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BIAS IN ISOTHERMAL TIME-TO-EVENT STUDIES DUE TO APPROACH TO TEST TEMPERATURE

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Abstract

Oxidative induction time (OIT), constant temperature stability (CTS) and isothermal crystallization are examples of isothermal time-to-event (TTE) measurements obtained using differential scanning calorimetry. In TTE experiments, a test specimen is heated/cooled at a constant rate from the setup temperature to an isothermal test temperature. Once the test temperature is achieved, a clock is started and the time to the thermal event (e.g., onset to oxidation, thermal decomposition or crystallization exotherm peak) is measured. Such TTE values may be used to rank stability of the material at the test temperature. Some portion of the reaction of interest, however, takes place during the pre-isothermal period as the test specimen approaches the test temperature. This amount of reaction is unmeasured and represents a bias in the resultant TTE value. An equation has been derived and numerically integrated to estimate this bias. This approach shows that the bias is dependent upon the activation energy of the test reaction, the heating/cooling rate used and the temperature range between the melting temperature and the test temperature. For commonly used heating rates, the bias for OIT and CTS tests is small. Further, the myth that isothermal crystallization kinetics determinations required high cooling rates is dispelled with the bias of less than 0.9 min resulting from heating rates as low as 10°C min^{-1}. Knowledge of magnitude of this bias permits the selection of experimental conditions without the expense of high heating/cooling rate apparatus or extra cost cooling accessories.

Keywords: bias, constant temperature stability, isothermal crystallization, kinetics, oxidative induction time

Introduction

Oxidative induction time (OIT) [1], constant temperature stability (CTS) [2] and isothermal crystallization are examples of isothermal time-to-event (TTE) measurements using differential scanning calorimetry. The TTE values are indexes used to rank event occurrence or stability at the test temperature with longer TTE values indicate higher stability. In TTE experiments, as shown in Fig. 1, a test specimen is heated/cooled at a constant rate from the setup temperature to an isothermal test temperature. Once the isothermal test temperature is achieved, a clock is started and the time to the thermal event (e.g., onset to oxidation, thermal decomposition

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or crystallization exotherm peak) is measured. Some portion of the reaction of interest, however, takes place during the pre-isothermal period as the test specimen approaches the test temperature. This amount of reaction is unmeasured and represents a bias in the resultant TTE value.

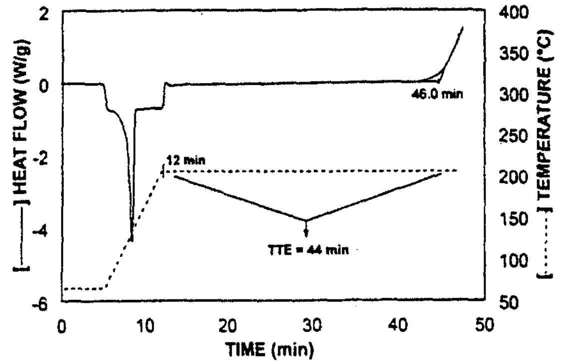

Fig. 1 Time-to-event experimental profile

In an earlier work, an expression, based upon the Arrhenius equation, was created for estimating the bias in oxidative induction time measurements due to the approach to the isothermal test temperature [3]. It was shown that the bias is dependent on the activation energy of the reaction and on the heating rate used to approach the test temperature. The bias itself was found to be less than 1.2 min for the most common heating rates and to be small when compared to most OIT values and to experimental repeatability.

This earlier oxidative induction time treatment is somewhat simplified, however, as the initial temperature is usually ambient, the test temperature is almost always 200°C, and the range between ambient and test temperature, as well as the activation energies, are large. This leads to the simplification that the reaction rate is insignificant at the start of the experiment and that the bias is not dependent upon the temperature range between ambient and the test temperature. Further, this earlier OIT work ignores that the test specimen sometimes undergoes a phase changed (i.e., melting) with the concomitant change in reaction rate, as the temperature is raised from ambient to the test temperature.

