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Thermal Analysis & Rheology

Recent Developments in the Application of Thermal Analysis to Polyolefins

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Introduction

Modern thermal analysis techniques have been used extensively in the area of polyolefin characterization. Historically, differential scanning calorimetry (DSC) has been used to measure melting points, heats of fusion and crystallization, oxidative induction time and glass transition temperature, whereas thermogravimetric analysis (TGA) has been employed in the determination of decomposition temperatures and rates, as well as thermal stability kinetic studies.

Recent developments involve the use of a sinusoidal heating rate to extract additional information from the classical thermal analysis experiments. In 1992, Modulated DSC® (MDSC®)[1] was introduced. This technique employs the use of a sinusoidal heating rate and then deconvolutes the resulting heat flow signal to generate heat capacity, as well as additional heat flow signals. MDSC has been used extensively in the area of materials characterization, particularly in the fields of polymer science, food science, and inorganic materials[2].

More recently, the sinusoidal heating rate has been applied to the field of TGA studies[3]. Modulated TGA™ (MTGA™) uses the same heating rate principle as MDSC, and deconvolutes the resultant weight loss signal to generate kinetic information about decomposition reactions. This technique is similar to the classical factor jump TGA decomposition kinetics and generates kinetic constants which are in good agreement with standard multiple heating rate techniques. In this paper, both MDSC and MTGA theory are discussed, as well as applications of both techniques to studies of linear polyethylene (HDPE). MDSC is used to measure relative sample morphology in a series of polyethylene materials, and the data are correlated to tensile breaking tests, and MTGA is used to generate kinetic constants for a polyethylene thermal decomposition.

MDSC Theory

In 1992, Reading[4] introduced the temperature sine wave forcing function to thermal analysis in the form known as Modulated DSC. In MDSC, a linear temperature ramp is modulated with a sinusoidal temperature oscillation (Figure 1) producing a corresponding oscillatory heat flow (*i.e.*, rate of heat transfer) proportional to physical properties of the test specimen (Figure 2). Deconvolution of the oscillatory temperature and heat flow lead to the separation of the overall heat flow into heat capacity and kinetic components, called reversing and nonreversing heat flow. The overall heat flow (dQ/dt) may be described as the sum of a heat capacity (heating rate dependent) term (Cpβ) (Cp = heat capacity, β = heating rate) and a kinetic (time and temperature-dependent) term [f(T,t)].

