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Application News

Thermal Analysis

No. T158A

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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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.

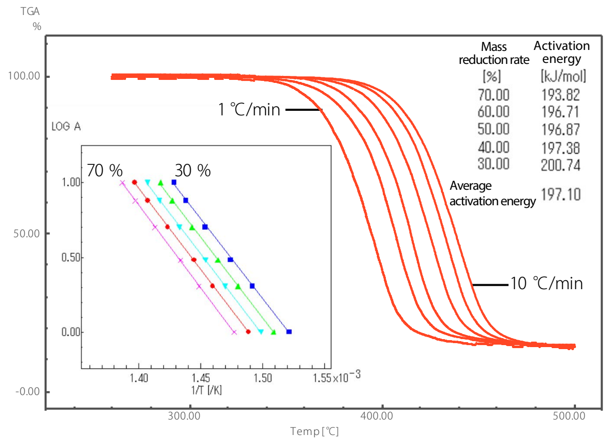

Fig. 1 TG Measurement Results of Thermal Decomposition of PET and Results of Reaction Rate Analysis

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.

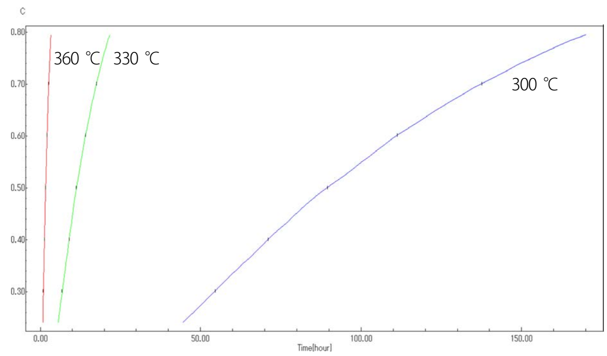

Fig. 2 Results of Isothermal Analysis of TG Measurement Results in Fig. 1

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.

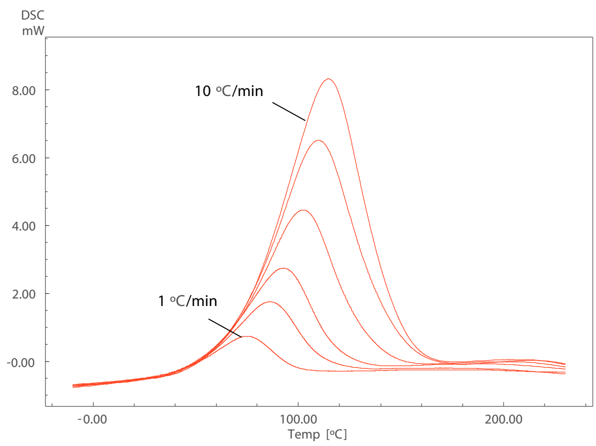

Fig. 3 DSC Measurement Results of Epoxy Resin

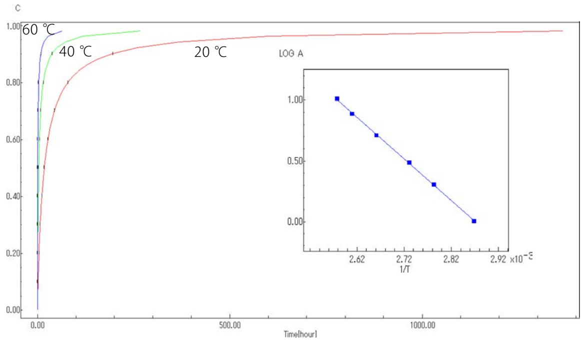

Fig. 4 Results of Reaction Rate Analysis and Isothermal Analysis of DSC Measurement Results in Fig. 3

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	3.69×10^{-1}	8.78×10^{-2}
	0.2	4.28	8.38×10^{-1}	2.00×10^{-1}
	0.3	7.43	1.45	3.47×10^{-1}
	0.4	1.17x10	2.30	5.47×10^{-1}
	0.5	1.79x10	3.51	8.36×10^{-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	1.97×10^{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. 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.

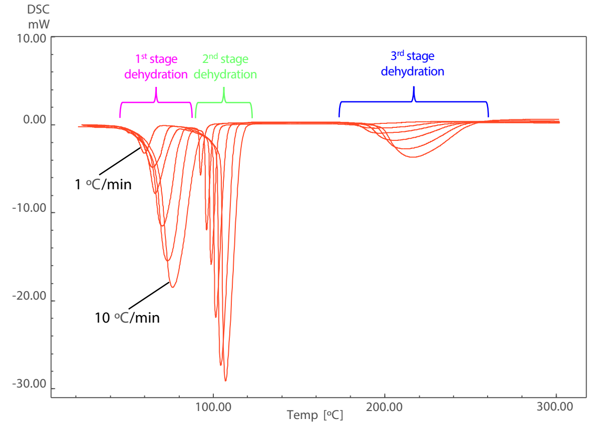

Fig. 5 DSC Measurement Results of Copper Sulfate Pentahydrate

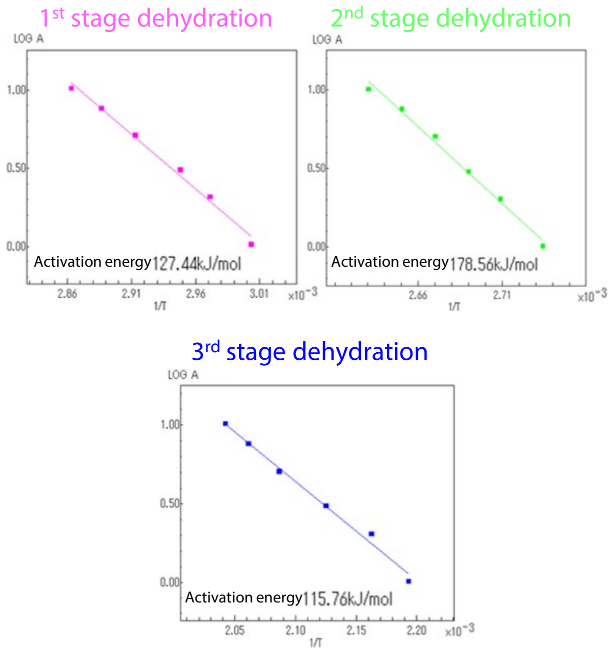

Fig. 6 Results of Reaction Rate Analysis of DSC Measurement Results in Fig. 5

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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