Other TTE cases of interest, such as thermal stability and thermoset cure are somewhat more complex. Phase changes, such as melting or glass transition, which affect the reaction rate and thus the TTE, often take place at temperatures between ambient temperature and the isothermal test temperature. For example, potassium chlorate, a common pyrotechnic, is quite stable in the solid, crystalline form but quickly decomposes once the specimen melts [4]. Other examples include thermoset cure where the crosslinking reaction occurs more rapidly above the melting temperature or the glass transition. These reactions, therefore, have a discontinuous change, from a slow to a fast reaction rate, at a specific transition temperature between ambient and the isothermal test temperature. These experimental conditions may be treated in an analogous manner to that of OIT but require modification to the mathematical treatment. Specifically, due to the wide variety of reaction mechanisms, the temperature range between the melting temperature and the test temperature becomes an experimental parameter in addition to the activation energy and the heating rate.

The case of polymer isothermal crystallization is even more complex, but is still treatable in the same manner. Here the initial temperature is that of the annealing temperature for the test specimen often 30°C above the melting temperature of the polymer [5]. The test specimen is then cooled to the isothermal test temperature below the melting temperature. No reaction takes place until the test temperature drops below the melting temperature of the specimen. Once below the melting temperature, the induction time decreases and the reaction rate increases with decreasing temperature leading to a positive value for the activation energy compared to the negative values seen in the oxidative induction time and thermal stability measurements.

Theory

The Arrhenius expression describes the relationship between the rate constant (k) and the temperature (T). For reactions whose rate increases with temperature, the Arrhenius expression becomes:

$$k(T) = Z \exp(-E/RT) \tag{1}$$

where $k(T)$ specific rate constant at temperature T (min^{-1}),
Z pre-exponential factor (min^{-1})
E activation energy (J mol^{-1}),
R molar gas constant (=8.3143 J (mol K)$^{-1}$), and
T absolute temperature (K).

The specific form of the rate equation (i.e., n-th order, Avrami, Šesták-Berggren, etc.) describing the reaction is unimportant provided that the fraction reacted is small (i. e., $\alpha \ll 1$).

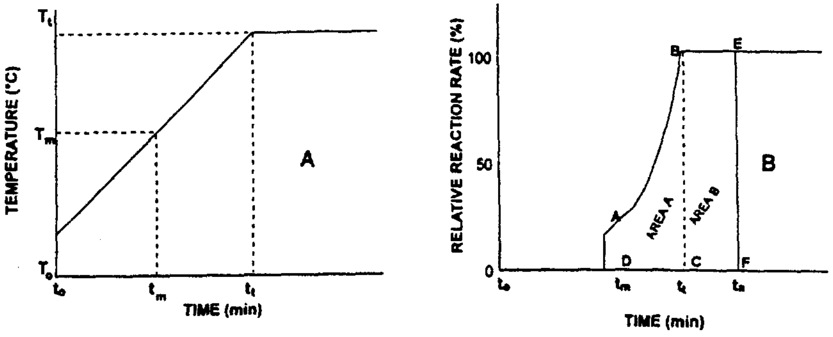

Fig. 2 Temperature (A), reaction rate profile (B)

A schematic diagram of a typical temperature program for a TTE experiment is shown in Fig. 2A. Temperature is displayed on the ordinate *vs.* time on the abscissa. Beginning at zero time (t_0) and ambient (or setup) temperature (T_0), the temperature is increased linearly to the isothermal test temperature (T_t) reached at time t_t. Along the way, the temperature may pass through the melting temperature (T_m) for the test specimen at a corresponding time of t_m.

