Invariant Kinetic Parameters of Polymer Thermolysis. I. Oxidative Degradation of Flame-Retardant Polyesters

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Synopsis

The paper gives an analysis of the data reported by J. D. Cooney and others. [J. Appl. Polym. Sci., 29, 911 (1984)] on the kinetics of oxidative degradation of flame-retardant polyesters [poly(ethylene terephthalate)]. A linear correlation is shown to exist between the parameters of the kinetic compensation effect. A formal interpretation of the correlation is given as well as its interpretation within two alternative polyester degradation schemes. The above correlation allowed the invariant kinetic parameters of the process $\log \hat{A} = 15.7 \pm 1.3$; $\hat{E} = 183 \pm 16$ (min^{-1}; kJ/mol) to be estimated, which seem to characterize the destruction of the polyester bond in the presence of oxygen. It is shown that $\hat{A}$ and $\hat{E}$ may be used to characterize the kinetics of polyester oxidative degradation during combustion, while the compensation parameter $\hat{T}_i$ may characterize the flame-retardant effect.

INTRODUCTION

J. D. Cooney et al.[1] have studied the kinetics of thermal oxidative degradation of four samples of flame-retardant commercial polyester [poly(ethylene terephthalate), PET] using the method of nonisothermal kinetics to find that the process proceeds at three separate stages, two of which actually merge as the heating rate increases. Flame retardants do not exert great influence on the decomposition of fabrics. They have used the parameters of the kinetic compensation effect (CE)

$$\log A = a_0 E + a_1 \tag{1}$$

to indicate changes in the decomposition kinetics due to the introduction of flame retardants. The kinetic parameters of all stages of the process were used to calculate a_0 and a_1. Bromine-containing flame retardants are found to have a greater effect on the polyester degradation kinetics compared to phosphorus-containing retardants. The effect if any, of the latter on the process kinetics is negligible.

Realization of the general CE for the three-stage process in Ref. 1 may be evidence of uniform degradation. This uniformity may be stipulated, for instance, by the destruction in the course of reaction of the $—H_2C—O—$ bonds[2] which is kinetically different owing to the structural nonuniformity of polymer macromolecules (irregular chaining and branching due to co-

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polymerizing impurities), differences in the end groups, and inhibiting effects of the decomposition products. Formally, such a situation corresponds to different conditions under which one and the same reaction proceeds.

The oxidative degradation of polyester is a complex process whose mechanism has not yet been studied thoroughly. Taking into account all possible elementary reactions for such processes proceeding by the radical mechanism gives an intricate expression for the effective velocity constant (K)[3]. The admixtures introduced into the fabrics produce different effects on individual elementary reactions and, consequently, on the entire decomposition process, which, depending on the nature of admixtures, alters the effective kinetic characteristics accordingly, including the CE parameters, used by Cooney et al.[1]

The stage nature of polyester thermolysis may be interpreted in an alternative way. When analyzing the available data, Petoukhov[4] concludes that PET decomposition mainly proceeds by the molecular mechanism. It is only at high temperatures (above 560 K) that thermolysis by the radical mechanism begins to predominate in an oxidizing atmosphere. Hence, linear heating may involve both mechanisms, first, a molecular and then a radical mechanism.

As the temperature range of the first peak is 520–590 K during poly(ethylene terephthalate) thermolysis,[1] this stage may be accounted molecular PET destruction, generating volatile and nonvolatile products that may be molecular destruction inhibitors. The second stage will then most probably correspond to radical decomposition, the third stage being decomposition of hard volatile products.

That three individual stages exist is of paramount importance in analyzing the mechanism of polyester degradation. However, for quantitative assessment of the polymer behavior during combustion, it is more important in the final analysis that the major loss of mass in the course of oxidative polyester degradation at high heating rates takes place practically for one macrostage.[1] In this case, when the kinetic results are extrapolated to the conditions in the combustion wave, polyester degradation may be considered as a one-stage process characterized by some effective kinetic parameters. The estimation of such parameters by the low-temperature nonisothermal data cited in Cooney's work is the concern of Part I of this work. These parameters are found not to be purely formal; they promote better understanding of the degradation process during combustion.

