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A COMPARISON OF VARIOUS ISOTHERMAL THERMOGRAVIMETRIC METHODS APPLIED TO THE DEGRADATION OF PVC

SATILMIŞ BASAN

Dept. of Chemistry, Cumhuriyet University, Sivas (Turkey)

OLGUN GÜVEN *

Dept. of Chemistry, Hacettepe University, 06532 Beytepe, Ankara (Turkey)

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ABSTRACT

Various isothermal methods of thermogravimetric analysis were applied to the degradation of poly(vinyl chloride) (PVC). The kinetic parameters, such as the reaction order, activation energy and pre-exponential factor, were evaluated according to existing differential and integral methods of analysis. The major drawbacks and advantages pertaining to five different methods were pointed out and discussed.

INTRODUCTION

In polymer and plastics science and technology, thermal methods of analysis find very wide use. Plastics encounter elevated temperatures at almost every step in the manufacturing, compounding and processing stages, and even in service, therefore a great deal of information is needed about their thermal behaviors.

Among different thermal analysis systems, dynamic thermogravimetry is a technique frequently used due to its simplicity and the advantage that only one thermogram is needed for the determination of all of the kinetic constants. There are many methods proposed for analyzing the dynamic thermograms in order to determine the kinetic constants of thermal degradations [1,2]. A comparison of these methods in the thermal degradation of polystyrene can be found in the work of Nishizaki et al. [1].

In dynamic thermogravimetry, since the sample is heated at a controlled heating rate, it is subjected to continuously changing (increasing) temperatures. This makes the characterization of the conversion function — which

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* To whom correspondence should be addressed.

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shows the dependence of the rate of change of the fraction reacted on the fraction remaining — extremely difficult. In order to characterize or determine this function, isothermal experiments must be carried out to separate out the effects of temperature change [3].

A number of methods for analyzing isothermal thermogravimetric data have been proposed and used in the literature in order to determine the kinetic constants. In this study, these different methods were applied to the thermal degradation of PVC and the results were compared after giving a brief survey of each method.

Determination of kinetic parameters in isothermal thermogravimetry

In the isothermal degradation studies, change in the weight of the sample is recorded as a function of time. The isothermal rate of decomposition is generally expressed by

$$-\frac{\mathrm{d}W}{\mathrm{d}t} = k'W^n \tag{1}$$

where W represents the weight at any time t, k' the rate constant and n the order of the reaction. The use of C, the conversion, instead of W in the analysis of thermograms has some advantages. The conversion, C, can be defined either with respect to initial weight of the sample, or weight at any moment during degradation, namely,

$$C = (W_0 - W)/W_0 = 1 - (W/W_0) \tag{2}$$

or

$$C' = (W_0 - W)/W = (W_0/W) - 1 \tag{3}$$

where C represents conversion with respect to the initial weight of the sample, W_0, and C' is the conversion with respect to the weight at any time, W. Substitution of W and $\mathrm{d}W$ from eqn. (2) into the first equation gives the following relation:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k'W_0^{n-1}(1 - C)^n \tag{4}$$

let $k'W_0^{n-1} = k$, then

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k(1 - C)^n \tag{5}$$

is obtained. The reaction rate constant, k, is expressed by the well-known Arrhenius equation:

$$k = A\ \exp(-E/RT) \tag{6}$$

Substitution of eqn. (6) into eqn. (5) gives

$$\frac{\mathrm{d}C}{\mathrm{d}t} = A\ \exp(-E/RT)(1 - C)^n \tag{7}$$

This is the general form of the kinetic expression used both in dynamic and isothermal thermogravimetry. The integral and differential form of the above equation with different approximations and assumptions are used in the analysis of isothermograms. In the following paragraphs these approaches are outlined.

In the pioneering work of Madorsky [4], the isothermal rate of conversion $(\mathrm{d}C/\mathrm{d}t)$ is directly plotted against the conversion C, and from the shapes of the curves the reaction order is deduced. The value of the initial rate obtained by extrapolation to zero conversion, or the rate at maximum conversion, is taken as the rate constant. The activation energy and pre-exponential factor are determined through the Arrhenius equation. The isothermal rate of conversion can be calculated either on the basis of initial sample weight $(\mathrm{d}C/\mathrm{d}t)$ or weight at any time $(\mathrm{d}C'/\mathrm{d}t)$.

The above method is modified by Friedman [5] in order to make the determination of activation energies at different conversions possible. In this method isothermal rates at certain conversions at certain different temperatures are plotted against $1/T$ values and from the slopes of a family of curves the activation energies at different conversions can be computed.