The corresponding reaction rate for the first few minutes of a TTE experiment may be modeled as presented in Fig. 2B. Here the relative reaction rate (the ratio of the reaction rate at a given temperature to that at the test temperature [i.e., $k(T)/k(T_t)$]) is displayed on the ordinate *vs.* time on the abscissa for the same time region as displayed in Fig. 2A. Some reaction takes place below the melting temperature (T_m), but this reaction rate is assumed to be insignificant until the melting temperature and time (t_m) is reached. At this point a discontinuous increase in the reaction rate is seen. The reaction rate then continues to increases exponentially until the isothermal test temperature and time are reached. Once the test temperature is achieved, the reaction rate is assumed to be constant. This assumption is reasonable early in the reaction process where the fraction reacted is small.

The amount of reaction which has taken place between the melting temperature and the test temperature is a bias underestimating the TTE value. This bias is represented in Fig. 2B by the Area *A* bounded by the points ABCD. The area is obtained by integrating Eq. (1) over the limits from the time the specimen melts (t_m) until the time the test temperature (t_t) is reached; that is, the interval of the temperature ramp between T_m and T_t.

$$\text{Area } A = \int_{t_m}^{t_t} k(T)\mathrm{d}t = Z\int_{t_m}^{t_t} \exp(-E/RT)\mathrm{d}t \tag{2}$$

For the constant heating rate region used to approach the test temperature, the heating rate (β) provides the relationship between the changing temperature ($\mathrm{d}T$) and the changing time ($\mathrm{d}t$); $\mathrm{d}t=\mathrm{d}T/\beta$ Substituting this relationship into Eq. (2) yields:

$$\text{Area } A = (Z/\beta)\int_{T_m}^{T_t} \exp(-E/RT)\mathrm{d}T \tag{3}$$

A second area, Area *B*, is described in Fig. 2B, which corresponds to the closed area BEFC. This area represents the amount of reaction which takes place at the test temperature over the time interval t_t to t_a. If t_a is selected so that Area *B* is equal to Area *A*, then t_a–t_t is equal to the bias in the TTE measurement due to the approach to test temperature reaction and is here called BIAS. Area *B* is equal to the reaction rate at the test temperature (T_t) multiplied by the BIAS.

$$\text{Area } B = k(T_t)\text{BIAS} = Z\exp(-E/RT_t)\text{BIAS} \tag{4}$$

Setting Eqs (3) and (4) equal to each other and solving for BIAS:

$$\mathrm{BIAS} = \left[\int_{T_m}^{T_t} \exp(-E/RT)\mathrm{d}T\right] / [(\beta \exp(-E/RT_t)] \qquad (5)$$

When the values for T_m , T_t and E are known, Eq. (5) may be evaluated. For convenience in the evaluation process, the exponential functions $\int \exp(-E/RT)\mathrm{d}T/\exp(-E/RT_t)$are collected into a term, called the Reaction Fraction (F), which has the units of temperature.

$$F = \left[\int_{T_m}^{T_t} \exp(-E/RT)\mathrm{d}T\right] / [\exp(-E/RT_t)] \qquad (6)$$

Equation (5) then reduces to the form:

$$\mathrm{BIAS} = F/\beta \qquad (7)$$

Values of the initial or melting temperature (T_0 or T_m), isothermal test temperature (T_t) and activation energy (E) are needed to solve Eqs (5, 6 and 7). Table 1 presents values for a number of example time-to-event measurements. Activation energy val-

Table 1 Kinetic Parameters for Thermal Stability Measurements

Material	Activation energy/kJ mol^{-1}	Temperature/°C		Reaction fraction (F)
		melting	test	
Oxidative induction time				
Polyethylene [6]	192	130	200	9.30
Polypropylene [6]	249	165	200	7.19
Rapeseed Oil [7]	72	<25	200	23.4
Lubricating Oil [8]	121	<25	200	14.5
Thermal stability				
4,4′-Azoxyanisole	148	119	307	17.8
Azidotriphenylmethane	147	65	227	13.4
Poly(acrylonitrile)	251	25	262	9.2
Polymer isothermal crystallization [9]				
Polyethylene	88	130	129	1.87
Nylon 6	357	205	222	5.10
Poly(ether ether ketone)	472	322	342	6.04
Poly(ethylene terephthalate)	1080	217	255	1.78

ues for TTE experiments are typically obtained using Eq. (8) derived by taking the logarithmic form of Eq. (1) and substituting the value of ln$k$ = –ln TTE+constant from the general rate equation at constant conversion. A plot of natural logarithm of the TTE value *vs.* the reciprocal of the absolute isothermal test temperature produces a straight line, the slope of which is equal to E/R. An OIT example plot is shown in Fig. 3.

