Kinetics Analysis of Insulating Material

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Yutaka Ichimura
Application Engineering Section

1.　Introduction

Kinetics analysis of thermal decomposition TG data has attracted attention as a way to evaluate the heat resistance of polymer material quickly. Several methods have been reported, including the Ozawa method, which is widely used for reaction kinetics analysis. It can obtain the chemical reaction activation energy and the constant temperature degradation time (the time until the reaction reaches a certain level at a constant temperature) from TG data at various heating rates. In this brief, polymer insulation material is analyzed using the Ozawa method.

2.　Kinetics Analysis using TG Measurements

Figure 1 shows the dehydration reaction data for calcium oxalate at four heating rates. As can be seen, the higher the heating rate, the more the TG curve shifts to a higher temperature. The Ozawa method transforms this temperature shift to a formula. It assumes that the reaction is a single reaction. When a one-step weight loss occurs as shown in Figure 1, reaction rate analysis is often performed. However, the thermal decomposition reaction of polymer materials is not a single reaction in many cases. In these cases, the heat resistance can be evaluated by performing the analysis assuming that the initial stage of the thermal decomposition reaction is a singular reaction section.
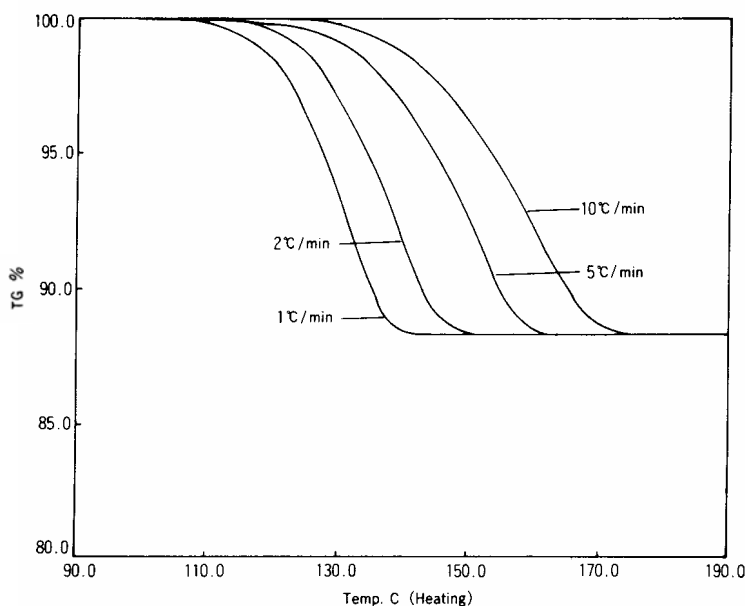

Figure 1　Dependence of Heating Rate of Calcium Oxalate Dehydration Reaction

Figure 2 shows the TG curves for the polymer insulation material measured at different heating rates. Figure 3 shows the 100% to 95% portion of this data analyzed using the Ozawa method. The activation energy is 113 kJ/mol. Furthermore, we know that when the temperature is held constant at 150°C, it takes 0.54 days for this reaction to advance 20%.
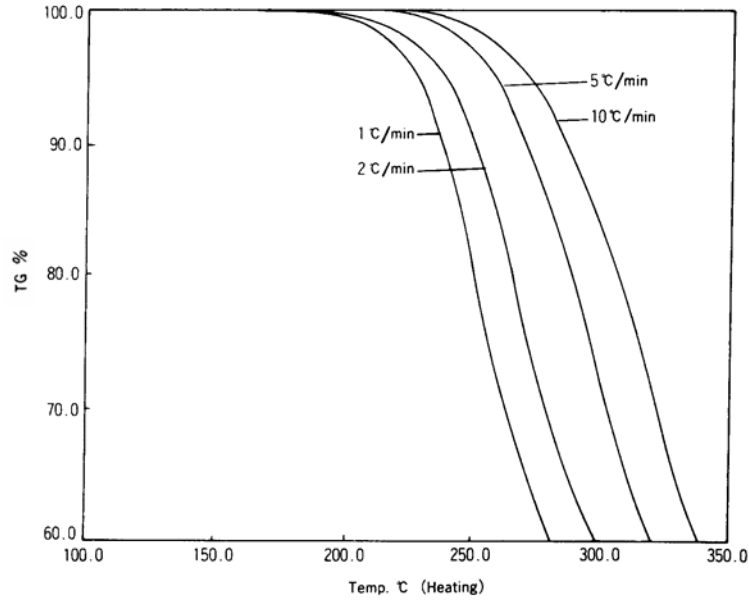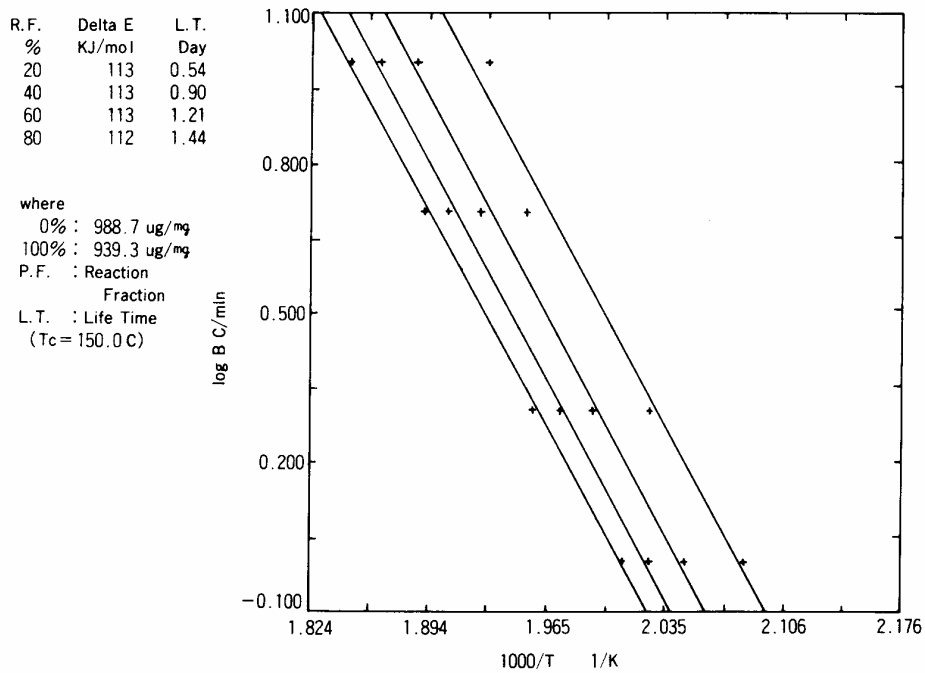

