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Thermal Analysis & Rheology

ESTIMATION OF BIAS IN THE OXIDATIVE INDUCTION TIME MEASUREMENT BY PRESSURE DSC

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ABSTRACT

Oxidative induction time (OIT) is defined as the time to the onset of oxidation of a test specimen exposed to an oxidizing gas at an elevated isothermal test temperature. In standard DSC, the oxidizing purge gas is initiated once the specimen has stabilized at the isothermal test temperature. In Pressure Differential Scanning Calorimetry, however, the test specimen is often exposed to the oxidizing atmosphere as the apparatus is heated from ambient to the isothermal test temperature. This approach creates a bias in the measurement due to undetected oxidation on heating. An expression, based upon the Arrhenius equation, is derived and then numerically integrated to obtain an estimation of the bias introduced into the OIT measurement by exposing the test specimen to oxygen at room temperature. The bias is dependent on the activation energy of the reaction and on the heating rate. The bias is found to be less than 1.2 minute for the most common heating rates, and is less than 3 minutes for the most extreme sets of experimental conditions. The bias is found to be small when compared to experimental repeatability of the OIT measurement and to the mean of OIT values. For this reason, it may be ignored in all but the most extreme cases of low activation energy, very slow heating rates, very low OIT values and high test temperatures. The ease-of-use benefits, achieved by exposing the test specimen to the reactive gas from the start of the experiment are likely to out weigh the small bias effect in most OIT measurements whether under Pressure DSC or standard DSC conditions.

A precursory study shows the same mathematical treatment can be used to estimate bias in other isothermal studies of kinetic phenomena such as isothermal polymer crystallization and isothermal reaction kinetics such as thermoset cure.

INTRODUCTION

Oxidative induction time (OIT) is defined as the time to the onset of oxidation of a test specimen exposed to an oxidizing gas at an elevated test temperature. OIT is used as an index to estimate the relative stability of materials to oxidation. It is typically used as a quality control tool and to rank the effectiveness of various oxidation inhibitors added to hydrocarbon products such as polymers, lubricating oils and greases as well as edible fats and oils. OIT measurements are commonly carried out using differential scanning calorimetry by temperature programming the specimen in an open sample pan from ambient to a test temperature under an inert atmosphere. Once the test temperature is reached and equilibrium is established, the purge gas is changed to an oxidizing gas (i.e., air or oxygen) and the clock is started. The elapsed time from the first oxygen exposure (t_o) to the onset of the oxidation (t_{onset}) is taken as the OIT value (see Figure 1). Oxidation is observed as an exothermic peak, although in most OIT experiments, only enough of the peak is recorded to determine its onset.
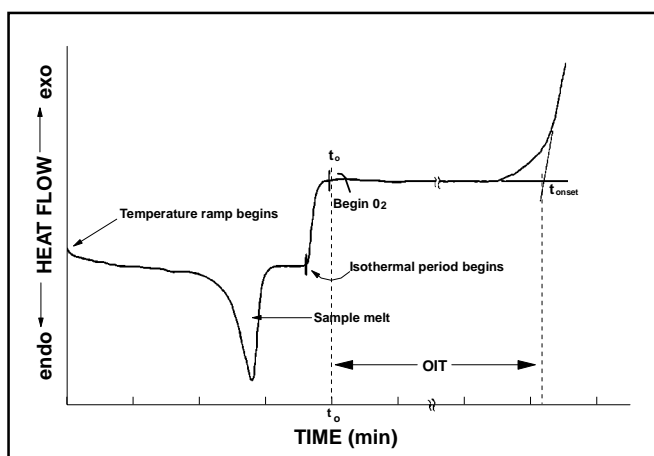
OIT EXPERIMENTAL CURVE

Figure 1

The temperature program used to achieve the OIT test conditions is made up of two parts. The first is the constant rate of temperature rise from ambient to the test temperature. The second portion is the establishment of the isothermal test temperature which is maintained until the experiment is terminated. The ramp rate to the isothermal test temperature is set as high as possible (to reduce analysis time) without overshooting the test temperature. The isothermal test temperature is typically selected to produce OIT values between 15 and 100 minutes; the higher value to limit analytical time and increase productivity, the lower value to limit the effect of measurement imprecision. Typical

isothermal test temperatures range between 150 and 210°[1,2,3]. The higher the test temperature, the lower the OIT value. The default for most OIT measurements is 200°C, with minor temperature adjustments being made depending upon the material being tested.

If a material is strongly stabilized, its OIT value may be quite long. In an attempt to reduce analytical time, the test temperature is sometimes elevated. Unfortunately, many oxidation inhibitors have an appreciable volatility at temperatures above 180°C and so increasing the test temperature results in the volatilization of the additives rather than in a measure of its chemical effectiveness. However, the OIT measurement may be accelerated at lower test temperature through the use of increased partial pressures of oxygen. Going from the 21% oxygen content of air as a reactant to 100% oxygen is one alternative. Another is making use of pressure DSC (PDSC).

