Some Remarks on the Use of Isothermal Thermogravimetric Data for the Evaluation of Kinetic Parameters. Applications for Degradation of Polymeric Materials

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ABSTRACT: A critical analysis of the isoconversional methods for evaluating kinetic parameters of decomposition of solids from isothermal thermogravimetric data is presented. An isoconversional integral method to evaluate the activation energy is suggested. This method allows removing the errors due the correction of the degradation time by subtracting the induction period to onset of the main reaction (also including the time required to heat the sample to the temperature at which the isotherm is recorded). This procedure was used to study the degradation of two series of polymeric materials, (a) poly(vinyl chloride)/acriloni-trile–butadiene–styrene (PVC/ABS) blends and (b) poly(vinyl chloride)/chlorinated poly(ethylene) (PVC/CPE) blends. The values obtained for the activation energy are in fairly good agreement with those obtained from the Prout–Tompkins model in case (a) and from nonisothermal data in case (b). © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 355–360, 2003

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INTRODUCTION

The thermogravimetric (TG) method offers information concerning the degradation of the polymeric materials in a relative short time. To record an isotherm, the sample is initially heated at a high rate from the start temperature to the selected degradation temperature and then held at this temperature for 2–3 h. It is assumed during the kinetic analysis of TG isotherms (i.e., mass versus time) that a rate-determining step occurs in the main reaction during the degradation of the investigated polymeric material. This rate-determining step is characterized by the kinetic triplet of activation energy, pre-exponential factor, and conversion function.[1] The activation energy can be equally well determined by isoconversional methods,[2–4] which do not need the explicit form of the conversion function. The use of these methods for TG isotherms raise the following problems: (1) the necessity of some corrections for the time and for the conversion degree, corresponding to the degradation that occurs during the heating of the sample at the chosen temperature; (2) the eventual existence of an induction period of degradation during which the kinetic parameters have different values with respect to the acceleration period;[5] and (3) the eventual existence of initial thermal shocks that occur until the temperature of thermal degradation settles down.

To solve these problems, the time values are corrected by subtracting t_0, the induction period to onset of the main reaction (also including the time required to heat the sample to temperature at which the isotherm is recorded).[3] The use of the TG method to record the degradation isotherm determines errors in the t_0 evaluation. These errors could determine errors in the values of kinetic parameters.

In this article we present an isoconversional integral procedure to evaluate the activation energy from TG isothermal data. The procedure allows avoiding time corrections for heating at the required temperature as well as for the induction period. This procedure was used for the kinetic analysis of some recent results[6,7] concerning (a) poly(vinyl chloride)/acrilonitrile–butadiene–styrene (PVC/ABS) blends and (b) poly(vinyl chloride)/chlorinated poly(ethylene) (PVC/CPE) blends.

METHODS

General considerations concerning the isoconversional methods used to evaluate the activation energy

The kinetics of the heterogeneous condensed phase reactions is usually descibed[2–4] by the equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = Af(\alpha)\exp\left(-\frac{E}{RT}\right) \qquad (1)$$

where α is the conversion degree, t is the time, k is the rate constant, T is the temperature, $f(\alpha)$ is the differential conversion function, A is the apparent pre-exponential factor, E stands for the apparent activation energy, and R is the gas constant. This equation describes the overall process and, consequently, we assume that the kinetic parameters are apparent. The differential conversion function $f(\alpha)$ describes, as an analytical equation, the physical (kinetic) model of the investigated process. There are several such equations in the literature and some of these are summarized in ref. 3.

As for most heterogeneous condensed phase reactions, the differential conversion function is not known *a priori*. Therefore, to evaluate E, isocoversional methods that do not need knowledge of the form of $f(\alpha)$ are used.[2–4] The differential isoconversional method for evaluation of the activation energy is based on the logarithmic form of eq. 1:

$$\ln \frac{d\alpha}{dt} = \ln Af(\alpha) - \frac{E}{RT} \qquad (2)$$

For α = constant, a plot of $\ln d\alpha/dt$ versus $(1/T)$ should be a straight line whose slope allows an evaluation of the activation energy.