$$\ln \mathrm{TTE} = [(E/R)1/T] + \text{constant} \tag{8}$$

The OIT values in Table 1 were obtained from the literature. The thermal stability values were obtained in our laboratory using thermal stability kinetics [10]. And the values for polymer isothermal crystallization were determined in our laboratories using the Šesták-Berggren equation, which is similar in form to the general rate equation but with an extra "auto-catalytic" parameter [9].

The evaluation of the Reaction Fraction requires the integration of the exponential terms in the numerator of Eq. (5). This is difficult to do exactly but may be estimated using numerical integration techniques. The numerical integration process used here, known as Simpson's Rule, is shown in Fig. 4, where the relative reaction

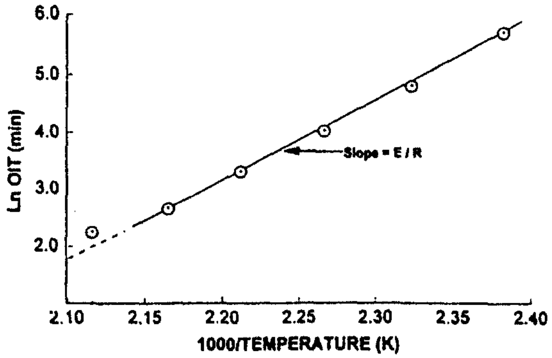

Fig. 3 Determination of activation energy

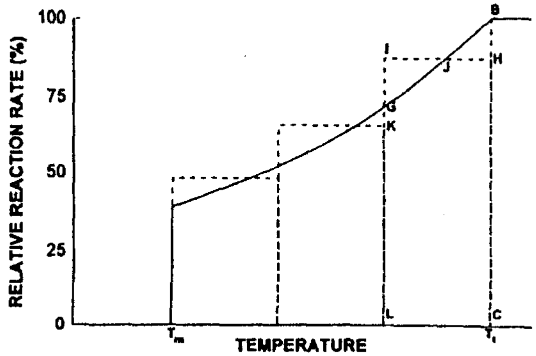

Fig. 4 Numerical integration

rate is plotted as the curved line on the ordinate with temperature on the abscissa. The area under the curve may be estimated using a series of rectangles with a temperature width multiplied by the reaction rate constant for the midpoint temperature for that temperature range. For example, the area BCLG may be estimated by the rectangle HCLI. The rectangle's over-estimation of the area JGI below the midpoint temperature approximates the area under-estimation BHJ above this value. By summing over all of the individual rectangles from the melting temperature to the test temperature, an estimation of the value for the fraction *F* may be obtained. A series of *F* values calculated for the representative set of oxidative induction time, thermal stability and polymer isothermal crystallization data are presented in Table 1.

Discussion

Values for the Reaction Fraction (*F*) from Table 1 may be inserted into Eq. (7) along with trial examples for the linear heating or cooling rate associated with the approach to isothermal test temperature. The BIAS for the Oxidative Induction Time test method is thus estimated to be very small even for modest heating rates. For example, the value for the BIAS for a heating rate of 20°C min^{-1}, called for in the standard Pressure DSC tests [11, 12], range from 0.5 to 1.2 min. These values may be compared to the OIT values of between 15 and 100 min and with the typical repeatability standard deviation of ca. 5 min to show that the bias is not significant.

