99	2.0	301
		2.13	4.0	284
		1.03	8.0	286

Fig. 4 SC-DSC data of 20 wt%DTBP/Toluene[11]
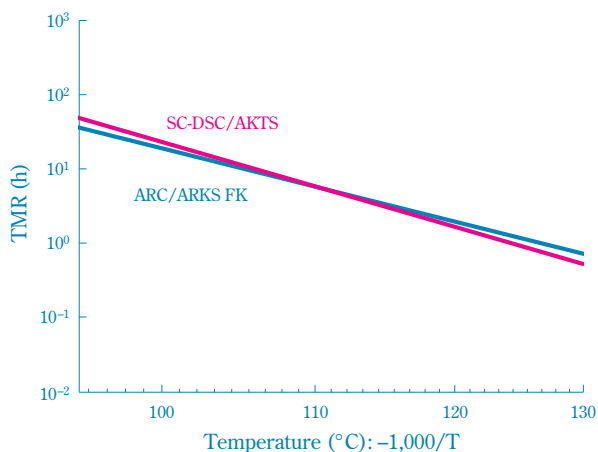
Fig. 5 Comparison of TMR versus temperature between ARC/ARKS FK and SC-DSC/AKTS simulations[11]

(3) TMR comparison of ARC/ARKS FK and SC-DSC/AKTS

A comparison of TMRs obtained from ARC/ARKS FK and SC-DSC/AKTS is shown in **Fig. 5**[11].

The close proximity of the TMRs of both methods confirms the consistency of the thermal stability evaluation results.

2. Application of the Friedman method to substances for which ARC measurement is difficult

We measured liquid compound A, handled by our company, using ARC and SC-DSC, and examined the applicability of the kinetic analysis by the Friedman method. When the compound A was measured by ARC, a temperature rise rate exceeding 10 °C/min, which is the capacity of the adiabatic control heater of our ARC, was observed even when the sample amount was reduced to 1 g (**Fig. 6**)[11]. Therefore, it was determined that analysis of this ARC measurement data would not yield reliable kinetic parameters.

On the other hand, since the full picture of exothermic behavior was obtained by SC-DSC, the kinetic analysis by the Friedman method was considered applicable. SC-DSC measurements were conducted at heating rates of 0.5, 1.0, 2.0, 4.0, and 8.0 °C/min (**Table 4, Fig. 7**)[11].

The results of SC-DSC/AKTS show that the standard deviation of 50 J/g of the exothermic value obtained by SC-DSC did not exceed 10% of the mean value of 503 J/g of the exothermic value, and the average correlation coefficient R was -0.991, not more than -0.990, thus the thermal analysis data met the suitability criteria. The obtained kinetic parameters were used to predict the temperature curve with an initial temperature of 67.5 °C, which is ADT_{24}, and the results are
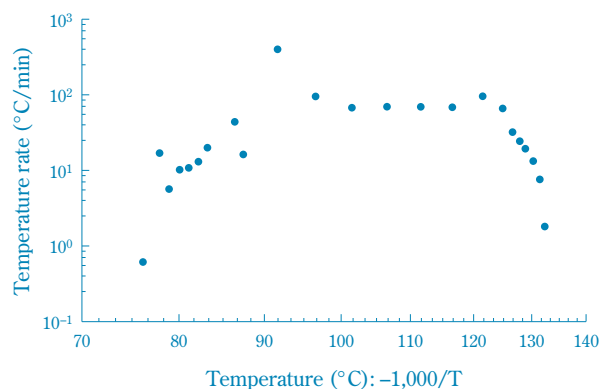
Fig. 6 Temperature rate profile versus temperature of compound A[11]

Table 4 Measurement conditions and results of SC-DSC (compound A)[11]

