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Application News

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Thermal Analysis

Reaction Rate Analysis by Thermal Analysis

Thermal stability tests of polymer materials and medical supplies require considerable time. However, it is possible to make predictions of the reaction rate in a short time (isothermal analysis) for chemical reactions that occur over extended periods of time at comparatively low temperatures, such as decomposition (deterioration) during storage, by carrying out a reaction rate analysis with a thermal analyzer. Because activation energy, which is an indicator of the ease of a reaction, can also be obtained, it is also possible to study conditions that enable stable storage of samples. This article introduces an example in which the activation energy of the chemical reactions in decomposition (deterioration), hardening (curing), and dehydration was obtained based on data acquired by TG-DTA measurements and DSC measurements by the reaction rate analysis programs in Shimadzu LabSolutions™ TA, and isothermal analyses of the reactions were conducted.

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Principles of Reaction Rate Analysis by TG and DSC

The principles of reaction rate analysis using the results of thermogravimetry (TG) and differential scanning calorimetry (DSC) measurements are presented below.

[Case of TG]

In case a reaction rate analysis is conducted by TG, the reaction rate equation is expressed as shown in ①.

$$\frac{dx}{dt} = \mathrm{Aexp}(-\frac{\Delta E}{RT})g(x) \quad \cdots \quad ①$$

x: reaction rate
A : frequency factor
ΔE: activation energy
R: gas constant
T: absolute temperature

Here, $g(x)$ is a function which is uniquely determined by x. If measurements of the mass of a sample are conducted at different heating rates in a chemical reaction that can be expressed by this equation, reactions in which a mass increase or decrease occurs will shift to the high temperature side as the heating rate becomes larger. Therefore, if the logarithm of the heating rate is plotted against the reciprocal of the temperature at the same reaction rate (i.e., same mass reduction rate) based on the results of these measurements, a straight line is obtained. The activation energy ΔE of the reaction can be obtained from the slope of this line.

[Case of DSC]

In case a reaction rate analysis is conducted by DSC, the equation of the reaction rate of the n-th reaction is expressed as shown in ②.

$$\frac{dx}{dt} = \mathrm{Aexp}(-\frac{\Delta E}{RT})(1-x)^n \quad \cdots \quad ②$$

If a chemical reaction which can be expressed by this equation is measured at different heating rates, the endothermic or exothermic peak corresponding to that reaction will shift to the high temperature side as the heating rate becomes larger. At this time, the position of the peak in the various measurements shows a constant reaction rate, independent of the heating rate. Therefore, if the logarithm of the heating rate is plotted against the reciprocal of the peak temperature, a straight line is obtained, and activation energy ΔE can be obtained from the slope of this line.

Furthermore, in both DSC measurements and TG measurements, it is possible to analyze the reaction time t at a certain temperature by the obtaining the converted time θ. The converted time θ in case of a constant temperature increase at a heating rate Φ is expressed by ③.

$$\theta = \frac{1}{\Phi}\int_{t_0}^{t} \exp(-\frac{\Delta E}{RT})dt \quad \cdots \quad ③$$

The converted time θ can be obtained by inserting the activation energy ΔE obtained by Eq. ① or Eq. ② into Eq. ③.

Here, the converted time θ in case of a measurement under a constant temperature is expressed by ④.

$$\theta = \exp(-\frac{\Delta E}{RT})t \quad \cdots \quad ④$$

If a reaction follows the reaction rate equation, θ will be the same in all cases, regardless of whether the measurements are conducted at a uniform heating rate or under a constant temperature. Based on this fact, when a sample is held at a constant temperature T, it is possible to obtain the reaction time t until the reaction rate x at that time is achieved by inserting the activation energy ΔE or the converted time θ obtained by Eqs. ① to ③ into Eq. ④, which expresses the conversion time in case of measurement under a constant temperature. This procedure is called isothermal analysis.

Thermal Decomposition of PET

Fig. 1 shows the TG measurement results when the thermal decomposition process of PET was measured at different heating rates, and the results of a reaction rate analysis using the TG measurement results. From these results, it can be understood that the activation energy for the thermal decomposition process of PET is approximately 197 kJ/mol.