The use of this method necessitates evaluating the curve $d\alpha/dt$ versus α for each recorded isotherm. To avoid the errors that affect the evaluation of $d\alpha/dt$ (the curve $d\alpha/dt$ versus α is determined by numeric derivation of the isotherm α versus t), an isoconversional integral method based on the integral form of eq. 1 is preferred:

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = At \exp\left(-\frac{E}{RT}\right) \qquad (3)$$

Equation 4 can be derived from eq. 3:

$$\ln t = \ln \frac{g(\alpha)}{A} + \frac{E}{RT} \qquad (4)$$

For α = const., a plot of versus $(1/T)$ should be a straight line whose slope allows an evaluation of the activation energy.

This method is also recommended by IEC 216 Standard[8] for the evaluation of the slope of the thermal lifetime straight line of electroinsulating polymeric materials. The relative long time of the accelerated thermal aging imposed by this Standard ($t > 500$ h) makes the preheating corrections unnecessary. These corrections are necessary when the TG method is used to determine the isotherm of degradation because this method requires relatively high temperatures and short times of recording. In addition, if the degradation of the polymer necessitates an induction period, a corresponding correction of t should be made. The accuracy of such corrections is relatively low. To avoid the introduction of supplementary errors generated in such a way, we suggest an integral isoconversional procedure. This procedure is based on the following relation that results at the integration of rate equation between α_0 and α:

$$g(\alpha, \alpha_0) = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = A(t_\alpha - t_{\alpha_0})exp\left(-\frac{E}{RT}\right) \quad (5)$$

Equation 6 can be derived from eq. 5:

$$\ln(t_\alpha - t_{\alpha_0}) = \ln\frac{g(\alpha, \alpha_0)}{A} + \frac{E_\alpha}{RT} \qquad (6)$$

where E_α is the activation energy value for the conversion degree α. For (α,α_0) = const., the plot of $\ln(t_\alpha - t_{\alpha_0})$ versus $(1/T)$ should be a straight line whose slope allows the evaluation of the activation energy.

If E_α does not depend on α, the value of the activation energy should not depend on α_0. An eventual dependence of E_α on α is reflected in the dependence of the activation energy on α_0.

RESULTS AND DISCUSSION

Application of procedure to the thermal degradation of some polymeric materials

Thermooxidative degradation of poly(vinyl chloride)/acrylonitrile–butadiene–stryrene (PVC/ABS) blends[6]

The isotherms of thermooxidative degradation at various temperatures (210, 220, 230, and 240°C) of PVC/ABS blends with different mass fraction of polymers (100/0, 90/0, 80/20, 50/50, and 0/100) are presented in ref. 6. The sample of blend was initially heated at a rate of 80 K min^{-1} from the starting temperature (50°C) to a selected degradation temperature and then held at this temperature for 180 min. The kinetic analysis was performed for $0.05 \le \alpha \le 0.30$. The isoconversional integral method based on eq. 6 was used to evaluate the activation energy. It was also shown[6] that the thermooxidative degradation of the investigated

TABLE I
Activation Energy Values for the Thermooxidative Degradation of PVC/ABS Blends[a]

α	PVC/ABS (100/0)			PVC/ABS (90/10)			PVC/ABS (80/20)		
	$E,$ kJ mol^{-1}	$E_{PT},$ kJ mol^{-1}	$e, \%$	$E,$ kJ mol^{-1}	$E_{PT},$ kJ mol^{-1}	$e, \%$	$E,$ kJ mol^{-1}	$E_{PT},$ kJ mol^{-1}	$e, \%$
0.05	117.3	125.8	7.25	99.7	125.5	25.88	104.7	129.2	23.40
0.10	120.4	125.8	4.49	104.8	125.5	19.75	108.3	129.2	19.30
0.15	121.5	125.8	3.54	107.2	125.5	17.07	111.1	129.2	16.29
0.20	121.3	125.8	3.71	108.9	125.5	15.24	112.6	129.2	14.74
0.25	121.3	125.8	3.71	110.1	125.5	13.99	114.9	129.2	12.45
0.30	121.3	125.8	3.71	111.1	125.5	12.96	114.9	129.2	12.45