Sample	Cell	Sample amount (mg)	Heating rate (°C/min)	Heat of decomposition (J/g)
Compound A	Gold plate	1.36	0.5	554
		0.61	1.0	497
		0.58	2.0	422
		1.25	4.0	522
		1.07	8.0	527
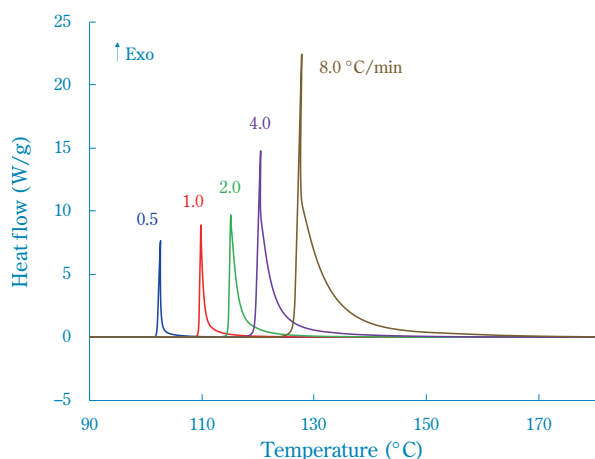
Fig. 7 SC-DSC data of compound A[11]
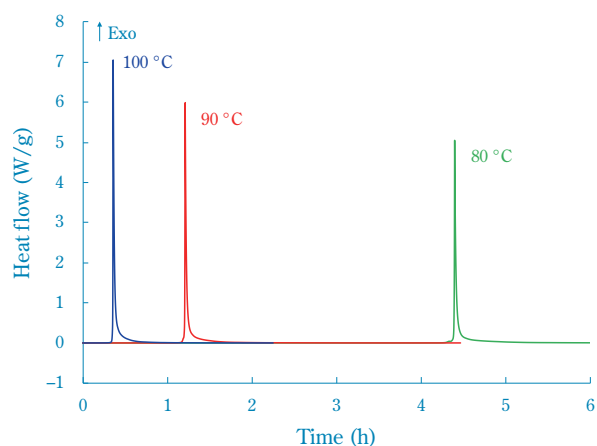
Fig. 9 Heat flow under isothermal conditions (simulation)[11]
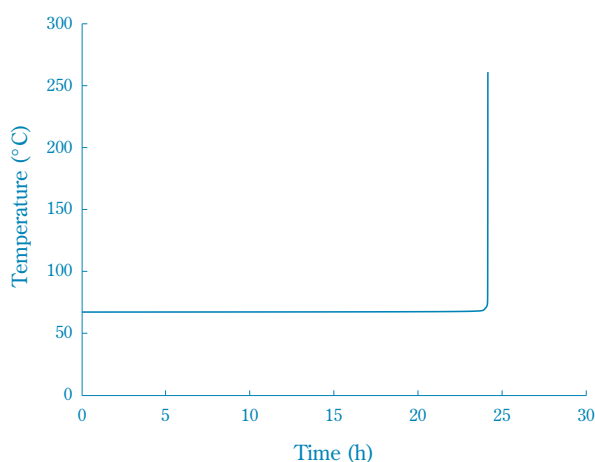
Fig. 8 Temperature curve of compound A under adiabatic conditions (simulation)[11]

shown in **Fig. 8**[11]. In addition, AKTS was used to predict the exothermic behavior under isothermal conditions (80, 90, and 100 °C), and the results are shown in **Fig. 9**[11]. The observed rapid increase in temperature and exothermic rate after a certain induction period suggests that the compound A is an autocatalytically decomposing substance. Since the thermal history of autocatalytically decomposing substances affects their thermal stability[7], control of reaction time is also important in the process of handling this compound.

This study revealed that the Friedman method based on SC-DSC measurement data can be used to analyze reaction rates even for substances that are difficult to measure with ARC to obtain correct data.