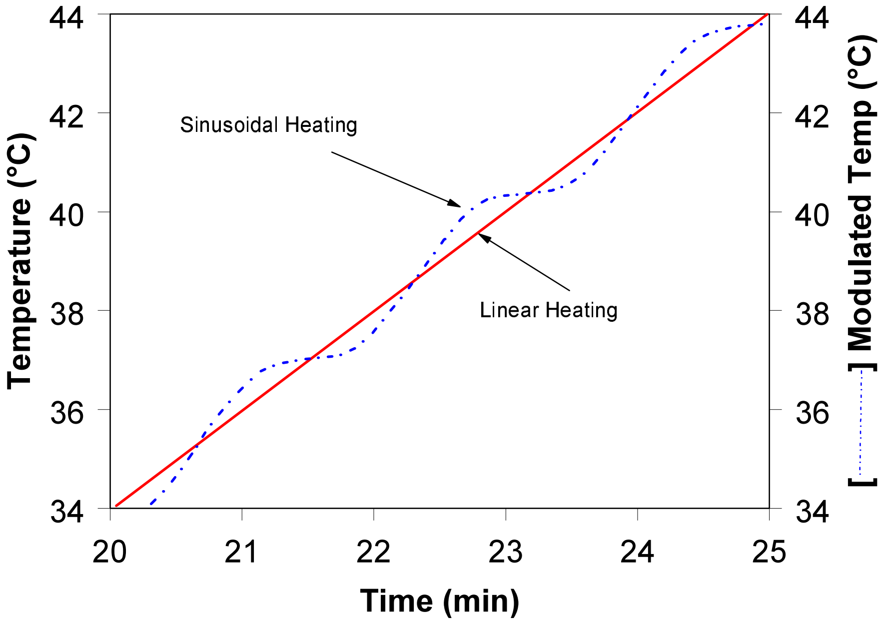

Figure 1

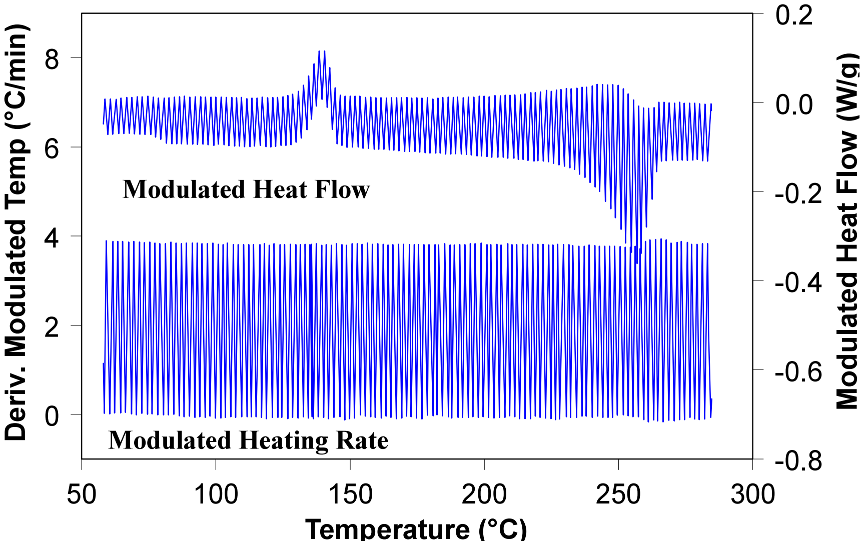

Figure 2

$$\frac{dQ}{dt} = Cp\beta + f(T,t) \qquad (1)$$

In this equation, Cp*β* describes the heat flow due to the heat capacity of the sample, and *f*(T,t) describes the heat flow due to kinetic phenomena such as crystallization, chemical reactions, melting, and thermosetting reactions. In standard DSC, the only signal output from the instrument is the total heat flow; the sum of all the thermal events occurring in the sample.