Using PDSC, the OIT test is conducted under slightly different experimental conditions than those used with the standard DSC. In PDSC, the specimen is pressurized with the reactive oxygen gas at room temperature, followed by temperature programming to the test temperature at a constant rate. The initial time for the OIT measurement (t_o) is taken when the programmed temperature reaches the test temperature (T_o).

These modified experimental conditions (exposing the sample to oxygen at the start of the temperature ramp conditions) raises the question, "how much oxidation takes place as the sample is programmed from ambient to the test temperature?" This oxidation results in an underestimation of the OIT value at the isothermal test temperature and represents a measurement bias.

THEORY

In kinetic expressions, such as those governing the OIT measurements, the relationship between the kinetic rate constant (k) and the temperature (T) is given by the Arrhenius expression.

$$k(T) = Z \exp(-E/RT) \qquad\qquad (1)$$

where:

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

The effect of the Arrhenius expression on the OIT measurement may be seen in Figure 2. Figure 2A is a schematic representation of the temperature program. The temperature program begins at ambient temperature and increases at a constant rate until the isothermal test temperature (T_o) is reach where it then remains constant until the end of the experiment. Figure 2B displays the relative reaction rate (the ratio of the reaction rate at a given temperature to that at the test temperature [i.e., $k(T) / k(T_t)$]) versus time for the same region as displayed in Figure 2A. The reaction rate is small at low temperatures and increases exponentially with temperature until the test temperature is reached. Once the test temperature is achieved, the reaction rate is assumed to be constant. (This model neglects, however, that some samples (e.g., polyolefins) undergo melting between ambient and the test temperature and that the reaction rate is different in the crystalline than in the amorphous form, [3]).

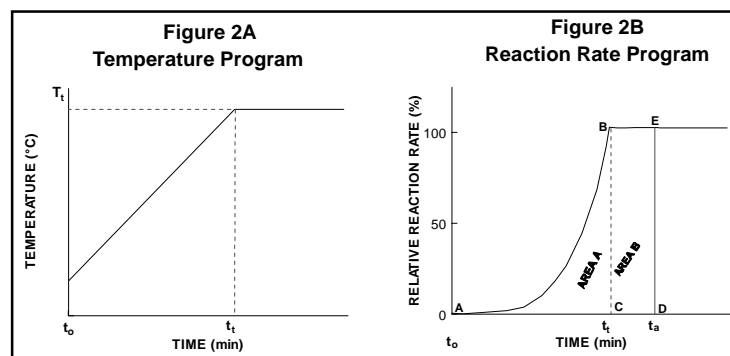## OIT TEMPERATURE REACTION RATE PROFILE

Figure 2

The amount of reaction which has taken place between ambient and the test temperature is a bias underestimating the OIT value. This bias is represented in Figure 2B by the Area A bounded by points ABC. This area is obtained by inte-grating equation (1) over the limits from the time of first exposure to oxygen (t_o) to the time the test temperature is reached (t_t), that is, the interval of the temperature ramp.

$$\text{Area A} = \int k\,(T)\ dt = Z \int \exp\,(-E/RT)\ dt \qquad\qquad (2)$$

For the constant heating rate region, the heating rate (β) provides the relationship between changing temperature (dT) and changing time (dt); $dt = dT / \beta$. Substituting this relationship into equation (2) yields:

$$\text{Area A} \;=\; \frac{Z \int \exp\,(-E/RT)\,dT}{\beta} \qquad\qquad (3)$$

A second Area B is described in Figure 2B which corresponds to the closed area BCDE. This area represents the amount of reaction which takes place at the test temperature over the time interval from t_t to t_a. This interval is selected so that Area B is equal to Area A. When this is done, $t_a - t_t$ is then equal to the bias in the OIT measurement due to the pre-test temperature reaction and is given the symbol ΔOIT. Area B is equal to the reaction rate at the test tempera-ture (T_t) multiplied by ΔOIT.

$$\text{Area B} = k(T_t) \times \Delta\text{OIT} = Z \exp\,(-E/RT_t) \times \Delta\text{OIT} \qquad\qquad (4)$$

Setting equations (3) and (4) equal to each other and solving for ΔOIT:

$$\Delta\text{OIT} \;=\; \frac{\int \exp\,(-E/RT)\,dT}{\beta \exp\,(-E/RT_t)} \qquad\qquad (5)$$