## Application of the Friedman method considering phase state of substances handled in process

There is a known case in which powder in the solid state during drying initiated a decomposition reaction and resulted in a chemical incident[14]. Determining the decomposition kinetic parameters in the solid state is important in determining safe process conditions. The aforementioned application of the Friedman method is in the liquid phase and there is no phase change, but the effect of melting may occur during exothermic behavior when evaluating thermal stability in the solid state. For such substances, it is difficult to analyze reaction rates from ARC measurement data taking into account the effect of melting, and reliable kinetic parameters cannot be determined. For some substances, SC-DSC measurements at dynamic mode or ARC measurements in Heat-Wait-Seek mode may only provide exothermic behavior in the liquid state. In such cases,

the hazard may be underestimated because the hazard is evaluated from decomposition kinetic parameters obtained in the liquid state rather than the solid state, which is the state actually being handled. Previous studies have pointed out that it may not be correct to apply decomposition kinetic parameters obtained in the liquid state to predict the exothermic behavior in the solid state of a substance that melts before or during decomposition[15]. For diaminomaleonitrile (DAMN) and compound B, handled by our company, both of which exhibit melting behavior before and during decomposition, we acquired their exothermic behaviors below their melting points using C80, which allows isothermal measurement with high sensitivity, and studied the data to obtain reliable kinetic parameters by using an AKTS-based kinetic analysis method (hereafter referred to as C80/AKTS).

1. When effects of melting appear during exotherm[16]

DAMN was subjected to SC-DSC measurement at a heating rate of 10 °C/min. The results showed a rapid exotherm after endotherm. Therefore, SC-DSC measurements were conducted at heating rates of 0.5, 1.0, 2.0, and 4.0 °C/min (**Fig. 10**)[16].

The endothermal peak observed at 10 °C/min was observed after the detection of a slight exotherm at 4.0 °C/min. At 0.5, 1.0, and 2.0 °C/min, exothermal peaks were observed at lower temperatures than the
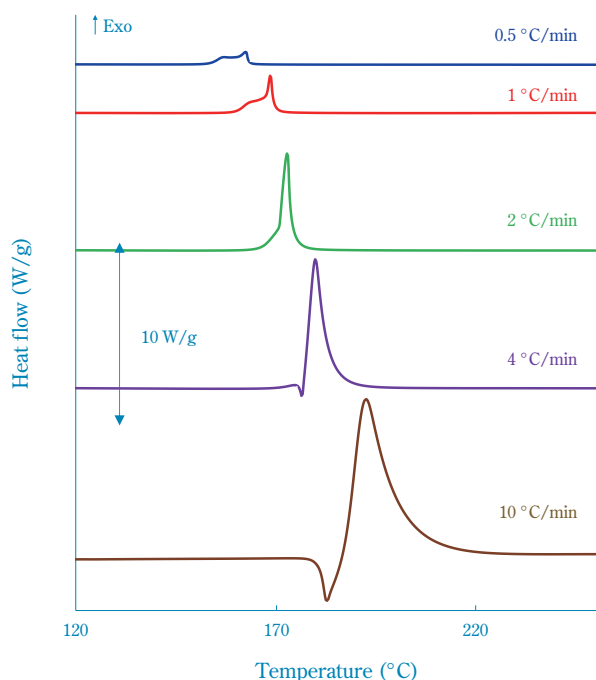
Fig. 10   SC-DSC data of DAMN[16]
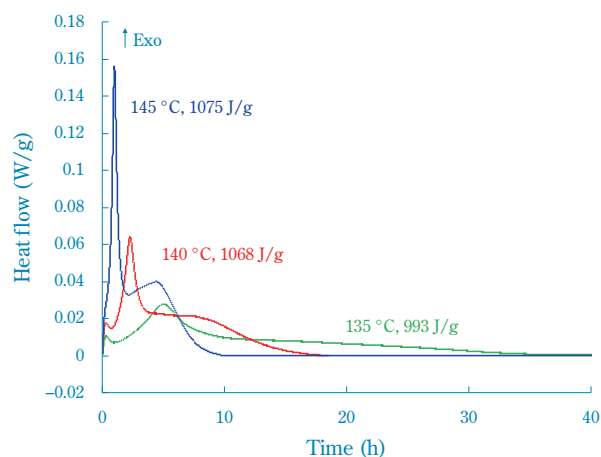
Fig. 11   C80 data of DAMN