[a] Data from ref. [6];
E = activation energy evaluated from the slope of the straight line ln t versus $(1/T)$;
E_{PT} = activation energy determined considering the Prout–Tompkins model; $e = \dfrac{E_{PT} - E}{E} \times 100$.

polymeric materials is described by the following equation:

$$g(\alpha) = \ln \frac{\alpha}{1 - \alpha} + C \qquad (7)$$

where C is a constant that correspond to the Prout–Tompkins model. The choice of this model by Klarić et al.[6] was suggested by the sigmoidal shape of isotherms, which indicates acceleration during the degradation process.

To evaluate the activation parameters with the equation that results from introducing eq. 7 in eq. 3, the aforementioned corrections of t are not necessary. These corrections are contained in the constant C, which depends on the temperature and reflects the "history" of the sample until the reaching of the isothermal temperature.

The values of the activation energy E as well as the relative deviations of E_{PT} (the activation energy evaluated using Prout–Tompkins model) with respect to those obtained by the isoconversional method, in which corrections of t were not made, are listed in Table I. The standard deviations of the activation energy values as well as the corresponding correlation coefficients of the linear regressions are not given in ref. 6. As one can see, the deviations (e) for the 100/0 samples are acceptable (<10%), whereas those for the 90/10 and 80/20 samples are relatively high. These high deviations could be due to (a) the possibility of an incorrect definition of the conversion degree or (b) the use of eq. 6 without corrections of t corresponding to the period of preheating and/or induction. Let us analyze these suppositions.

The possibility of wrong definition of the conversion degree. If the reaction yields one or more gaseous products and the evolved gas composition is constant, α values can be calculated from the mass loss up to time t, $m_0 - m_t$, divided by the mass loss corresponding to completion of reaction, $m_0 - m_f$ by $\alpha = (m_0 - m_t)/(m_0 - m_f)$.[3] In ref. 6, the degree of conversion is considered

as $\alpha = (m_0 - m_t)/m_0$, although several reactions occur at the degradation of the investigated materials. The latter generates doubts concerning the correct verification of the Prout–Tompkins model. To verify the correctness of this model and to evaluate exactly the rate constant we used the method suggested by Nawada and Sreedharan,[9] which does not necessitate the knowledge of the final value of the mass loss corresponding to the investigated process. The method is based on the observation that for an isotherm, the ratio of two α values does not depend on the final mass loss. Consequently, the ratios $R = \alpha_i/\alpha_j$ could be used to evaluate $k(T)$, even when the degree of conversion was evaluated using an incorrect value of the final mass loss.

The following relationship can be written from eqs. 3 and 7 for the Prout–Tompkins model:

$$\alpha = \frac{D \exp(kt)}{1 + D \exp(kt)} \qquad (8)$$

where $D = \exp(-C)$.

Three points of the isotherm $[(\alpha_1, t_1), (\alpha_2, t_2),$ and $(\alpha_3, t_3)]$ are considered. Simple algebraic calculations based on eq. 8 lead to the following relation:

$$(R_{12} - 1)e^{k(t_1 - t_3)} - (R_{13} - 1)e^{k(t_1 - t_2)} + R_{13} - R_{12} = 0 \qquad (9)$$

TABLE II
Values of α_1, α_2, and α_3 Used in Eq. 9 for Evaluation of k

α_1	α_2	α_3	R_{12}	R_{13}
0.05	0.10	0.15	0.5	0.3333
0.05	0.10	0.20	0.5	0.25
0.05	0.10	0.25	0.5	0.20
0.05	0.10	0.30	0.5	0.1667
0.10	0.15	0.20	0.6667	0.5
0.10	0.15	0.25	0.6667	0.4
0.10	0.15	0.30	0.6667	0.3333

