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A COMPACT METHOD FOR THE KINETIC ANALYSIS OF ISOTHERMAL THERMOGRAVIMETRIC CURVES

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ABSTRACT

A new method of analysis for the determination of kinetic parameters from isothermal weight loss curves is proposed. By applying this compact method it is possible to follow the change of the order of a reaction with temperature and the dependence of the activation energy on the extent of the reaction from a single diagram. The values of the kinetic parameters determined by this method are in very good agreement with the values obtained by various methods of thermogravimetric analysis.

INTRODUCTION

When detailed information on the thermal degradation behaviour of any substance (polymer, composite, coal, etc.) is required, isothermal thermogravimetry becomes one of the major techniques to be applied. The kinetic parameters determined by dynamic thermogravimetry are the overall averages of the relevant parameters for a series of reactions taking place in the temperature and conversion intervals studied. The determination of individual kinetic parameters, like reaction order, activation energy and pre-exponential factors at certain conversions or some specified temperatures, is possible through an isothermal weight loss study.

A number of methods have been developed for the kinetic analysis of isothermograms and these are briefly outlined and compared in our previous paper [1]. In this communication a more compact method is proposed for the determination of kinetic parameters and its advantages over the existing methods are discussed.

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If we write the general equation relating the rate of conversion to the fraction remaining:

$$\frac{dC}{dt} = k(1 - C)^n \tag{1}$$

(where C is the conversion with respect to initial weight of the sample, k the reaction rate constant, and n the order of the reaction) by substituting the Arrhenius expression instead of k one obtains

$$\frac{dC}{dt} = A \exp(-E/RT)(1 - C)^n \tag{2}$$

which, by taking the logarithm of both sides can be cast into

$$\ln(dC/dt) = \ln A - E/RT + n \ln(1 - C) \tag{3}$$

As can be seen from eqn. (3), $\ln(dC/dt)$ is a first order function of both $1/T$ and $\ln(1 - C)$. In order to take into account both variables (i.e. temperature and conversion) simultaneously, $\ln(dC/dt)$ values can be plotted against the combined form of these variables, i.e. $1/T + \ln(1 - C)$. At this point $1/T$ should be multiplied by 10^3 in order to bring the order of magnitudes of both terms to the same level.

A plot of $\ln(dC/dt)$ vs. $10^3/T + \ln(1 - C)$ should give two families of lines with one group having positive and the other group with negative slopes. According to eqn. (3) slopes of the lines (lines with negative slopes) corresponding to certain conversion values will give the $-E/R$ values for the specific conversion considered whereas the slope obtained from the line (lines with positive slopes) drawn for a certain temperature will directly give the order of the reaction for that temperature.

When intercepts of these lines are considered, it is possible to obtain two sets of values from the two families of lines. The intercept of the lines drawn for constant temperatures will be equal to $\ln A + n \ln(1 - C)$, whereas the intercept obtained from the lines corresponding to various conversions will give the $\ln A - E/RT$ value. Since n and E values were previously determined from the slopes, now it is possible to calculate the pre-exponential factor, A, from the intercepts corresponding either to a certain temperature and/or conversion value. Moreover, the natural logarithm of A for zero conversion is identical to the intercept value of the line drawn for zero conversion, since the $\ln A + n \ln(1 - C)$ term becomes $\ln A$ at $C = 0$.

The results of the above-mentioned method of analysis applied to the isothermal weight loss curves of a poly(vinyl chloride) (PVC) sample heated at four different temperatures are given in the following.

EXPERIMENTAL

Detailed information on the characteristics of the PVC sample used in this study [2] and experimental details of the thermogravimetric work [3] have already been published elsewhere.

RESULTS AND DISCUSSION

The isothermal weight loss curves given in fig. 1 of a preceeding paper [1] are used in the kinetic analysis. The two families of lines mentioned in the Introduction are constructed by plotting $\ln(dC/dt)$ values against the combined variables $\ln(1-C)+10^3/T$, and are given in Fig. 1. As has already been described in the Introduction, and as indicated by the lines, four lines with positive slopes correspond to the four temperatures, i.e. 240, 250, 260 and 270 °C, and the seven lines with negative slopes correspond to conversions ranging from 0.0 to 32.5%. Since in the time period (200 min) covered in this study, 32.5% conversion is not reached at 240 °C, only three points were available to draw the line at this conversion.

The order of the reaction, activation energy and pre-exponential factor computed from the slopes of the lines in Fig. 1 are listed in Table 1. As can be seen from this table, it is possible to determine a wide range of kinetic parameters by using this method of analysis. The values of the kinetic parameters determined by this method are in good accordance with the

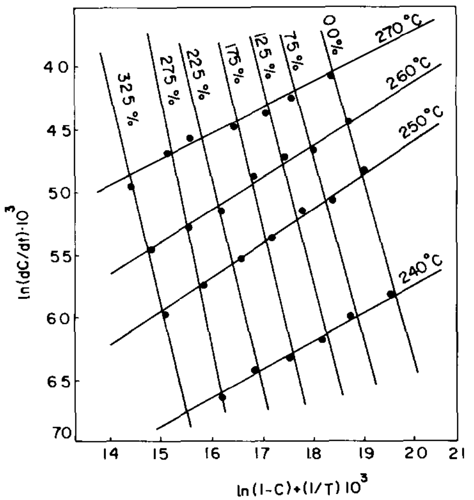

Fig. 1. Plot of $\ln(dC/dt)$ vs. $\ln(1-C)+10^3/T$.

TABLE 1

The reaction order, activation energy and pre-exponential factor determined for the thermal degradation of PVC according to the compact method proposed in this paper

Temp. (°C)	Order (n)	Conversion (c)	E (kcal mol^{-1})	$A \times 10^{-10}$	Corr [a]
240	2.24			0.95	0.986
250	2.64			0.72	0.983
260	2.57			0.73	0.971
270	1.67			3.67	0.982
		0.0	29.78	1.82	0.980
		2.5	30.63	2.21	0.982
		7.5	31.18	1.91	0.980
		12.5	32.50	2.67	0.965
		17.5	34.56	5.95	0.981
		22.5	34.25	4.39	0.987
		27.5	40.17	4.32	0.995

[a] Correlation coefficients of the lines in Fig. 1.

values computed by other methods [1]. This method comprises all the advantages pertinent to other existing methods of kinetic analysis.

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