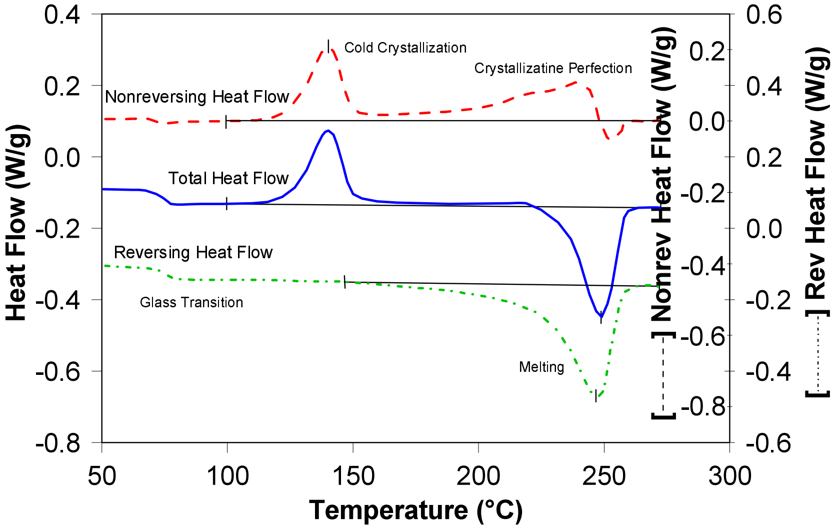

Figure 3

Modulated DSC allows for the separation of total heat flow into two constituents, which provides for increased understanding of the phenomena occurring simultaneously in the sample. Figure 3 contains the deconvoluted heat flow signals for a sample of quench-cooled polyethylene-terephthalate (PET). The total heat flow signal is the same as would be derived form a standard DSC experiment at the same underlying heating rate. This signal represents the sum of all the thermal events. The *Reversing Heat Flow* is the heat capacity component of the total heat flow (Cp*β*), and contains the heat capacity-related events such as the glass transition, and melting of the sample. The *Nonreversing Heat Flow* is the kinetic component of the total heat flow [*f*(T,t)], and contains the kinetically-controlled thermal events such as the cold crystallization, and crystalline perfection which occurs upon heating the sample into the melting region. This crystalline perfection is not resolved in the total heat flow signal, as it occurs simultaneous with the more energetic melting process, and is thus concealed beneath the large melting. It is this ability to resolve previously undetectable transitions which has made MDSC an invaluable tool in the field of polymer characterization.

MTGA Theory

Kinetics is the study of the dependence of the extent or rate of a chemical reaction on time and temperature. Anyone who dries washed clothes knows that if the temperature of the drying process is higher, the clothes will dry faster. This is a kinetic intuition and drying is one of the oldest (and still most important) uses of kinetics.

Those who study kinetics do so with mathematical models which quantify the relationship between the rate of reaction, time and temperature. Once a suitable model is available, it may be used to predict future performance. The chief benefit of kinetics is the ability to predict performance at temperatures and times which are not easily tested. For example, an engineer designing a product for a 40 year lifetime, must use kinetic information to estimate performance into the future since we can't wait 40 years to do end-use testing

The utility of thermogravimetric analysis with respect to kinetics comes from the nature of the TGA measurement. Specifically, TGA measures mass loss, which provides all of the information commonly needed to evaluate a weight loss kinetic process such as drying.

Perhaps the most popular mathematical tool for evaluating kinetics of weight loss reactions is the Flynn and Wall[5] method. This approach is described in an ASTM standard method E1641[6] and may be used to estimate the thermal endurance through ASTM standard E1877[7].

The Flynn and Wall method is a multi-heating rate approach where four or more rates between 1 and 10 °C/min are used to follow the weight loss process. From the increase in temperature of the weight loss resulting from the increase in heating rate, kinetic parameters are obtained. Due to the number of slow heating rate experiments required, the Flynn and Wall approach often takes several days to gather the required information. Productivity pressures urge us to look for an even shorter method to obtain kinetic parameters.

Modulated thermogravimetry (MTGA) is a new approach to obtain kinetic information which does so in a single, time-saving experiment. In MTGA, similar to MDSC, an oscillatory temperature program is superimposed on top of the linear underlying heating rate used in traditional TGA experiments. This produces an oscillatory rate of weight loss from which kinetic information may be derived. In Equation 1, it was shown that the total heat flow from a standard DSC experiment could be divided into two parts; a heating-rate dependent part and a kinetic component. By analogy, the corresponding oscillatory temperature equation for thermogravimetry is given by :

$$\frac{dw}{dt} = C\beta + f(T,t) \qquad (2)$$

where the rate of weight loss (dw/dt) is analogous to the rate of heat flow in DSC. In the TGA case, however, the first term, proportional to the rate of heating, is zero and Equation 2 reduces to the common kinetic expression where the rate of weight loss is directly proportional to the kinetic term.

For the study of chemical reactions, the kinetic term in equations 1 and 2 [i.e.,$f(t,T)$] is often modeled using two equations. The first of these, the rate equation, describes the relationship between the rate of reaction and amount of material. The second, the Arrhenius equation, describes the temperature dependence. These two equations are commonly combined into a single form:

$$\frac{da}{dt} = Z[f(a)]\exp\left(\frac{-E}{RT}\right) \qquad (3)$$

where:
a = reaction fraction
da / dt = rate of reaction
Z = pre-exponential factor
f(a) = kinetic expression
exp = exponent of the natural logarithm base e
E = activation energy
R = gas constant
T = absolute temperature.

