

Estimation of Kinetic Parameters During Teflon Degradation from Linearized Differential TGA Traces

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Synopsis

In a recent communication,¹ mathematical expressions were derived for obtaining kinetic parameters during polymer pyrolyses from linearized DTA traces. The approximate method developed is now extended to differential TGA traces in this paper and is applied to polytetrafluorethylene (Teflon). The results obtained are compared with those obtained from more elaborate procedures.

Experimental

To a thermogravimetric apparatus (TGA) (Aminco Thermograv) was attached a differentiator which was designed and constructed in these laboratories.^{2,3} Teflon samples (DuPont) of 200 mg. were used. TGA and differential TGA traces (DTGA) were obtained simultaneously.

Theory

In a previous paper,¹ it was shown that when the peak height, ΔT , is linear with respect to temperature T for two DTA traces, mathematical expressions could be obtained for estimating reaction order n and activation energy, E , for the left-hand side and the right-hand side of the DTA peaks. From eqs. (1) and (2) of the previous paper,¹ it can be readily shown that similar mathematical expressions hold for DTGA traces when the height of the DTGA trace (R_t) ($R_t \equiv -dW_c/dt$) is linear with respect to temperature. When such is true or approximately true, then expressions (1) and (2) can be readily obtained for the right- and left-hand sides of the peaks, respectively.

$$W_c = W_{0,c}[(T_f - T)/(T_f - T_0)]^2 \quad (1)$$

and

$$W_c = W_{0,c}\{[T_f - T_i - z(T - T_i)]/(T_f - T_i)\} \quad (2)$$

where W_c and $W_{0,c}$ denote active weight or weight fraction of polymer remaining and polymer initially present, respectively, during a pyrolysis; $z = (T - T_i)/(T_p - T_i)$; T_0 is the initial reaction temperature; T_i and

T_f are the temperatures corresponding to the intersection of the base line with the linearized portion of the DTGA trace on the left-hand side of the peak and the right-hand side of the peak, respectively (cf. Fig. 1 of ref. 1); and T_p denotes the temperature corresponding to the intersection of the linearized portions of the left-hand and right-hand sides of the DTGA peak.

Estimation of n

We may write, employing the Arrhenius equation,

$$-dW_c/dt = R_t = Ze^{-E/RT} W_c^n \quad (3)$$

By utilizing eqs. (1) and (2), eqs. (4) and (5) may be obtained for the right-hand and left-hand sides of the DTGA peak, respectively;

$$R_t = Ze^{-E/RT} W_{0,c}^n [(T_f - T)/(T_f - T_0)]^{2n} \quad (4)$$

and

$$R_t = Ze^{-E/RT} W_{0,c}^n [T_f - T_t - z(T - T_t)/T_f - T_t]^n \quad (5)$$

By using two heating rates, $(RH)_1$ and $(RH)_2$, and employing isothermals, eqs. (4) and (5) may be converted into eqs. (4a) and (5a), respectively,

$$\log \frac{R_{t,1}}{R_{t,2}} = 2n \log \frac{(T_f - T)_1}{(T_f - T)_2} + \log \left\{ \left[\frac{(W_{0,c})_1}{(W_{0,c})_2} \right]^n \left[\frac{(T_f - T_0)_2}{(T_f - T_0)_1} \right]^{2n} \right\} \quad (4a)$$

$$\log \frac{R_{t,1}}{R_{t,2}} = n \log \frac{F(T)_1}{F(T)_2} + \log \left[\frac{(W_{0,c})_1 (T_f - T_t)_2}{(W_{0,c})_2 (T_f - T_t)_1} \right]^n \quad (5a)$$

where $F(T) = T_f - T_t - z(T - T_t)$.

Estimation of E

Once the reaction order n has been evaluated by means of eqs. (4a) and/or (5a), values of E may be obtained by utilizing eqs. (4) and/or (5). Thus, for the right-hand side of the DTGA peak,

$$\log R_t - 2n \log (T_f - T) = -E/2.3RT + \log \left[\frac{Z(W_{0,c})^n}{(T_f - T_0)^{2n}} \right] \quad (6)$$

and for the left-hand side of the DTGA peak,

$$\log R_t - n \log F(T) = -E/2.3RT + \log [Z(W_{0,c})^n / (T_f - T_t)^n] \quad (7)$$

Results and Discussion

In Figure 1 are shown DTGA traces for Teflon for two different heating rates. Due to the very great steepness of the right-hand side of the peaks, the method previously outlined for the estimation of n and E could only

be applied to the left-hand side of the peaks. The left-hand side of the peaks are only very approximately linear and therefore the results obtained will be approximate at best.

The value of n for Teflon was estimated from eq. (5a) and the corresponding plot is shown in Figure 2. A value of $n = 1.0$ was obtained. From eq. (7) a value of E of about 61 kcal./mole was obtained (see Fig. 2). In order to check these values, the more elaborate method of Freeman⁴ was applied to the corresponding primary thermograms obtained for weight versus temperature at heating rates of 5.3. and 7.1°C./min. The following average values of n and E were obtained: 0.85 and 63 kcal./mole, respectively. Thus, there appears to be good agreement between the method in this paper which utilized automatically obtained DTGA traces and a

