

DIFFERENCE EQUATION METHOD OF ANALYSING ISOTHERMAL THERMOGRAVIMETRIC DATA

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Difference equation method has been suggested to evaluate the kinetic parameter of the degradation of polymers under isothermal condition. The method is simple and applicable to degradation process for any value of n , the reaction order. By using one simple method all the kinetic parameters cannot be obtained in other methods only by difference equation.

In the study of the thermal degradation of polymers, the weight change of a sample is recorded as a function of time. Madorsky [1] has proposed a method for obtaining the kinetic parameters, in which the rate constant is taken as proportional to the maximum rate of degradation at a particular temperature. The method suffers from the limitation that, while the activation energy can be estimated, this is difficult in the case of the pre-exponential factor and the order of reaction.

In the present communication, a method of difference equations [2, 3] has been used in the kinetic analysis of the oxidative degradation of polystyrene and styrene-acrylonitrile copolymer.

Theoretical considerations

A typical difference equation can be expressed in the general form

$$X_{t+1} = F(X_t)$$

where X_t is a quantity at time t , and X_{t+1} is the quantity at time $(t + 1)$, where unity represents a unit of time.

In the thermal decomposition of materials, the rate of decomposition has the following form:

$$-\frac{dW}{dt} = kW^n \quad (1)$$

where W is the fractional residual weight of the sample, t is the time, and k and n are the rate constant and the order of reaction, respectively.

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Using eq. (1), the difference equations for zero, first and n th (where $n > 1$ or $n < 1$) order reactions are as follows [4],

$$W_{t+\Delta t} = W_t - k\Delta t \text{ (zero-order)} \quad (2a)$$

$$W_{t+\Delta t} = W_t e^{-k\Delta t} \text{ (1st-order)} \quad (2b)$$

$$\frac{1}{(W_{t+\Delta t})^{n-1}} = \frac{1}{W_t^n} + (n-1)k \cdot \Delta t \text{ (nth-order)} \quad (2c)$$

where W_t is the fractional residual weight at time t , and $W_{t+\Delta t}$ is the value at $(t + \Delta t)$. From a plot of the fractional residual weights at time $(t + \Delta t)$ as a function of the residual weights at time t , according to eqs (2a), (b) or (c), k and n can be evaluated.

The values of A and ΔE can be calculated from a plot of $\log k$ vs. $\frac{1}{T}$ as usual according to the Arrhenius equation, where A , ΔE and T are the pre-exponential factor, the activation energy and the absolute temperature. Thus, the kinetic parameters ΔE , n and A are determined from isothermal analytical data.

The order of reaction, n , was evaluated for the process using relation (3), given by Chatterjee [5]:

$$n = \frac{\Delta \log \left(-\frac{dW}{dt} \right)}{\Delta \log W} \quad (T = \text{constant}) \quad (3)$$

The method uses two TG curves from two different weights of test samples.

Experimental

Polystyrene (general-purpose granules) was obtained from Polychem. (India) Ltd., Bombay, and was used without purification in powder form. Styrene-acrylonitrile powder was also used without purification.

A 50 mg sample of polymer was weighed into a platinum crucible and the residual weights were recorded regularly every 30 minutes by a chemical balance in a constant-temperature furnace.

Results and discussion

The results of isothermal thermogravimetry at various temperatures (fractional residual weights) are plotted as a function of time in Figs 1 and 2 for polystyrene and styrene-acrylonitrile copolymer (SAN). The residual weights at time $(t + \Delta t)$ were plotted as a function of residual weight at time t , as shown in Figs (3a) and (3b). The TG data for polystyrene and SAN fitted well with eq. (2b). The slopes

Table 1
Results of kinetic analysis by various methods

Polymer	From eq. (2)			From the Madorsky method ΔE , kcal/mole	From the Chatterjee method n	Literature values	
	n	ΔE , kcal/mole	A , min^{-1}			n	ΔE , kcal/mole
Polystyrene	1	30	3.86×10^{10}	34.3	1	0 to 1* [6]	29 ± 2 [7]
SAN	1	29.8	5.5×10^9	23.49	1		

* The value refers to the degradation in vacuum.