endothermal onset temperature at 10 °C/min, and no endothermal peak was observed. Since the melting point of DAMN is 180 °C[17], the endothermal peaks observed at 4.0 and 10 °C/min are considered to be endothermal peaks due to melting. The decomposition exotherm of DAMN was found to occur both in the solid state and in the liquid state after melting. The reaction rate was analyzed from this heating measurement data by the Friedman method, and the results did not meet the suitability criteria for thermal analysis data. This is most likely due to the endothermal peaks observed at 4.0 and 10 °C/min, and we considered it necessary to analyze this on the basis of the decomposition exothermic behavior in the solid state. Therefore, isothermal measurements (135, 140, and 145 °C) by C80 below the melting point of DAMN (180 °C) were conducted to obtain data on the decomposition exothermic behavior of DAMN in the solid state (**Fig. 11**).
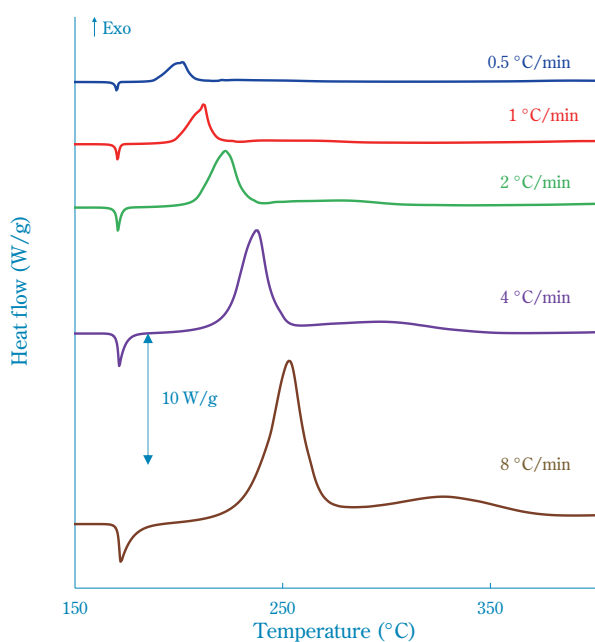
The reaction rate was analyzed by AKTS based on C80 isothermal data. The standard deviation of 46 J/g of the heat of decomposition did not exceed 10% of the mean value of 1045 J/g of the heat, and the mean correlation coefficient R was −0.993, which was not more than −0.990, thus the thermal analysis data met the suitability criteria. For substances that show melting effects during exotherm, the kinetic analysis by the Friedman method could be applied by using C80 measurement data below the melting point.

2. When exothermic behavior appears after melting[16]

Compound B was subjected to SC-DSC measurement at heating rates of 0.5, 1.0, 2.0, 4.0, and 8.0 °C/min. The results showed no exothermic behavior in the temperature range below the melting point (170 °C)
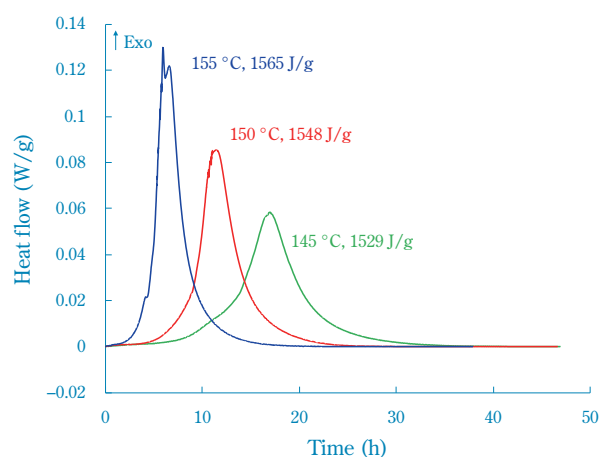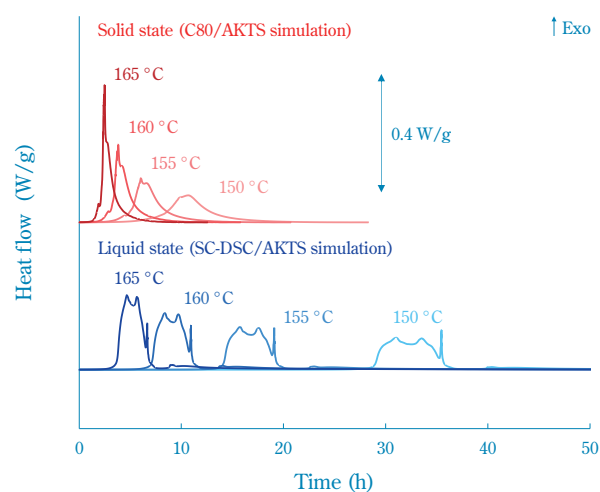
Table 5 Measurement conditions and results of SC-DSC (compound B)[16]