The estimation is based on the correlation of the values of a_0 and a_1 type, and allows one to find the parameters $\hat{A}$ and $\hat{E}$ referred to as invariant because they are independent of the heating rate and the form of the kinetic function $f(a)$. The physicochemical and geometric interpretation of the method of $\hat{A}$ and $\hat{E}$ estimation is given elsewhere. Work by Lesnikovich and colleague concern both its possible application to nonisothermal data,[6,7] and mathematical and statistical substantiation.[8] The expediency of using this approach to estimate the kinetic parameters of fuel polymer binder combustion is also shown by Lesnikovich.[9] Following the above works, the correlation of the values of a_0 and a_1 type completes the chain of relations

$$\log K = \log A - \frac{E}{2.3\,RT};$$

(2)

$$\log A \ = \ \log \hat{K} \ + \ \frac{E}{2.3 \, R\hat{T}};$$

(3)

$$\log \hat{K} \ = \ \log \hat{A} \ - \ \frac{\hat{E}}{2.3 \, R\hat{T}},$$

(4)

where $\wedge$ denotes an invariant quantity; K is the velocity constant; $a_0 = \frac{1}{2.3} R\hat{T}$; $a_1 = \log \hat{K}$. Geometrically, the invariant quantities mean that they are coordinates of the intersection point of the straight lines determined by the preceding equation in the equation chain. Thus, it is well known that, in the case of the CE, the Arrhenius lines form a pencil. Similarly, the correlation of a_0 and a_1 consists with a pencil of lines [Eq.(1)] with vertex coordinates $(\log \hat{A}; \hat{E})$. In other words, correlation [Eq.(4)] is the Arrhenius equation for the vertices of the pencils of primary Arrhenius lines. Therefore, $\hat{A}$ and $\hat{E}$ found from this correlation are independent of a number of secondary factors affecting A and E in original Arrhenius Eq. (2) and are invariant in this sense.

RESULTS AND DISCUSSION

In this case of flame-retardant polyester degradation, such secondary factors are the heating rate. Flame-retardant effect, as well as the causes of the division of the entire process into stages. In fact, as seen from Figure 1, a_0 and a_1 show a satisfactory correlation with the correlation factor $/ r / = 0.9978$. The values of $\hat{A}$ and $\hat{E}$, found through the simple regression analysis using average a_0 and a_1 values, constituted 15.7 ± 1.3 and 183 ± 16 (A /min^{-1}; E/kJ mole^{-1}), respectively.

In order to specify the meaning of $\hat{A}$ and $\hat{E}$ we have obtained, and to find the causes of the dependence in Figure 1, let us represent oxidative polyester degradation at each of the three stages in the simplest uniform terms
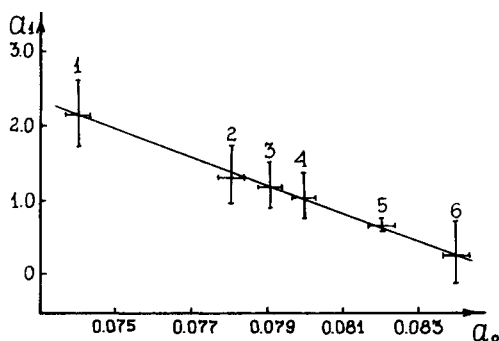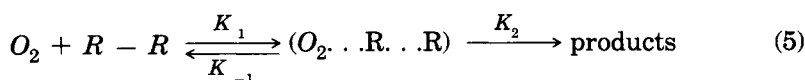
$$O_2 + R - R \underset{K_{-1}}{\overset{K_1}{\rightleftarrows}} (O_2 \ldots R \ldots R) \overset{K_2}{\longrightarrow} \text{products}$$

(5)

Fig. 1. Correlation of compensation parameters estimated by Cooney et al.:[1] 1, TRIS; 2, AB19; 3, T54; 4, MICH; 5, T271; 6, 900F.

At $K_{-1} >> K_2$ in the quasistationary approximation

$$K = \frac{K_1}{K_{-1}} \cdot K_2 \qquad (6)$$

Note that a similar expression for the effective velocity constant K is also obtained in a quasiequilibrium approximation provided, for example, that the process includes the formation of an intermediate compound, as is assumed in the case of polyester pyrolysis.[4] Similar combinations of elementary constants for the starting, propagation, and stopping of the chain are encountered in radical-chain processes.[10]

As noted above, polyester destruction is a complex process, and the constants in the expressions of type in Eq. (6) are not elementary. When affected by the above factors (structural nonuniformity, admixtures, impurities, reaction products), they may change, thus causing K to alter and three individual stages to appear.