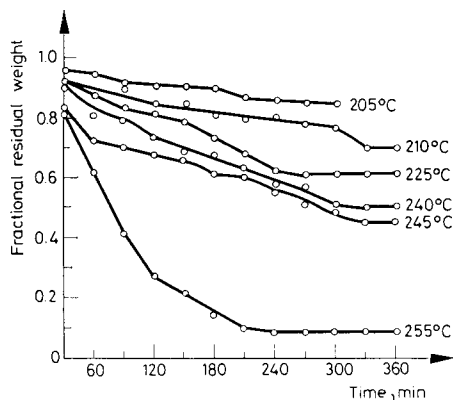


Fig. 1. TG curves given by polystyrene at different temperatures (degradation in air)

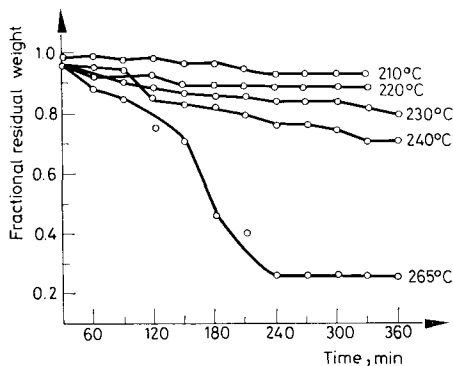


Fig. 2. TG curves given by SAN at different temperatures (degradation in air)

(hence k) were determined by the least squares method for the two samples at various temperatures. The values of k thus obtained were plotted as a function of $\frac{1000}{T}$ to evaluate A and ΔE (in kcal/mole). The results are shown in Table 1.

The values of ΔE obtained by the Madorsky method and n by the Chatterjee method are given in column 2 of Table 1.

As may be seen from the above procedure, the method described in this paper is simple, and applicable to a degradation process for any value of n . By using one

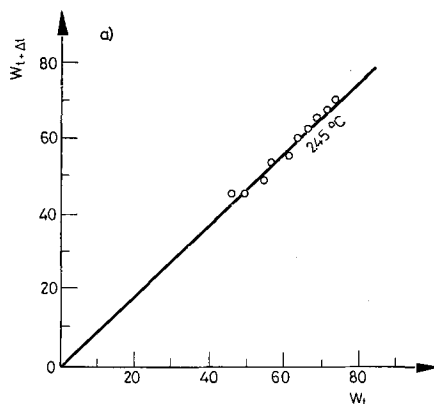


Fig. 3(a). Plot of W at $(t + \Delta t)$ vs. W at t for polystyrene

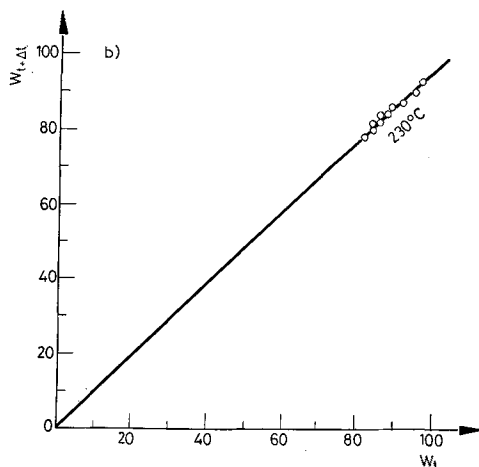


Fig. 3(b). Plot of W at $(t + \Delta t)$ vs. W at t for SAN

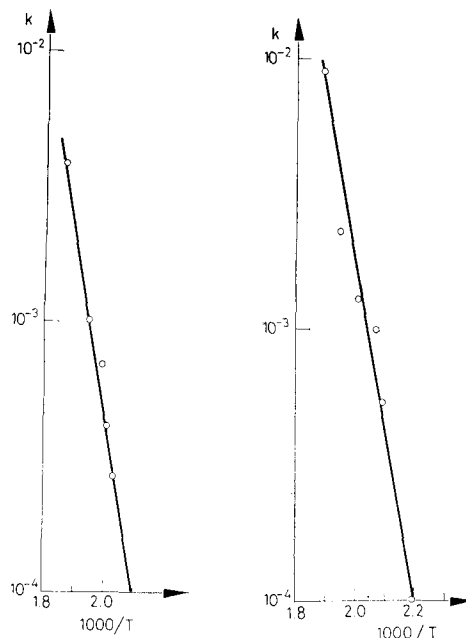


Fig. 4. Logarithm of the rate of degradation of polystyrene in air as a function of absolute temperature

Fig. 5. Logarithm of the rate of degradation of SAN in air as a function of absolute temperature

simple method, all the kinetic parameters cannot be obtained in other methods than the difference equation method.

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