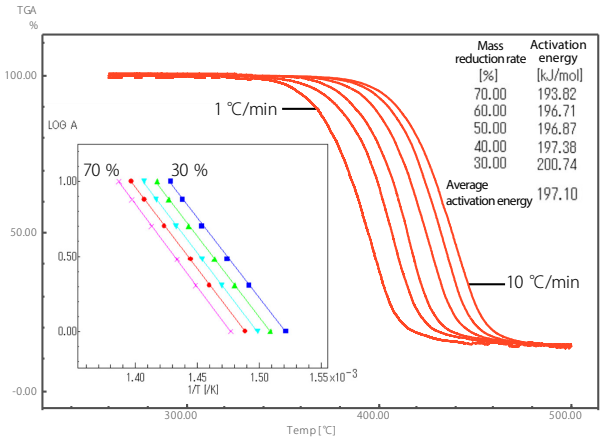

Fig. 1 TG Measurement Results of Thermal Decomposition of PET and Results of Reaction Rate Analysis

Next, Fig. 2 and Table 1 show the results of an isothermal analysis of the measurement results in Fig. 1. These results show that approximately 2.7 h is necessary for 70 % decomposition (mass reduction) when PET is held at 360 °C, but approximately 138 h is necessary for the same decomposition when the PET is held at 300 °C. Although actual measurement of the reaction under low temperature conditions would require significant time, in this analysis, the progress of the reaction at low temperature was predicted based on the TG measurement results obtained at high temperatures from 400 °C to 600 °C.

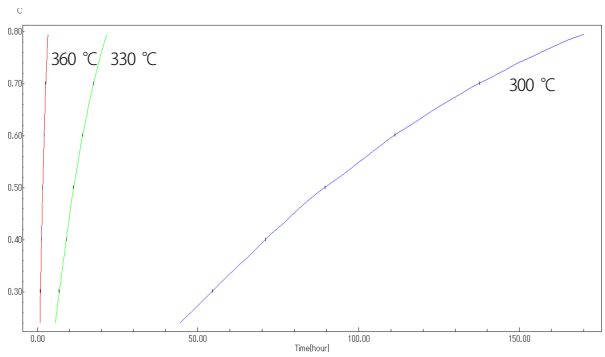

Fig. 2 Results of Isothermal Analysis of TG Measurement Results in Fig. 1

Table 1 Results of Isothermal Analysis of TG Measurement Results in Fig. 1

Activation energy	197.10kJ/mol			
Analysis temperature		300.00°C	330.00°C	360.00°C
Reaction time [hour]				
	0.30	5.46x10	6.98	1.08
	0.40	7.12x10	9.11	1.42
	0.50	8.97x10	1.15x10	1.78
	0.60	1.11x10^2	1.42x10	2.21
70 % reduction →	0.70	1.38x10^2	1.76x10	2.74

Curing of Epoxy Resin

DSC measurements at different heating rates were carried out for a two-part liquid epoxy resin adhesive, in which hardening (curing) proceeds with time after the two liquids are mixed, and a reaction rate analysis and isothermal analysis were conducted. Fig. 3 shows the DSC measurement results, and Fig. 4 and Table 2 show the results of the reaction rate analysis and the isothermal analysis.

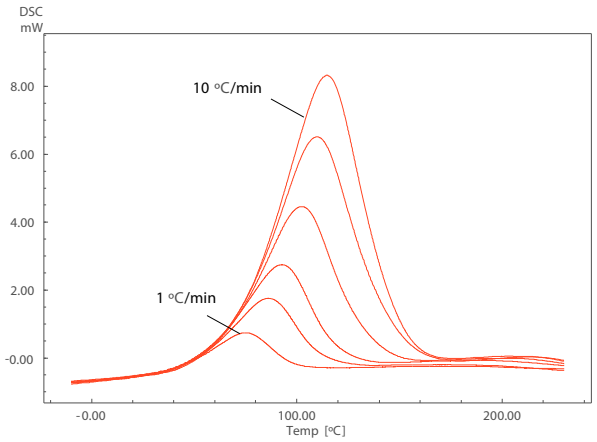

Fig. 3 DSC Measurement Results of Epoxy Resin

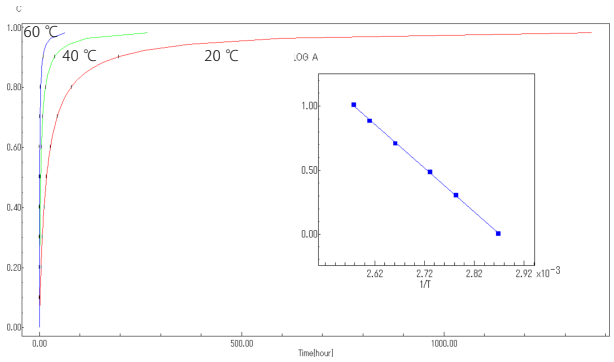

Fig. 4 Results of Reaction Rate Analysis and Isothermal Analysis of DSC Measurement Results in Fig. 3

Table 2 Results of Reaction Rate Analysis and Isothermal Analysis of DSC Measurement Results in Fig. 3