It is seen that Eq. (6) agrees with Eq. (2) since Eq. (6) yields a complete analog of Eq. (2):

$$\log K = \log A - \frac{E}{2.3\,RT}$$

where $A = \dfrac{A_2 \cdot A_1}{A_{-1}}$; $E = E_2 - E_{-1} + E_1$.

Further, we shall use the condition according to which the CE must take place for the process under study. As at the i-th point of intersection of the Arrhenius lines $K = K_i$, then for Eq. (5) the i-th CE will be written as:

$$\log A_1 - \log A_{-1} + \log A_2 = \log \hat{K}_i + \frac{E_2 - E_{-1} + E_1}{2.3\,RT_i} \qquad (7)$$

(in Cooney et al. $i = 1,\ldots,6$).[1]

If the kinetic parameters of the limiting stage with K_2 do not change with the realization of the CE, then the CE obeys the linear dependence of $\log A_1 - \log A_{-1}$ on $E_1 - E_{-1}$ with a slope $\dfrac{1}{2.3\,R\hat{T}_i}$. Since there are no restrictions imposed on the free CE term, it must hold at any of its values, including 0, when the CE is of the form:

$$\log A_1 - \log A_{-1} = \frac{E_1 - E_{-1}}{2.3\,R\hat{T}_i} \qquad (8)$$

It follows from Equations (7) and (8) that

$$\log \hat{K}_i = \log A_2 - \frac{E_2}{2.3\,R\hat{T}_i} \qquad (9)$$

Because Eq. (9) is valid for all i points, $\log A_2 = \log \hat{A}$, $E_2 = \hat{E}$. Thus, log

$\hat{K}$ versus $1/\hat{T}$ yields the kinetic parameters of the stage corresponding with the K_2. In other words, the fulfillment of relation (8) is consistent with the equality $K_1 = K_{-1}$, i.e., $K = K_2$. The variable subscript i in Eq. (8) means that the CE is realized i times (under i different conditions affecting log $A_1 - \log A_{-1}$, $E_1 - E_{-1}$ in different ways). A certain $\hat{T}_i$ corresponds to each of these conditions.

Equation (4) a_0 versus a_1, formally means that the origin of the coordinates (log $A_1 - \log A_{-1}$) versus ($E_1 - E_{-1}$) is transferred from the vertex of the pencil of lines described by Equation (8). The transformation of coordinates, which agrees with Equations (7)–(9), is shown schematically in Figure 2. The physical meaning of the reasons leading to Eq. (4) is that the reaction or a set of reactions for which the CE takes place, is complicated by yet another process to which K_2 corresponds in Eq. (3). In the general case, its velocity constant enters K as a cofactor and does not depend on the factors causing the CE.

Form (8) for the CE may be attributed to entropy–enthalpy compensation[11] for the stage with K_1 and K_{-1}. More trivial reasons[12] which are, in particular, connected with the nonelementary nature of these stages, are also possible. In nonisothermal kinetics, the CE may be apparent, for which $\hat{T}_i$ corresponds to a maximum reaction rate.[13] In the case under consideration, a uniform CE for all three stages is most interesting. We think this may be explained by that the value of $\hat{T}_i$ for each separate i is close to the characteristic temperature (T_d)[14] of intensive decomposition of polymer with a certain flame retardant. According to Shlensky[14], $K = K_0$

$$\exp\left[-\frac{E}{R}\left(\frac{1}{T} \cdot \frac{1}{T_d}\right)\right],$$ where $K_0 = K$ at $T = T_d$. Obviously, this expression