Sample	Cell	Sample amount (mg)	Heating rate (°C/min)	Latent heat of melting (J/g)	Heat of decomposition (J/g)
		1.82	0.5	−153	2807
		1.62	1.0	−143	2560
Compound B	Gold plate	1.59	2.0	−144	2608
		1.10	4.0	−149	2538
		0.96	8.0	−156	2501

Fig. 12 SC-DSC data of compound B[16]

Fig. 13 C80 data of compound B

Fig. 14 Comparison of heat flow under isothermal conditions between SC-DSC/AKTS and C80/AKTS simulations[16]

(**Table 5**, **Fig. 12**)[16]. On the other hand, when C80 isothermal measurements below the melting point (145, 150, and 155 °C) were conducted, exotherm was observed. The heat of decomposition was 1529 to 1565 J/g, which deviated from the SC-DSC value measured after melting (2501 to 2807 J/g) (**Fig. 13**). This suggests that compound B undergoes exothermal decomposition in both the solid state and the liquid state after melting, and that the exothermic behavior differs depending on the phase state. The results also suggest that isothermal measurements below the melting point are necessary to confirm decomposition progress in the solid state.

Next, in order to verify the validity of extrapolating the prediction of exothermic behavior in the temperature region below the melting point from the kinetic parameters obtained in the liquid state, isothermal measurements at 150 to 165 °C, below the melting point (170 °C) of the compound, were predicted from the kinetic parameters in the solid and liquid states,

respectively (**Fig. 14**)[16]. Kinetic parameters in the solid state were obtained from C80 isothermal measurement data under multiple conditions (145, 150, and 155 °C) by analyzing the reaction rate by AKTS. The standard deviation of the heat of decomposition, 18 J/g, did not exceed 10% of the mean heat of decomposition of 1547 J/g, and the mean correlation coefficient R was −0.992, which is not more than −0.990, thus the thermal

analysis data met the suitability criteria. On the other hand, the kinetic parameters in the liquid state were obtained by analyzing the reaction rate by AKTS based on the heating measurement results of SC-DSC. The standard deviation of the heat of decomposition, 121 J/g, did not exceed 10% of the mean heat of decomposition of 2603 J/g, and the mean correlation coefficient R was −0.990, which is not more than −0.990, thus the thermal analysis data met the suitability criteria.

Comparing the predicted results of exothermic behavior under isothermal conditions at 150 °C, the exothermal peak was observed after 31 hours when the kinetic parameters in the liquid state were applied, whereas the exothermal peak was observed after 10 hours when the kinetic parameters in the solid state were applied, which is shorter time to the peak than when the kinetic parameters in the liquid state were extrapolated. Similarly, shorter peak times were observed for other temperatures equal to or lower than the melting point, suggesting that analytical methods that extrapolate kinetic parameters obtained in the liquid state to the solid state may underestimate the risk. Therefore, when predicting the exothermic behavior of the solid state, it was found necessary to analyze the reaction rate and determine the kinetic parameters based on the results of isothermal measurements using C80 data below the melting point.