TABLE III
Kinetic Parameters for PVC/ABS Blends Obtained with Eq. 9

T, °C/Parameter	$\bar{k}$, min^{-1} PVA/ABS (100/0)	$\bar{k}$, min^{-1} PVA/ABS (90/10)	$\bar{k}$, min^{-1} PVA/ABS (80/20)
210	0.0421 (± 0.0048)	0.0580 (± 0.0021)	0.051 (± 0.0034)
220	0.0777 (± 0.0078)	0.0983 (± 0.0052)	0.0882 (± 0.0017)
230	0.1605 (± 0.0077)	0.1829 (± 0.0080)	0.1849 (± 0.0089)
240	0.3058 (± 0.0225)	0.3483 (± 0.0182)	0.2913 (± 0.0027)
E,[a] kJ mol^{-1}	137.5 (± 4.0)	123.4 (± 5.5)	122.9 (± 7.1)
A',[a] min^{-1}	31.044 (± 0.957)	27.856 (± 1.326)	27.612 (± 1.726)
$-r$[b]	0.99917	0.99803	0.99664

[a] E' and A' are activation parameters obtained from the parameters of the straight line $\ln \bar{k}$ versus $(1/T)$.
[b] r is the correlation coefficient of the linear regression $\ln \bar{k}$ versus $(1/T)$.

Solving this equation numerically provides the value of k.

The values of the triplet $(\alpha_1, \alpha_2, \alpha_3)$ introduced in eq. 9 are listed in Table II. The values of the obtained rate constants as well as of the activation parameters are shown in Table III. The resulting k values differ from the values reported in ref. 6, although there are no significant differences between the E values calculated by us and those evaluated in ref. 6 using the Prout–Tompkins model. It should be noted that close values for E are obtained for the following kinetic models: exponential law [$g(\alpha) = \ln \alpha + C$]; power law [$g(\alpha) = \alpha^{1/n}$, with $n = 2$]; Avrami–Eforeev [$g(\alpha) = [-\ln(1 - \alpha)]^{1/n}$, with $n = 2, 3,$ and 4]. It appears that for a series of kinetic models, E is practically independent on the form of $g(\alpha)$. Similar results were reported previously.[10] In the cases analyzed in this paper, this independence of E on the kinetic model could be due to the use of a relatively small range of conversion degree ($0.05 \leq \alpha \leq 0.30$) as well.

The use of the isoconversional procedure based on equation 6. The E values calculated by the isoconversional procedure suggested in this paper are shown in Table IV. The relative deviation of the activation energy

obtained by the Prout–Tompkins model compared with those obtained by the isoconversional method are also shown. One can easily see that the method suggested in this paper leads to activation energy values that are in better agreement with those obtained considering the degradation according to the Prout–Tompkins model. Thus, the high deviations mentioned in Table I are eliminated.

Thermal degradation of poly(vinyl chloride)/chlorinated poly(ethylene) (PVC/CPE) blends

The results obtained following an investigation of the isothermal and nonisothermal degradation in nitrogen flow of PVC/CPE blends of different mass fraction of polymers (100/0, 90/10, 80/20, 70/30, 50/50, and 0/100) are presented in ref. 7. The nonisothermal degradation was investigated by a thermogravimetric method at the heating rates of 2.5, 5, 10, and 20 Kmin^{-1}. The isothermal degradation was performed at 240, 250, 260, and 270°C. In the latter case, the sample was initially heated at the rate of 80 Kmin^{-1} from the start (50°C) to the selected temperature and

TABLE IV
Activation Energy Values Obtained by the Isoconversional Procedure Based on Eq. 6 (for $\alpha_0 = 0.05$) for PVC/ABS Blends[a]