coincides in form with the expression that may easily be obtained by substituting Eq. (3) into Eq. (2). If both expressions describe adequately the temperature dependence of K, then $T_{d_i} = \hat{T}_i$. The values of $a_0{}^1$ for TRIS, AB19, T54, MICH, T271, and 900F give, correspondingly, $\hat{T}_1 \approx 705$, $\hat{T}_2 \approx 670$, $\hat{T}_3 \approx 660$, $\hat{T}_4 \approx 650$, $\hat{T}_5 \approx 640$, and $\hat{T}_6 \approx 620\ K$, which lie in the region of intensive polyester decomposition.
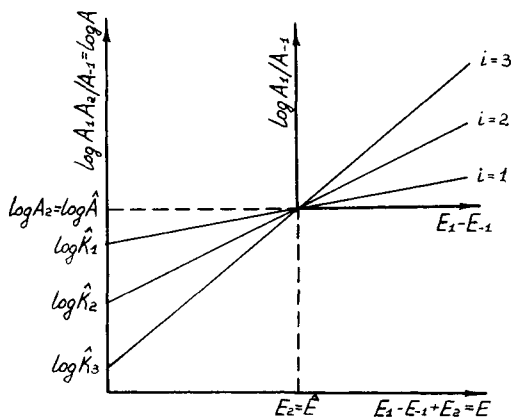

Fig. 2. Coordinate transformation corresponding to Equations (7), (8), and (9) for three lines at different $\hat{T}_i$.

However, as the temperatures T_{d_i} and $\hat{T}_i$ are not known with high enough accuracy, the alternative interpretation in Eq. (4) cannot be ruled out either. It is based on the assumption that all three stages are different reactions. The entire three-stage process may schematically be written down as:

$$R - R \xrightarrow{K_1} R' - R' \xrightarrow{K_2} R'' \xrightarrow{K_3} P$$
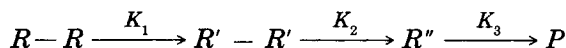
A single CE for the three stages may be attributed, in this case, to the apparent nature of this effect when $\hat{T}_i$ is equal to the harmonic mean value of the experimental temperatures.[15] Here the following set of linear equations holds

$$\log A_1 ij = a_{0i} E_{1ij} + a_{1i}$$
$$\log A_2 ij = a_{0i} E_{2ij} + a_{1i} \qquad (10)$$
$$\log A_3 ij = a_{0i} E_{3ij} + a_{1i}$$

(j is the ordinal number of α values for which A and E are calculated by Cooney[1] by the Ozawa method). From Eq. (10)

$$a_{0i} = \frac{\log A_{1ij} - \log A_{3ij}}{E_{1ij} - E_{3ij}}$$

and

$$a_{1i} = \log A_{2ij} - \frac{\log A_{1ij} - \log A_{3ij}}{E_{1ij} - E_{3ij}} E_{2ij} \qquad (11)$$

Following the data of Cooney et al.,[1] with changing i (i.e., flame retardant) and j (i.e., α from 0.5 to 0.8 corresponding to the second stage) A_2 and E_2 change, but scarcely and they may be considered constant and roughly equal to A_2 and E_2 for the polymer without the flame retardant. When the flame retardant is introduced, the values of $\log A_1$; $\log A_3$; E_1, and E_3 may vary to give new values of a_0 and a_1 for each i-th flame retardant, that is, to new apparent CEs and Equation (4). In accordance with the above, the flame retardant may principally affect the first and/or the third stage of PET decomposition. Thus, A_2 and E_2 for pure polymer are approximately estimated from Equation (11) similarly to Equation (4), in other words, the kinetic parameters of the second stage, which are presumably caused by polyester decomposition and proceed by the radical mechanism, prove to be invariant.

It is worth noting that the value of $\hat{A}$ is close to the theoretical value of the pre-exponential factor in the reactions of homolytic break of chemical bonds. Recently, a great bulk of experimental data on the kinetics of gas-phase homolysis reactions of the type $R = R \rightleftarrows R' + R'$ were processed statistically to find that the effective mean value of $\log A = 14.6$ (A/s^{-1}) or 16.4 (A/min^{-1}).[16] The numerical values of $\log \hat{A}$ and $\hat{E}$, together with the analysis of the alternative schemes, make it credible that these values

do have the kinetic characteristics for chemical break of polyester bonds (in the presence of O_2), which are probably single carbon–oxygen (ester —H_2C—O—) bonds[4] (for C-C bonds in pyrolysis of polybutadiene rubbers we have found $\hat{E} = 249\text{-}284$ kJ·mol^{-1}).[9]

The values of log $\hat{A}$ and $\hat{E}$ within the errors coincide with the "global" log A and E found by Cooney et al.[1] for the second stage of decomposition of the control sample T54 by the method suggested by Ozawa (15.9±0.6 and 182.6±7.5), Friedman (13.1±0.3 and 201.0±8.5), and Kissinger ($E=202.1±6.7$). As the algorithm for $\hat{A}$ and $\hat{E}$ computation excludes the effect of the nonisothermal data processing method on these values,[6,9] we may conclude that the methods of Cooney yield rather correct results.[1] In this case, the above coincidence supports the assignment of $\hat{A}$ and $\hat{E}$ to the ether bond-breaking process. At the same time, it should be noted that the three methods do not always yield close results. This is all the more true of a wider range of methods used to process nonisothermal kinetic data. This results in the problem of giving preference to the values of A and E obtained by different methods which may be solved through estimating $\hat{A}$ and $\hat{E}$.