3. Example of application to solid mixture C, a mixture handled by our company

SC-DSC measurements were conducted to evaluate the thermal stability of mixture C, which contains compound B as a major component during the drying process (**Fig. 15**), and exotherm was observed after the endothermic peak. Based on the composition of the mixture C, this endothermic peak was determined to be due to melting, so C80 isothermal measurements (120, 125, and 130 °C) were conducted below the temperature at which the endothermal peak was detected (141 °C) (**Fig. 16**).

The C80 results indicate that the thermal decomposition reaction proceeds even in the region below the onset temperature of the endothermal peak. Therefore, the reaction rate was analyzed by AKTS using C80 isothermal measurement data for multiple conditions below the onset temperature of the endothermal peak. The standard deviation of the heat of decomposition, 19 J/g, did not exceed 10% of the mean heat of 747.7 J/g, and the mean correlation coefficient R was

−0.995, which is not more than −0.990, thus the thermal analysis data met the suitability criteria. Assuming that the mixture decomposes in the solid state without the influence of melting, the relationship between an arbitrary temperature and TMR in this case is shown in **Fig. 17**.
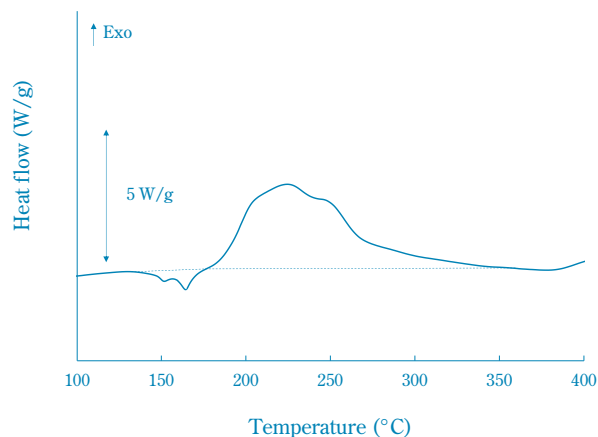

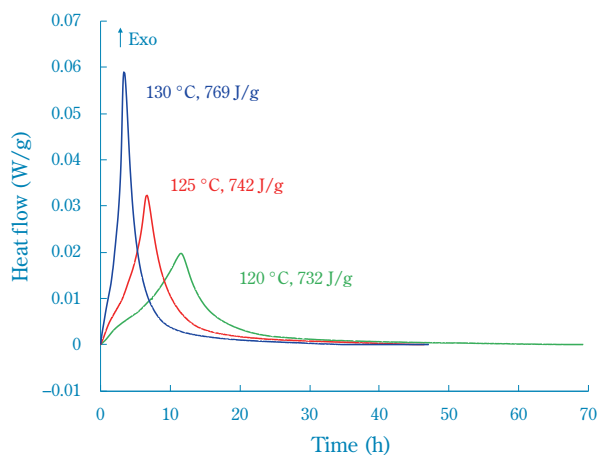**Fig. 15** SC-DSC data of mixture C (10 °C/min)
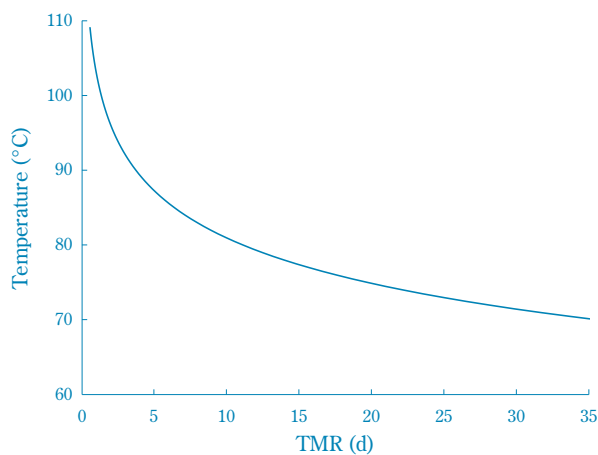

Fig. 16 C80 data of mixture C

Fig. 17 Temperature versus TMR of mixture C (simulation)

In the process of drying this mixture, it is important to determine safety measures to ensure that the mixture does not stay at a temperature for a long period of time beyond the predetermined time, in addition to controlling temperature in a way that takes into account a TMR which sufficiently allows emergency measures to be taken.