Some authors prefer to use the general rate equation as given by eqn. (5) after taking the logarithm of both sides of the equation [6,7].

$$\ln\left(\frac{\mathrm{d}C}{\mathrm{d}t}\right) = \ln k + n \ln(1 - C) \tag{8}$$

From the graphs of $\ln(\mathrm{d}C/\mathrm{d}t)$ vs. $\ln(1 - C)$ one can obtain the rate constant from the intercept and the reaction order from the slope of the lines. The determination of k at different temperatures will further give the relevant activation energy and pre-exponential factor values.

The methods outlined in the preceding paragraphs all take into consideration the differential form of the kinetic equation, mainly based on the general rate law. In all of these methods it is very important to determine the $(\mathrm{d}C/\mathrm{d}t)$ values accurately from the isothermograms.

In addition to differential methods outlined so far, there are also integral methods of analysis which are used in isothermal thermogravimetry. A brief discussion of these methods is given in the following sections.

In the method proposed by Flynn [8], a semi-quantitative form of eqn. (5) is used in order to process the raw data directly from the isothermograms. If we rearrange eqn. (5)

$$\int_0^c \frac{\mathrm{d}C}{\mathrm{f}(c)} = \int_0^t k \, \mathrm{d}t \tag{9}$$

after taking the integral, we have

$$\mathrm{F}(c) = kt \tag{10}$$

by taking the logarithm of both sides of eqn. (10) and substituting k from the Arrhenius equation, one obtains

$$\ln t = \ln \mathrm{F}(c) - \ln A + E/RT \tag{11}$$

If the order of the reaction does not change in the temperature and conversion intervals studied, then ln F(c) will have a constant value. From lines obtained by plotting ln t vs. $1/T$, the slopes will give the activation energies at certain conversions.

Wilkinson [9], on the other hand, by integrating eqn. (5) obtained the following:

$$(1 - C)^{1-n} = 1 - n + (n - 1)kt \tag{12}$$

If a binomial expansion is applied to the left-hand side of eqn. (12) and it is rearranged, the final form of Wilkinson's equation is obtained [10]:

$$t/C = 1/k + n/2t \tag{13}$$

According to eqn. (13), plots of t/C vs. t will give straight lines with slopes equal to half of the reaction order and intercepts which are the reciprocal of the rate constant. By computing the rate constants at different temperatures, one can easily calculate the activation energy and pre-exponential factor of the thermal degradation reaction.

EXPERIMENTAL

The properties of the PVC sample used throughout this study have already been published elsewhere [11,12].

Isothermal thermogravimetric curves of the PVC sample were recorded using a Shimadzu DT-30 type thermal analyzer. Approximately 5 mg PVC films were placed in the Pt sample holders and the thermal degradations were carried out in dynamic nitrogen atmosphere with a flow rate of 25 ml min^{-1} at four different temperatures, viz. 240, 250, 260 and 270 °C for a period of 200 min. The Pt pans carrying the PVC samples were directly inserted into the furnace which was brought to the desired temperature in advance, in order to avoid a temperature lag.

RESULTS AND DISCUSSION

The various methods of isothermal thermogravimetric analysis mentioned in the Introduction were applied to the thermograms shown in Fig. 1. Typical isothermal weight loss curves for PVC heated at four different temperatures are given in this figure. Figures 2 and 3 show the application of Madorsky's method where $(\mathrm{d}C/\mathrm{d}t)$ and $(\mathrm{d}C'/\mathrm{d}t)$ were plotted against

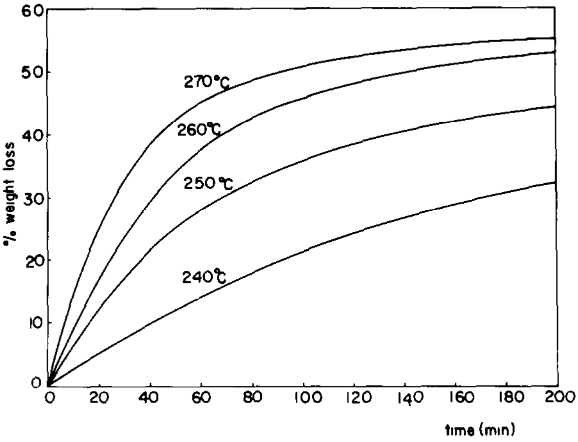

Fig. 1. Isothermal weight loss curves of PVC at four different temperatures.

conversion, respectively. From the parabolic shapes of the curves it is possible to deduce the order of the reaction to be 2. The rate constants pertaining to isothermal weight losses at four different temperatures were determined from Figs. 2 and 3 as the rate at zero conversion or the rate at maximum weight loss. These two sets of k values were plotted against $1/T$ in Fig. 4. The activation energies and pre-exponential factors determined from the slopes and intercepts of these lines are given in Table 1 together with the results obtained according to Friedman's approach.