As to the accuracy of log $\hat{A}$ and $\hat{E}$ values, it seems to be less than the accuracy of the above values for T54 or the values obtained by any one of the methods. The latter, however, characterizes the error in approximation or in reproducibility, if the experiments were repeated, rather than giving a systematic error of the method. The calculation of $\hat{A}$ and $\hat{E}$ implies[6,9] the application of various data processing methods and different kinetic functions. Therefore, systematic errors in separate methods become random in method of $\hat{A}$ and $\hat{E}$ estimation and the error comes across in the determination of these kinetic parameters, which are characterized more objectively. Comparison of the errors in log $\hat{A}$ and $\hat{E}$ with the above values of log A and E for T54 on the boundaries of the confidence intervals shows that log A ranges within 16.5–12.8 = 3.7 while the range for log $\hat{A}$ is 2.6. A similar picture is valid for E errors. Thus, in reality, the method of $\hat{A}$ and $\hat{E}$ estimation gives less uncertainty in the kinetic parameter values.

In conclusion, although oxidative degradation of flame-retardant polyester is a complex process, Cooney's use of the compensation parameters a_0 and a_1 to characterize changes in the kinetics of the process seems to have grounds. However, as follows from the authors' study, a single equation may give a more complete quantitative characteristic of the effect of temperature and flame retardant as well as of the process behavior in the initial polymer on K. Irrespective of the real process mechanism, this equation will be obtained from Eqs. (2)–(4) in the form:

$$K = \hat{A}\ exp\left(-\frac{\hat{E}}{R\hat{T}_i}\right) exp\left(\frac{E}{R\hat{T}_i}\right) exp\left(-\frac{E}{RT}\right) \tag{12}$$

where $\hat{A}$ and $\hat{E}$ characterize polymer degradation; $\hat{T}_i$ is the effect of the i-th flame retardant on polymer degradation; E is the temperature effect on a complex set of flame-retardant polymer processes. Note also that it is Eq. (4) from which one draws the conclusion that flame retardants do not change the nature of the polymer process. In fact, the common line (Fig.

1) contains both the points for polyester with admixtures and the points for two samples without flame retardants which serve the purpose of comparison.

In accordance with other works,[14,17,18] the polymer temperature cannot exceed some limit value. Perhaps, during combustion the polymer temperature T_{si} in the reaction layer is close to $T_{di} = \hat{T}_i$. The experimental data give evidence[2] that for pure polyester $T_s \approx 650\,K$, while for flame retardant polyester $T_s \approx 720\,K$, which agrees with the $\hat{T}_i$ values. Hence, in the case of polymer combustion we may assume $T_{si} = \hat{T}_i$. Then Eq. (12) is reduced to give $K = \hat{A}\,\exp\left(-\dfrac{\hat{E}}{R\hat{T}_i}\right)$. The latter means that for characterizing the polymer degradation kinetics quantitative combustion models may include invariant kinetic parameters $\hat{A}$ and $\hat{E}$ along with the compensation parameter $\hat{T}_i$ for the flame retardant effect. It is probable that $\hat{T}_i$ is greater than $\hat{T}$ for untreated polymer when flame retardant influences flame gas-phase reactions. this condition will intensify flame retardant polymer decomposition, which is necessary to ensure combustion. When flame retardant influences on solid-phase processes, $\hat{T}$ is greater than $\hat{T}_i$ for untreated polymer, which corresponds to decrease of K and to inhibit of polymer decomposition.

To conclude, we emphasize the scientific and applied importance of the problem of estimating the invariant kinetic polymer decomposition parameters, including $\hat{T}_i$. In Part II we shall discuss some methodologic features of determination of these invariants based on the butyl rubber pyrolysis.

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