α	PVA/ABS (100/0) E, kJ mol^{-1}	r	e, %	e', %	PVA/ABS (90/10) E, kJ mol^{-1}	r	e, %	e', %	PVA/ABS (80/20) E, kJ mol^{-1}	r	e, %	e', %
0.10	132.4 (± 4.6)	0.9988	−4.98	+3.85	124.6 (± 6.0)	0.9977	+0.72	−0.96	120.9 (± 7.2)	0.9965	+6.87	+1.65
0.15	131.4 (± 4.3)	0.9989	−4.26	+4.64	124.8 (± 6.1)	0.9976	+0.56	−1.12	124.8 (± 7.2)	0.9967	+3.53	−1.52
0.20	128.8 (± 4.5)	0.9988	−2.40	+6.67	125.5 (± 6.4)	0.9974	0.00	−1.67	125.5 (± 7.2)	0.9967	+2.95	−2.07
0.25	127.5 (± 5.3)	0.9983	−1.33	+7.84	125.4 (± 6.7)	0.9971	+0.08	−1.60	128.3 (± 6.9)	0.9971	+0.70	−4.21
0.30	125.6 (± 7.0)	0.9969	+0.16	+9.47	125.3 (± 7.8)	0.9967	+0.16	−1.52	128.4 (± 7.5)	0.9966	+0.62	−4.28

[a] E = value of the activation energy obtained from the slope of the straight line $\ln(t_\alpha - t_{\alpha_0})$ versus $(1/T)$; r = correlation coefficient of the linear regression $\ln(t_\alpha - t_{\alpha_0})$ versus $(1/T)$; $e = \dfrac{E_{PT} - E}{E} \times 100$, where E_{PT} have the values listed in Table I; $e' = \dfrac{E' - E}{E} \times 100$, where E' has the values listed in Table III.

TABLE V
Activation Energy Values for Thermal Degradation of PVC/CPE Blends[a]

	PVC/CPE (100/0)			PVC/CPE (90/10)			PVC/CPE (80/20)		
α	E_{FWO}, kJ mol^{-1}	E, kJ mol^{-1}	e, %	E_{FWO}, kJ mol^{-1}	E, kJ mol^{-1}	e,%	E_{FWO}, kJ mol^{-1}	E, kJ mol^{-1}	e, %
0.05	143.3	103.0	−28.12	122.6	99.3	−19.00	124.5	100.6	−14.38
0.10	141.2	109.5	−22.45	119.4	104.3	−12.65	122.6	104.8	−14.52
0.15	138.9	112.0	−19.37	118.3	104.4	−11.75	120.6	107.5	−10.86
0.20	137.2	114.0	−16.91	116.8	106.0	−9.25	120.3	107.8	−10.39
0.25	136.0	116.3	−14.48	115.4	106.5	−7.71	120.4	106.8	−11.30
0.30	135.3	118.5	−12.42	115.7	107.0	−7.52	120.7	104.0	−13.84

[a] From ref. 7; E_{FWO} = activation energy obtained from nonisothermal data by Flynn–Wall–Ozawa method;

E = activation energy obtained from isothermal data using the straight line ln t versus $(1/T)$; $e = \dfrac{E - E_{FWO}}{E_{FWO}} \times 100$.

then held at this temperature for 120 min. For kinetic analysis, the conversion degree range $0.05 \leq \alpha \leq 0.30$ was used.

To evaluate the activation energy from nonisothermal data, the isoconversional integral method of Flynn–Wall–Ozawa[11, 12] was used. The method based on eq. 4 without time corrections was applied to the isothermal data. The results obtained for the 100/0, 90/10, and 80/20 samples are listed in Table V. The standard deviations of the activation energy values as well as the corresponding correlation coefficients of the linear regressions are not given in ref. 7. Relatively large differences among the values of nonisothermal and isothermal activation energy are noted (except the 90/10 sample for $\alpha = 0.20$, 0.25, and 0.30; $|e| < 10\%$). These deviations are even higher than those reported between the E values determined from isothermal data.