The three thermal stability materials in Table 1 are candidates for a reference material for DSC kinetic tests such as those of Constant Temperature Stability [2] or thermal stability [10]. In the CST, a temperature is sought at which the material may be held for two hours or more without initiation of the exothermic runaway reaction. The method calls for the test specimen to be heated from ambient to the test temperature in less than 10 minutes. Heating rates between 20 and 35°C min^{-1} are commonly used. The BIAS for undetected reaction observed during heating is obtained by dividing the Reaction Fraction of Table 1 by these heating rates. The BIAS calculated for these heating rates range from 0.3 to 0.9 min. Again this value is insignificant compared to the 120 min minimum for the test method.

The final example is that of polymer isothermal crystallization with activation energy values for representative polymers presented in Table 1. These polymers range from "fast" crystallizers such as polyethylene, through intermediate crystallizing rate examples of nylon and PEEK, to the "slow" crystallizers such as poly(ethylene terephthalate). The isothermal crystallization case is especially interesting as it is commonly believed that very high cooling rates ($\geq$100°C min^{-1}) are required for this measurement. However, Foreman and coworkers showed quite acceptable results when cooling rates as low as 5°C min^{-1} are used [9] . Dividing the Reaction Fractions of Table 1 by trial cooling rates shows why this is possible. The BIAS values thus obtained range between 0.2 and 0.6 min for the modest cooling rate of 10 °C min^{-1}. This is small compared to the 5 to 100 min TTE times typically encountered in an isotherm crystallization kinetics experiment.

Conclusion

This approach, based on the Arrhenius equation, shows that the bias introduced into time-to-event experiments by the process of linearly temperature programming to the test temperature is dependent upon the activation energy of the test reaction, the heating/cooling rate used and the temperature range between the melting temperature at the test temperature. For commonly used heating rates, the bias for Oxidative Induction Time and Constant Temperature Stability tests is small compared to the OIT values and the experimental times. Further, the myth that isothermal crystallization kinetics determinations required high cooling rates is dispelled with the bias of less than 0.9 min resulting from heating rates as low as 10°C min^{-1}. Knowledge of magnitude of these bias values permits the selection of experimental apparatus and conditions without the expense of high heating/cooling rate apparatus or extra cost cooling accessories.

References

1 ASTM D3895-95, "Oxidative Induction Time of Polyolefins by DSC", American Society for Testing and Materials.
2 ASTM E0487-79, "Constant Temperature Stability of Chemical Materials", American Society for Testing and Materials.
3 R. L. Blaine and S. M. Marcus, "Estimation of Bias in the Oxidative Induction Time Measurement by Pressure DSC" Oxidative Behavior of Materials by Thermal Analytical Techniques, ASTM STP 1326, A.T. Riga and G.H. Patterson, Eds., American Society for Testing and Materials, 1997.
4 J. A. Conkling, Chemistry of Pyrotechnics, Marcel Dekker, New York, 1985.
5 ASTM E0794-95, "Melting and Crystallization Temperatures by Thermal Analysis", American Society for Testing and Materials.
6 D. I. Marshall, E. J. George, J. N. Turnipseed and J. L. Glenn, Polym. Eng. Sci., 13 (1973) 415.
7 B. Kowalski, Thermochim. Acta, 156 (1989) 347.
8 J. A. Walker and W. Tsang, Soc Autom. Eng. Tech. Paper 801383, (1980).
9 J. A. Foreman and R. L. Blaine, "Isothermal Crystallization Made Easy; A Simple Model and Modest Cooling Rates", 41st Ann. Tech. Conf. Soc. Plasts. Eng., Vol. 2 (1995) 2409.
10 ASTM E0698-79, "Arrhenius Kinetic Constants for Thermally Unstable Materials", American Society for Testing and Materials.
11 ASTM D5483-93, "Oxidation Induction Time of Lubricating Greases by PDSC", American Society for Testing and Materials.
12 ASTM D5885-96, "Oxidative Induction Time of Polyolefin Geosynthetics by PDSC", American Society for Testing and Materials.