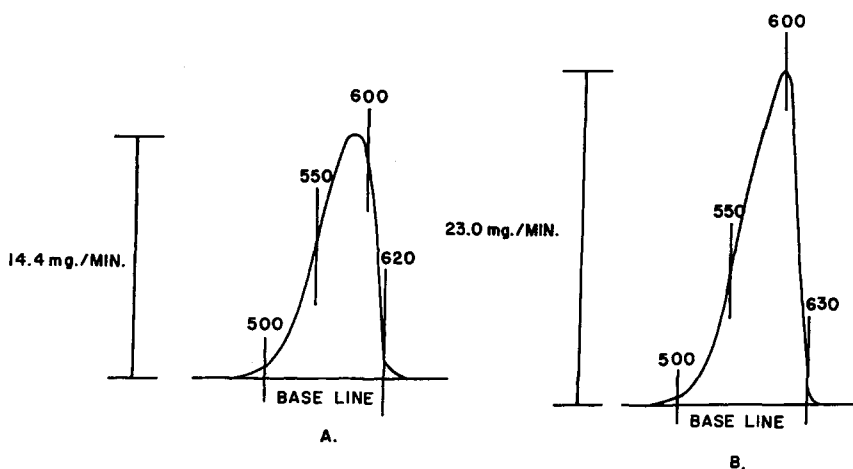


Fig. 1. Differential TGA traces for Teflon: (A) 5.3°C./min.; (B) 7.1°C./min.

more exacting method⁴ which employed "hand" differentiation of TGA traces. (However, the relatively low value of E obtained cannot be accounted for.)

As in the case of linearized DTA traces,¹ it should be noted that when the right-hand side of the DTGA peak is utilized (linearization is good), it is not necessary that the left-hand side of the DTGA peak show good linearity. However, when the left-hand side of the DTGA peak is used (shows good linearity), the right-hand side of the DTGA peak must also possess good linearity. Where possible, values for both sides of the DTGA peak should be obtained as a check.

Advantages and disadvantages of the method employed in this paper for estimating E and n are: (1) changes in n (and E) with conversion may be detected; (2) the method is relatively simple; (3) two DTGA traces are required; (4) it may be difficult at times to readily obtain two DTGA

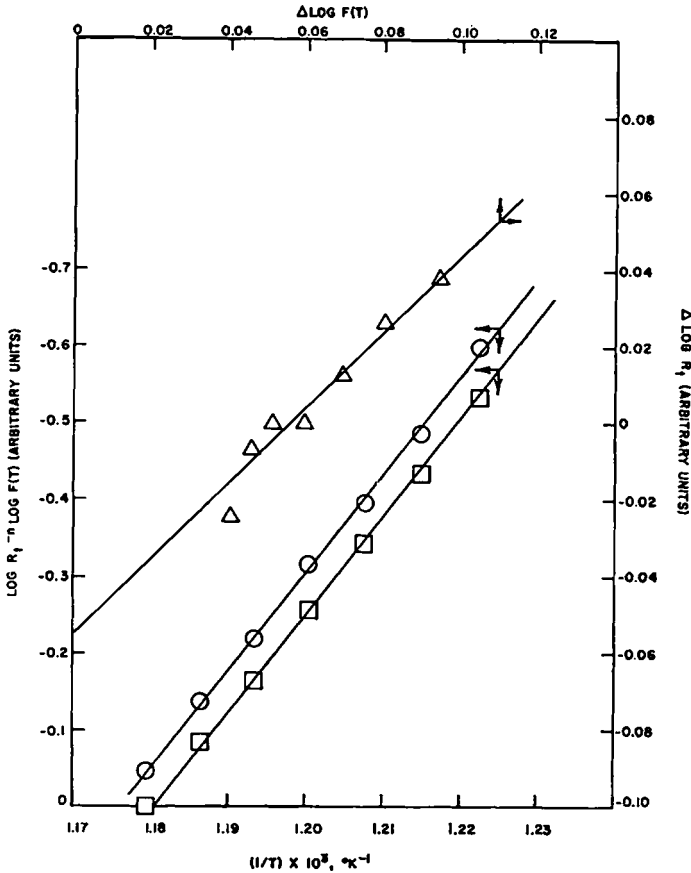


Fig. 2. Estimation of n and E by eqs. (5a) and (7), respectively:
(O) 7.1°C./min.; (□) 5.3°C./min.

traces for the same material at two different heating rates which overlap sufficiently so that the method can be employed.

References

1. L. Reich, *J. Appl. Polymer Sci.*, in press.
2. N. Lockhart, Picatinny Arsenal Tech. Memo. 49-63, Nov. 1962.
3. S. H. T. Lee, H. Will, and D. W. Levi, Picatinny Arsenal Tech. Rept. 3321, July 1966.
4. D. A. Anderson and E. S. Freeman, *J. Polymer Sci.*, **54**, 253 (1961).

Résumé

On a étendu une méthode utilisée préalablement pour les traces DTA linéarisées pour la linéarisation de traces thermogravimétriques différentielles en vue d'estimer les paramètres cinétiques en cours de pyrolyse de polymères. Par cette méthode deux traces thermogravimétriques différentielles sont utilisées. La méthode est appliquée au poly-tétrafluoro-éthylène (teflon). L'accord avec les valeurs obtenues par cette méthode

et une méthode plus élaborée est bon. Les avantages et désavantages de la méthode sont soumis à discussion.

Zusammenfassung

Eine früher für linearisierte DTA-Kurven verwendete Methode wird auf linearisierte differential-thermogravimetrische (DTGA) Kurven zur Bestimmung der kinetischen Parameter während der Polymerpyrolyse erweitert. Bei dieser Methode werden zwei DTGA-Kurven verwendet. Die Methode wird auf Polytetrafluoräthylen (Teflon) angewendet. Die Übereinstimmung der nach dieser Methode erhaltenen Werte mit den nach einer anspruchsvolleren erhaltenen ist gut. Vor- und Nachteile der Methode werden diskutiert.

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