The linearity of the Flynn–Wall–Ozawa curves suggests the same degradation mechanism at all the heating rates tested. It would be expected that the same mechanism should be valid for the isothermal degradation. Consequently, the activation energy values obtained from isothermal data should be close to those obtained from nonisothermal data. The uncorrected values of t at the evaluation of the activation energy from isothermal data are the reason of the mentioned relatively high differences between E and E_{FWO} listed

in Table V. As previously shown, the corrections could be avoided by using the isoconversional procedure based on eq. 6. The results obtained by the application of this procedure are shown in Table VI. For the 90/10 and 80/20 samples, the straight lines ln $(t_\alpha - t_{\alpha\ 0})$ versus $(1/T)$ exhibit correlation coefficients >0.9981. In these cases, the values of the standard deviation are relatively small. For the 100/0 sample, $0.9845 \leq r \leq 0.9910$. Consequently, for this sample, the standard deviations of E values are relatively high. This statement can be explained by the relatively high errors in E determined by the small values of the differences $(t_\alpha - t_{\alpha\ 0})$ that correspond to the highest degradation rate of the 100/0 sample.

The results in Table VI show that applying the procedure suggested in this work to isothermal data values results in activation energy values that are in fairly good agreement with those obtained from nonisothermal data using the Flynn–Wall–Ozawa isoconversional method. Consequently, the thermal degradation mechanism of PVC/CPE blends is the same in isothermal and nonisothermal conditions.

CONCLUSIONS

The isoconversional methods for kinetic analysis of isothermal data obtained by isothermal thermo-

TABLE VI
Activation Energy Values Obtained from Isothermal Data Using the Integral Isoconversional Procedure Based on Eq. 6 (for $\alpha_0 = 0.05$) for PVC/CPE Blends[a]

	100/0			90/10			80/20		
α	E, kJ mol^{-1}	r	e, %	E, kJ mol^{-1}	r	e, %	E, kJ mol^{-1}	r	e, %
0.10	139.4 (± 15.2)	0.9883	−1.27	130.5 (± 2.0)	0.9998	+9.30	121.5 (± 4.1)	0.9989	−0.09
0.15	134.2 (± 12.8)	0.9910	−3.38	125.5 (± 2.5)	0.9996	+6.09	123.1 (± 1.1)	0.9999	+2.07
0.20	131.0 (± 13.6)	0.9894	−4.52	121.2 (± 3.3)	0.9992	+3.77	118.8 (± 1.6)	0.9998	−1.25
0.25	129.6 (± 4.8)	0.9874	−4.71	118.8 (± 4.2)	0.9988	+2.95	113.6 (± 2.4)	0.9996	−5.65
0.30	126.5 (± 5.7)	0.9845	−6.50	117.1 (± 5.1)	0.9981	+1.21	106.5 (± 2.3)	0.9995	−11.76

[a] E = value of the activation energy obtained from the slope of the straight line ln$(t_\alpha - t_{\alpha_0})$ versus $(1/T)$;

r = correlation coefficient of the linear regression ln$(t_\alpha - t_{\alpha_0})$ versus $(1/T)$; $e = \dfrac{E - E_{FWO}}{E_{FWO}} \times 100$.

gravimetry in investigations of the decomposition of solid compounds were analyzed. An isoconversional integral procedure to evaluate the activation energy was suggested. This procedure removes the errors due the usual corrections of the degradation time. The suggested procedure was used for the kinetic analysis of (a) thermooxidative degradation of PVC/ABS blends and (b) thermal degradation of PVC/CPE blends. In the first case (a), the values of the activation energy obtained by the suggested procedure are in a fairly good agreement with those obtained by the Prout–Tompkins model. In the second case (b), the values of the activation energy obtained by the suggested procedure agree with those obtained from nonisothermal data by the Flynn–Wall–Ozawa method.

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