Figure 2   TG results for Polymer insulation material

Figure 3   Kinetic Analysis results

3. Ozawa Method of Kinetic Analysis

3-1. Determination of Activation Energy

When a reaction follows the Arrhenius law, the reaction rate can be expressed using the following formula.

$$\frac{dx}{dt} = A\exp(-\frac{\Delta E}{RT}) \cdot f(x) \quad \cdots\cdots (1)$$

Where,
- x : Reaction quantity
- t : Time
- A : Frequency Factor
- ΔE : Activation Energy
- R : Gas constant
- T : Absolute Temperature
- f(x) : Function of x

Because the heating rate is constant in TG measurements, the following equation is formed.

$$\frac{dT}{dt} = B \quad \cdots\cdots (2)$$

Where, B : Heating rate

When equation 2 is inserted into equation 1, the following equation is formed through separation of variables and integration.

$$\int_{x_0}^{x} \frac{dx}{f(x)} = \frac{A}{B}\int_{T_0}^{T} \exp\left(-\frac{\Delta E}{RT}\right) dT \quad \cdots\cdots (3)$$

When equation 3 is integrated by parts, the following equation is formed.

$$F(x) - F(x_0) = \frac{A\,\Delta E}{B \cdot R}\left\{ P\left(\frac{\Delta E}{RT}\right) - P\left(\frac{\Delta E}{RT_0}\right)\right\} \quad \cdots\cdots (4)$$

Where, $F(x) = \int \frac{dx}{f(x)}$

$$P(y) = \frac{e}{y} - \int_{y}^{\infty} \frac{e}{y}dy$$

When item 1 is much larger than item 2 on the right side of equation 4 and x_1 is set as $x_0=0$, a constant results.

$$\frac{A \cdot \Delta E}{B \cdot R} P\left(\frac{\Delta E}{RT}\right) = const.$$

P(y) can be approximated by the following formula.

$$\log P\ (y) \fallingdotseq -2.315 - 0.4567y \quad (20 < y < 60) \quad \cdots\cdots (5)$$

Equation 5 is then applied to equation 4.

$$-\log B - 0.4567\frac{\Delta E}{RT} = \text{const.} \quad \cdots\cdots (6)$$

The following equation is formed by setting items corresponding to x_1 as B_1, T_1, items corresponding to x_2 as B_2, T_2, and so on for a certain reaction amount.

$$-\log B_1 - 0.4567\frac{E}{RT_1} = -\log B_2 - 0.4567\frac{E}{RT_2}$$

$$= \ldots\ldots = \text{const.} \quad \cdots\cdots (7)$$

The activation energy (E) is obtained from the slope of the plot of logB, the data of the various heating rates (B), against 1/T.

3.2 Determination of Constant Temperature Degradation Time

At a constant temperature, T is not dependent on time, so the following equation is formed when equation 1 is integrated.

$$\int_{x_0}^{x}\frac{dx}{f\ (x)} = A\int_{t_0}^{t_0+\tau} \exp\ \left[-\frac{\Delta E}{RT}\right]\ dt$$

$$= A\exp\ \left[-\frac{\Delta E}{RT}\right]\ \cdot\ \tau \quad \cdots\cdots (8)$$

where τ is the time for the change from reaction x_0 to x.

The following equation is formed from equation 3 and equation 8.

$$\tau = \frac{\displaystyle\int_{T_0}^{T} \exp\ \left(\frac{\Delta E}{RT}\right)\ dT}{B\exp\ \left(-\frac{\Delta E}{RT}\right)} \quad \cdots\cdots (9)$$

Constant temperature degradation time is calculated from equation 9.