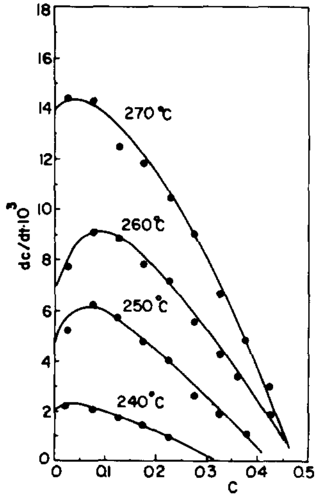

Fig. 2. Change of rate of degradation with conversion (based on the initial weight of the sample).

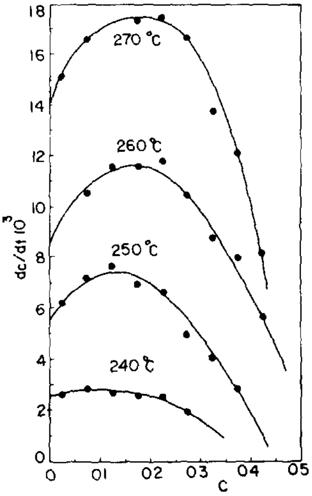

Fig. 3. Change of rate of degradation with conversion (based on the weight of the sample at any given time).

In order to apply the general form of rate equation to isothermograms, ln(dC/dt) vs. ln(1 − C) graphs were prepared and are shown in Fig. 5. According to eqn. (8) slopes of these lines give the order of the reaction, and the intercept can be used to calculate the rate constants at different temperatures. Application of the Arrhenius equation to the rate constant obtained from Fig. 5 yields the activation energy and pre-exponential factor as shown in Fig. 6.

Figure 7 represents the kinetic analysis of the curves shown in Fig. 1 according to Flynn's method. Values of ln t were plotted against 1/T as

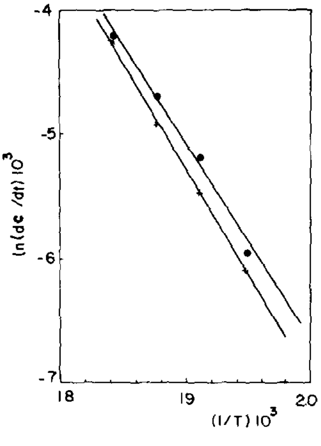

Fig. 4. Arrhenius plot of k values obtained by Madorsky's method.

TABLE 1

Kinetic parameters determined according to various isothermal methods of thermogravimetric analysis

Method	Temp.	Order	Corr. [c]	Conv.	E (kcal mol^{-1})	A	Corr. [c]
Madorsky [4]		2			32.46 [a1]	1.77×10^{11}	0.996
					31.40 [a2]		0.981
		2			33.00 [b1]	2.77×10^{11}	0.989
					33.54 [b2]		0.976
Friedman [5]				5	31.92		0.979
				10	34.81		0.970
				15	37.79		0.968
				20	41.79		0.978
				25	42.92		0.983
General rate equation [6]	240	3.50	0.983		28.72	6.70×10^{9}	0.972
	250	2.80	0.982				
	260	2.75	0.963				
	270	1.80	0.992				
Flynn [8]				5	30.63		0.982
				10	30.93		0.984
				15	31.45		0.979
				20	32.74		0.978
				25	34.12		0.981
				30	35.16		0.986
Wilkinson [9]	240	2.66	0.996		31.45	8.95×10^{10}	0.986
	250	2.60	0.993				
	260	2.60	0.996				
	270	2.45	0.993				

[a1,a2] From the intercept and maximum rate in Fig. 2, respectively.

[b1,b2] From the intercept and maximum rate in Fig. 3, respectively.

[c] Correlation coefficients of the lines in related figures.

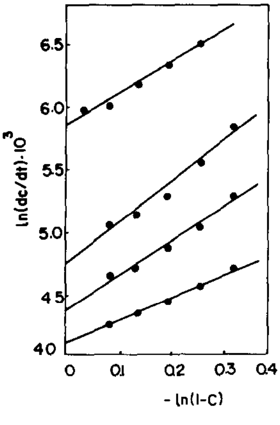

Fig. 5. Application of the general rate equation to the data of Fig. 1.

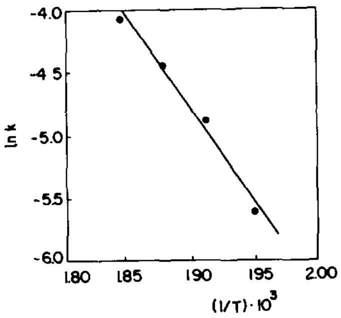

Fig. 6. Application of the Arrhenius equation to k values determined from the general rate equation.