Values of the isothermal test temperature (T_t) and activation energy (E) parameters are needed to solve equation (5). Many OIT tests are carried out at 200°C ($= 473$ K). This value is selected for the value for the value of T_t in this evalua-tion. The second parameter, activation energy, is determined from a series of OIT measurements of the same material at several isothermal test temperautures. According to equation (6) below (derived by taking the logarithmic form of equation (1) and substituting the value of ln k = -ln OIT + constant from the general rate equation at constant conver-sion), a plot of the natural logarithm of OIT versus the reciprocal of the absolute isothermal test temperature produces a straight line, the slope of which is equal to E/R.

$$\ln \text{OIT} = [(E/R) \times 1/T] + \text{constant} \qquad\qquad (6)$$

Figure 3 illustrates such a data treatment for a polyethylene sample tested under 3.5 MPa (500 psig) pressure of oxygen, using a PDSC cell.
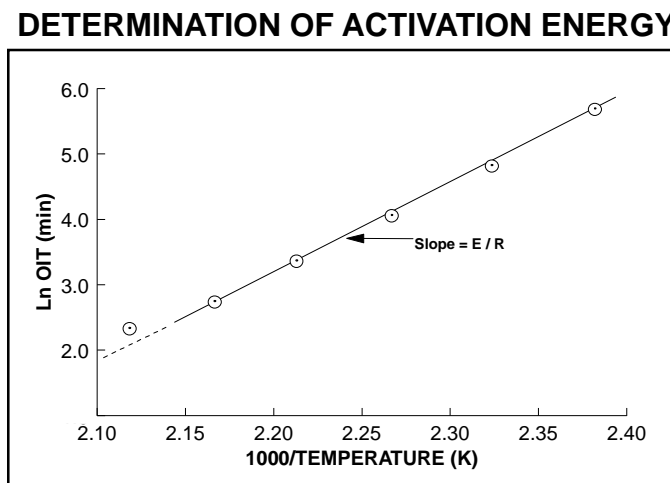
DETERMINATION OF ACTIVATION ENERGY

Figure 3

Activation energy values for OIT measurements for three common classes of materials (edible oils, polyolefins and lubricants) to which the OIT procedure is applied are collected in Table 1. The values for E for these materials range from a low of 70 to a high 250 kJ/mol with a value of 130 kJ/mol as an average.

Table 1
TYPICAL OIT ACTIVATION ENERGIES

Material	Activation Energy (kJ/mol)	Reference
Corn Oil	99	[7]
Peanut Oil	110	[4]
Rapeseed Oil	72	[7]
Soybean Oil	67	[7]
Sunflower Oil	85	[7]
Polyethylene	89	[11]
Polyethylene	165	[6]
Polyethylene	192	[9]
Polyethylene, Cross-linked	144	[8]
Polypropylene	249	[9]
Lubricating Oil*	121	[12]
Lubricating Grease*	146	[10]

* Pressure DSC at 3.4 MPa (500 psig) oxygen. All others at ambient pressure.

With appropriate values for T_t and E selected, equation (5) may be evaluated. For convenience, the exponential terms, $\int \exp(-E/RT)\, dT / \exp(-E/RT_t)$, are collected into a fraction (F) which has the units of temperature. Equation (5) then takes the form:

$$\Delta OIT = F/\beta \qquad\qquad\qquad\qquad (7)$$

The evaluation of F requires the integration of the exponential term in the numerator. This is difficult to do exactly but may be estimated using numerical integration techniques.

The numerical integration process, known as Simpson's Rule, is shown in Figure 4 where the relative reaction rate is plotted as the curved line with temperature as the abscissa. The area under the curve may be estimated using a series of rectangles with a temperature width 2°C multiplied by the reaction rate constant for the midpoint temperature for that 2°C range. For example, the area BCFG may be estimated by the rectangle HCFI. The rectangle's over estimation of the area (JGI) below the midpoint temperature approximates the area underestimation (BHJ) above this value. By summing all of the individual rectangles from ambient to the test temperature, an estimation of the value for the fraction F may be obtained. Table 2 shows a series of F values calculated for representative activation energies covering the range of interest for OIT studies.
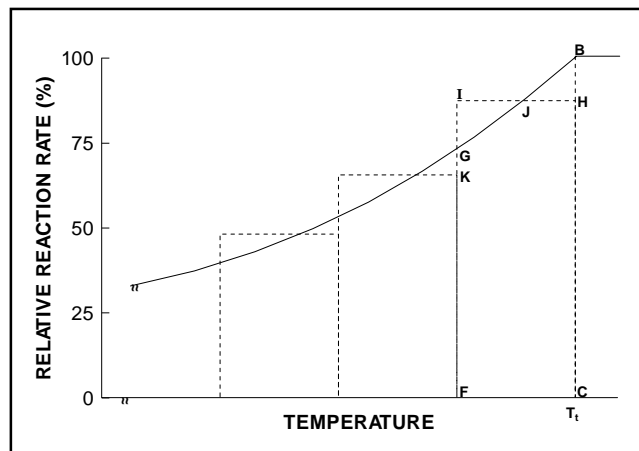
NUMERICAL INTEGRATION

Figure 4

With these values in hand, the effect of heating rate (β) on the value of the OIT bias (ΔOIT) may be estimated from equation (7). Table 3 presents ΔOIT values for common heating rates for 70, 130 and 250 kJ/mol, the minimum, average and maximum activation energy values of Table 2.