Activation energy	62.21kJ/mol			
Analysis temperature		20.00°C	40.00°C	60.00°C
Reaction time [hour]				
	0.1	1.88	3.69x10^{-1}	8.78x10^{-2}
	0.2	4.28	8.38x10^{-1}	2.00x10^{-1}
	0.3	7.43	1.45	3.47x10^{-1}
	0.4	1.17x10	2.30	5.47x10^{-1}
	0.5	1.79x10	3.51	8.36x10^{-1}
	0.6	2.75x10	5.39	1.28
	0.7	4.42x10	8.67	2.06
	0.8	7.97x10	1.56x10	3.72
90 % curing →	0.9	1.97x10^2	3.86x10	9.19

From the results of the reaction rate analysis, the activation energy of the curing reaction of the epoxy resin is approximately 62.2 kJ/mol. The results of the isothermal analysis showed that 90 % progress of curing requires 197 h when the sample is held at 20 °C. This analysis makes it possible to evaluate the optimum curing temperature and time for thermosetting resins, which are important in actual industrial processes.

Dehydration of Copper Sulfate Pentahydrate

Copper sulfate pentahydrate contains five water molecules, which dehydrate in the three stages of 2 molecules, 2 molecules, and 1 molecule when heated. Because these respective dehydration reactions are endothermic reactions, the dehydration process was measured by DSC at different heating rates, and a reaction rate analysis was carried out. Fig. 5 shows the DSC measurement results, and Fig. 6 shows the results of the reaction rate analysis.

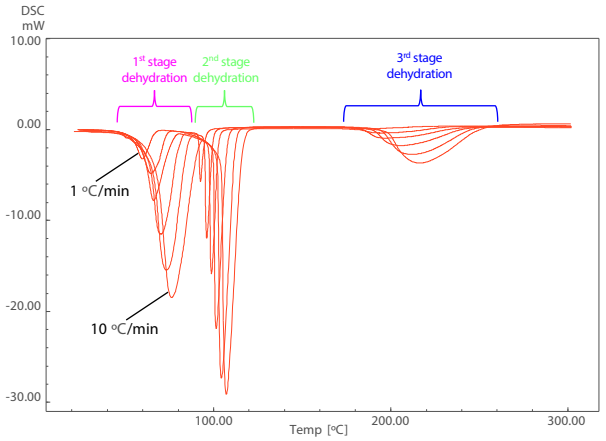

Fig. 5 DSC Measurement Results of Copper Sulfate Pentahydrate

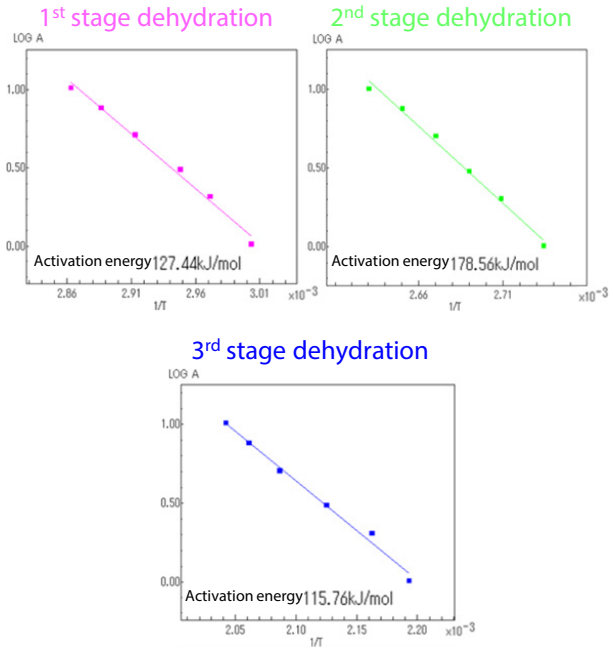

Fig. 6 Results of Reaction Rate Analysis of DSC Measurement Results in Fig. 5

From Fig. 5, it can be understood that the dehydration reaction occurs in three distinct stages. The results of the reaction rate analysis of the dehydration reactions in Fig. 6 show that the dehydration reactions have different activation energies of approximately 127.4 kJ/mol for the 1st stage, 178.6 kJ/mol for the 2nd stage, and 115.8 kJ/mol for the 3rd stage, indicating that there are differences in the bonding states of the respective water molecules.

Conclusion

In this article, the reaction time and activation energy of various types of reactions were obtained by reaction rate analyses. The progress of a reaction at desired points in time when a sample is held at a certain temperature can be determined by conducting an isothermal analysis, and the external energy necessary to induce the reaction can also be determined by obtaining the activation energy of that reaction. Based on these results, it is possible to study stable storage methods for samples under various external environmental conditions such as light and temperature, and make predictions of the reaction rate of chemical reactions that occur over long periods of time, such as deterioration due to oxidation, based on the results of short duration measurements.

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