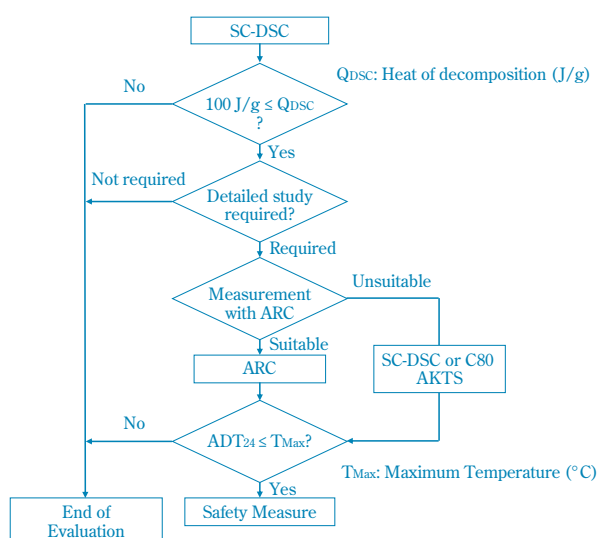## Improved thermal stability evaluation flowchart[2), 11)]

We have improved the previously applied thermal stability evaluation flowchart and have started using a new thermal stability evaluation flowchart by adding kinetic analysis by AKTS (**Fig. 18**)[11)]. In this evaluation flow, the SC-DSC is initially conducted as a screening test to determine whether a detailed study is required. If the need for a detailed study using kinetic parameters is determined, the applicability of ARC measurements in the detailed study will be examined by predicting the temperature reached under adiabatic conditions, the maximum exothermic rate, the complexity of the decomposition reaction, and the need to obtain kinetic parameters in the solid state from the SC-DSC measurements. If it is determined to be valid, the reaction rate is analyzed from the ARC measurement results and ADT_{24} is calculated. If it is determined to be not valid, SC-DSC and C80 are measured under multiple conditions and the reaction rate is analyzed by AKTS to calculate ADT_{24}. By comparing the ADT_{24} obtained from these studies with the maximum temperature T_{Max} (the higher of either the

maximum operating temperature or the heating medium temperature)[2)], the need for additional safety measures is determined.

By applying this thermal stability evaluation flowchart, it will be possible to determine the kinetic parameters for substances for which it has been difficult to determine the kinetic parameters by ARC measurements, and to study appropriate operating conditions, operating procedures, and safety measures by estimating the exothermic behavior in the process.

Conclusion

In order to prevent incidents caused by runaway reactions, the thermal stability of the substances handled must be accurately determined, and appropriate process conditions and safety measures must be planned and implemented. In this paper, we introduced measurement and analytical methods for kinetics analysis using the Friedman method, taking into account the phase state of substances handled in the process, and examples of application of the method to compounds handled by our company. The Friedman method is considered to be highly practical for complex thermal decomposition reactions because it does not require the assumption of a reaction model. In addition, it is important to select appropriate thermal analysis tests and analytical methods for thermal stability evaluation in accordance with the characteristics of the substance, handling conditions, and evaluation objectives, and to evaluate them comprehensively. We would like this paper to contribute to the prevention of incidents caused by runaway reactions.

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Fig. 18 Thermal stability evaluation flow chart[11)]

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PROFILE

Ryotaro ITOH

Sumitomo Chemical Co., Ltd.
Production & Safety
Fundamental Technology Center
Researcher