Table 2
EFFECT OF ACTIVATION ENERGY ON REACTION FRACTION F
(T_t = 200°C = 473K)

Activation Energy (kJ/mol)	Reaction Fraction F (K)
70	24.01
100	17.29
130	13.51
150	11.79
200	8.94
250	7.20

DISCUSSION

Table 3 shows that the OIT bias is smallest for high activation energy materials (such as polypropylene) and high heating rates. It is largest for the lower activation energy materials (such as the edible oils) and low heating rates. For the typical heating rate of 20°C, the bias due to oxygen exposure at the start of the OIT experiment, is less than 1.2 minutes. The importance of this 1.2 minute bias may be assessed by comparing it first to the mean value of OIT measurements and secondly, to the precision of the OIT measurement itself.

Table 3
EFFECT OF HEATING RATE AND ACTIVATION ENERGY ON THE OIT BIAS
(Test Temperature = 200°C)

Activation Energy (kJ/mol)	Heating Rate (°C/min)	OIT Bias (min)
70	5	4.8
	10	2.4
	20	1.2
	40	0.6
130	5	2.7
	10	1.4
	20	0.7
	40	0.3
250	5	1.4
	10	0.7
	20	0.4
	40	0.2

The Pressure DSC measurement of OIT is ordinarily applied to very stable materials. In the geosynthetic industry where the OIT measure is made on waste pit liners, the value for OIT is typically 300 to 1000 minutes. Clearly, a bias of 1.2 minutes in such a measurement is trivial. More commonly, however, the OIT value for other materials is between 15 and 100 minutes. For the shorter of these time periods, the bias begins to be significant. In cases of low OIT values, a second comparison is made to the repeatability of the OIT measurement, as discussed below.

ASTM standard test methods, including those for OIT, contain repeatability (within laboratory precision) information derived from interlaboratory test programs. These results show that repeatability tends to be relatively constant for a particular class of materials and is only a weak function of the OIT value itself. The best obtainable precision for OIT values are ca. 2 minutes while the pooled standard deviation for a variety of materials is around 5 minutes [1,2,3]. Comparing the repeatability of the OIT test with the bias induced by exposing the test specimen to oxygen from ambient temperature, shows the bias to be smaller than obtainable precision.

CONCLUSION

The bias introduced into the OIT measurement by exposing the test specimen to oxygen at room temperature and then ramping to the test temperature is found to be small when compared to the experimental repeatability and to the mean values of the OIT values. For this reason, it may be ignored in all but the most extreme cases of low activation energy, very slow heating rates, and high test temperatures. The ease-of-use benefits, achieved by exposing the test specimen to the reactive gas from the start of the experiment are likely to outweigh the small bias effect in most OIT measurement whether under Pressure DSC or standard DSC conditions.

Extension to Isothermal Crystallization and Isothermal Kinetics

This same procedure may be used with other types of experiments where the temperature is ramped to a specific test temperature where the time to a thermal event is measured. Two additional examples include polymer isothermal crystallization and isothermal kinetics such as thermoset cure. In isothermal crystallization, the test temperature is approached from higher temperatures. For isothermal kinetics, the test temperature is approached from lower temperatures as with the OIT measurement.

Table 4 lists some of the activation energies for isothermal crystallization reactions determined in our laboratory using the Stestak Berggren equation, which is similar in form to the general rate equation [5]. Polyethylene is considered to be a "fast" crystallizing material with its activation energy of 88 kJ/mol while poly(ethylene terephthalate) is considered to be a slow crystallizer at 1080 kJ/mole. Comparing these activation energies to the bias values listed in Table 3, shows that, except for the very lowest of activation energies, even for modest temperature rates of cooling (e.g., 10°C/min) this procedure may be used for isothermal crystallization with a bias of less than 1 minute.

For thermoset cure reactions, activation energies are often in the range of 60 to 100 kJ/mol. These values are low compared to most OIT and polymer crystallization reactions. By comparison to Table 3, such low activation energy curing reactions benefit from a very rapid temperature rise to the test temperature.

Table 4
ACTIVATION ENERGY FOR ISOTHERMAL CRYSTALLIZATION [5]

Material	Activation Energy (kJ/mol)
Polyethylene	88
Nylon 6	357
PEEK	472
PET	1080

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