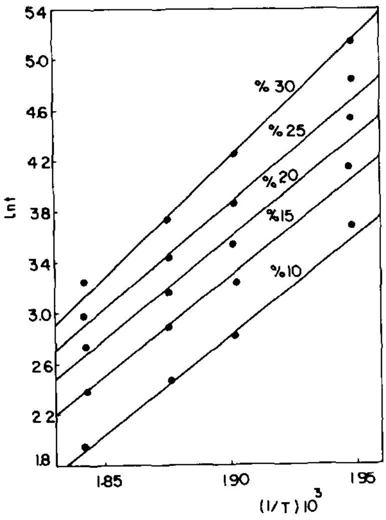

Fig. 7. Relationship between ln t and $1/T$ as given by Flynn's method.

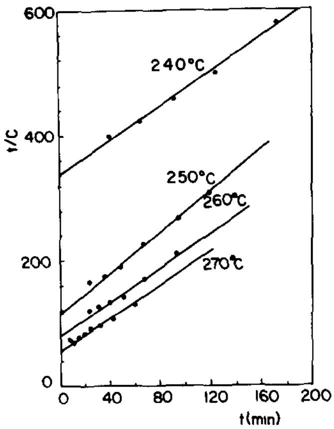

Fig. 8. Plot of t/c vs. time according to Wilkinson's method.

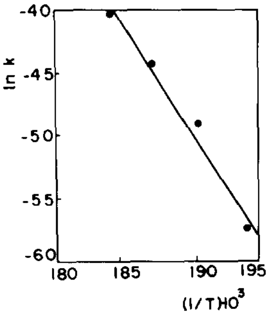

Fig. 9. Arrhenius plot of data obtained from Fig. 8.

dictated by eqn. (11). The lines obtained in Fig. 7 refer to different extents of conversions between 10 and 30%. Activation energies pertaining to these conversions were computed from the slopes and are listed in Table 1.

The method proposed by Wilkinson is applied to the thermal degradation of PVC and results are presented in Figs. 8 and 9. By plotting t/C vs. time at four temperatures it is possible to obtain the reciprocal of k from the intercepts and half of the reaction order from the slopes of Fig. 8. Figure 9 is the Arrhenius plot of the data obtained from Fig. 8. Numerical values of these parameters are given in Table 1.

In any kinetic analysis it is generally aimed to determine the order of a reaction, the activation energy and the pre-exponential factor. These values are determined following the methods described in the Introduction, and are collected in Table 1. All three kinetic parameters can be determined by Madorsky's method; however, the determination of reaction order from the shape of a conversion curve is a major drawback of this method. It is not possible to follow the change of activation energy with the extent of conversion using this technique. This latter disadvantage has been overcome in Friedman's approach.

In addition to all three kinetic parameters it is also possible to investigate the change of reaction order with temperature and conversion using the general rate law. The activation energy and the pre-exponential factor of the reaction, however, can only be calculated for the initial rate of decomposition but not for any extent of conversion.

In the above-mentioned methods, it is necessary to determine the rate at every conversion either by drawing tangents to the curves given in Fig. 1 or by taking the derivative of the isothermograms. In Flynn's method, however, the raw data of Fig. 1 can be directly processed to find the kinetic parameters. From plots of ln t vs. $1/T$ the activation energy corresponding to any conversion can be directly calculated from the slope of the lines. On the other hand, since intercept involves the sum of ln F(c) and ln A terms it is not possible to find the order and pre-exponential factor of the decomposition reaction. It is, however, a direct and rapid method of determination of activation energies.

Wilkinson's method also carries the advantage of using the conversion, *c*, and time, *t*, values directly from the curves in Fig. 1 for the determination of kinetic parameters. Due to the approximations introduced in binomial expansion, however, the applicability of Wilkinson's equation is limited to 40% conversions. Although it is possible to follow whether the reaction order changes with time or temperature by this method, the activation energy and pre-exponential factor can only be determined for the initial decompositions.

Activation energy of the thermal degradation of the same PVC sample was determined by dynamic thermogravimetry to be 43.2 kcal mol^{-1} [12]. The values reported in Table 1 for various methods are somewhat below this value. This discrepancy is not surprising if one considers the wide temperature range covered in dynamic thermogravimetry as compared to four temperatures studied here. If the E values given in Table 1 for higher extents of conversions are considered, the results get closer to that determined by dynamic thermogravimetry. This is the major advantage of the isothermal method over dynamic thermogravimetry, i.e. to follow the change in the kinetic parameters with conversion.

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