

Measurement of Activation Energy Using Reaction Rate Analysis Program

Activation energy must be measured for the evaluation of thermal stability of heat resisting high polymer materials, composite materials, and pharmaceuticals or for the quantitative evaluation of curing reaction of epoxy resins. Reaction rate parameters, including activation energy and reaction order, can be determined by thermal analysis.

These parameters can be calculated easily and quickly from the variation of decomposition temperature depending on heating rates or from the change of endothermic or exothermic temperature, using specimen heating rate as a parameter.

Decomposition reaction is the subject of reaction rate analysis with thermo-gravimetric analyzer (TGA). Chemical reaction that has no gravimetric change can be measured with a differential scanning calorimeter (DSC).

The following is an example of some measurements of the activation energy of various chemical reactions, using the reaction rate analysis program which offers an easy way for calculation of reaction rate parameters from data obtained with TGA and DSC.

Principle

[TG] The following equation is basically used in reaction rate analysis with TG

$$\frac{dx}{dt} = A \cdot \exp\left(-\frac{\Delta E}{RT}\right) \cdot g(x)$$

x: reaction ratio R: Gas constant
 A: Frequency factor T: Absolute temperature
 ΔE: Activation energy g(x): an unconditionally obtainable function

Time θ converted to the time in constant rate heating is expressed by the following equation

$$\theta = \frac{1}{\phi} \int_{T_1}^T \exp\left(-\frac{\Delta E}{RT}\right) \cdot dT$$

θ in constant rate heating is equal to that of constant temperature heating as long as the reaction value is constant.

Plotting the logarithms of a reciprocal number for the temperature at a given reaction ratio versus the heating rate produces a straight line, from the inclination of which activation energy can be determined.

High polymer materials

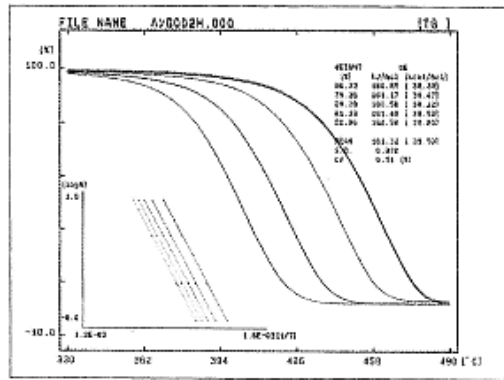


Fig.1 Activation Energy of Decomposition Reaction of Nylon-6

[DSC]

Reaction speed for n-order reaction is expressed by the following equation in case of DSC.

$$\frac{dx}{dt} = A \cdot \exp\left(-\frac{\Delta E}{RT}\right) (1-x)^{n-1}$$

where n represents a reaction order.

DSC measurement of a chemical reaction expressed by the above equation at different heating rates results in the shifting of exothermic and endothermic peaks of each chemical reaction toward the higher temperature side as the heating rate increases.

Plotting the logarithms of the reciprocal number for the peak temperature and the heating rate produces a straight line as the peak points have an almost constant reaction ratio. Activation energy is determined by the inclination of this straight line.

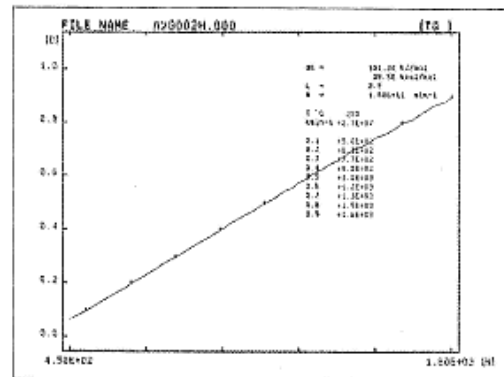


Fig.2 Estimation of Decomposition of Nylon-6

Fig 2 is a plotted curve of the decreasing ratio at each temperature versus the time needed for the decrease both calculated from the activation energy and reaction order in Fig.1 It is known from this plotted curve that 500 hours is spent for 10% decrease at 250 °C.

Inorganic materials

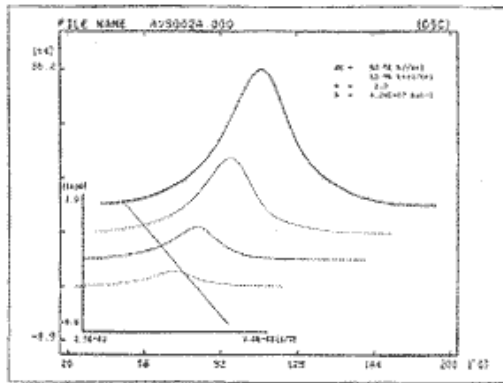


Fig.5 Activation Energy at Curing Reaction of Epoxy Resin

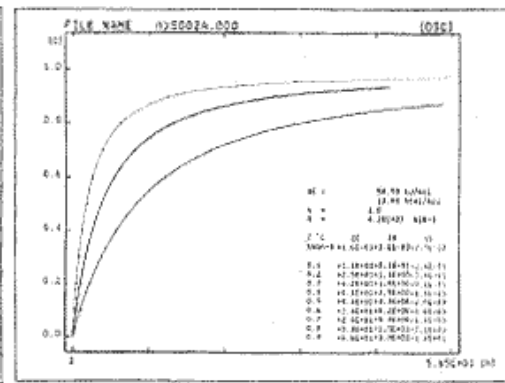


Fig.6 Curing Time of Epoxy Resin

Dehydration reaction

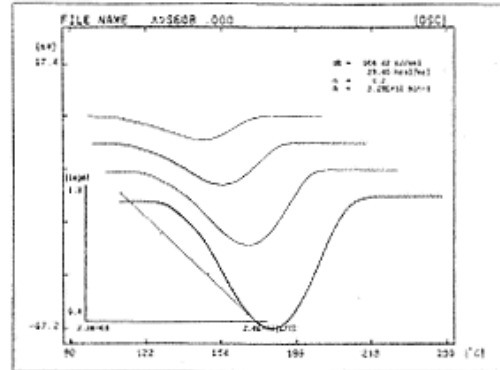


Fig.7 Activation Energy at Decomposition Reaction of Sodium Hydrogen Carbonate

* Please be advised that data obtained before the implementation of the current Weights and Measures Law may be presented in terms of gravimetric unit.



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