Activation energy (E) is considered to be the most important of the kinetic parameters as it describes how the reaction changes as a function of temperature. In Modulated TGA, activation energy is described by the equation:

$$E = \frac{R(T^2 - A^2)L}{2A} \tag{4}$$

where T is the average temperature, A is the temperature amplitude and L is the ratio of the natural logarithm of the maximum and minimum rate of weight loss taken at adjacent half cycles of the sine wave. This equation may be said to be "model-free" as it does not depend on knowledge of the kinetic function for its calculation. However, many decomposition and volatilization reactions may be described using first order kinetics where the value for pre-exponential factor is determined using the relationship

$$1n\,Z = \left[\frac{da}{(1-a)}\right] + \frac{E}{RT} \tag{5}$$

The values for T, A and L are obtained by deconvolution of the oscillatory temperature program and the resultant oscillatory rate of weight loss using real-time discreet Fourier transform, (DFT). The use of DFT produces the continuous determination of kinetic parameters which are then stored in the data file at each data collection point along with the raw experimental information. Moreover, the real time availability of these kinetic parameters permits them to be used to control experimental conditions or to be plotted as a function of other important experimental parameters.

Applications

Experimental

In all of the standard experiments, the material analyzed was linear polyethylene, NIST standard 1475A. For MDSC experiments, the purge gas was helium flowing at 25 ml/min. For MTGA, the purge gas was nitrogen flowing at 100 ml/min. The MDSC conditions were as follows: β= 1.5°C/min., A = ±0.159°C, period = 40 seconds. The MTGA conditions were as follows:

β= 2°C/min, A = ±5°C, period = 200 seconds.

Results and Discussion

MDSC

A series of modulated DSC experiments were performed to determine the relative sample morphology of six different HDPE specimens intended for use in underground storage tanks. Previously, the manufacturer had been relying on a 300 hour tensile breaking test to determine the suitability of the individual HDPE specimens. However, this test proved to be costly both in time and money. Therefore, the manufacturer was interested in investigating alternative testing methods for quality control procedures.

In the 300 hour tensile breaking test, the material was deemed suitable if the test bar withstood the tensile force for the entire time period. If the bar broke before 300 hours, the material failed the test. More amorphous polymers tend to creep under load. The amount of amorphous material present will affect the creep time of the sample, prior to failure or breakage. Samples of high crystalline content would be expected to creep very little, thus expediting the time to breakage.

Differential scanning calorimetry was first investigated for this application because of its sensitivity to changes in crystallinity. DSC is an efficient means to measure the heat of fusion of a material, which is directly proportional to the material's degree of crystallinity. Modulated DSC adds to the sensitivity of the technique in its ability to separate reversing melting from nonreversing melting. The former is associated with amorphous materials which crystallize upon heating, only to re-melt as the temperature is increased further. Non-reversing melting is associated with the highly crystalline domains of the sample, present before any thermal history is applied to the material.

The sensitivity of MDSC to subtle changes in crystallinity is illustrated in a series of standard experiments. In these tests, a sample of HDPE (13.5 mg) was initially quench cooled from above the melt by rapid immersion in liquid N_2. This was done to impose minimal crystallinity in the sample. The modulated DSC experiment described in the previous section was performed on the sample, between 100°C and 145°C, which encompasses the melting region of the polymer. The sample was then control cooled from above the melt at 0.5°C/min. This slow cooling rate would be expected to impart a much higher degree of crystallinity to the sample. The MDSC experiment was then repeated. The identical MDSC experiment was performed on the sample after cooling at rates of 1, 2, 4, 8, 16, and 32°C/min. The MDSC results for the sample cooled at 0.5°C/min are shown in Figure 4. The measured total heat of fusion (total heat flow) is resolved into both the reversing heat flow and the nonreversing heat flow signals. As discussed above, the non-reversing heat flow peak is proportional to the crystalline domain in the sample prior to heating. The reversing peak represents the more amorphous domain of the sample which can melt reversibly.

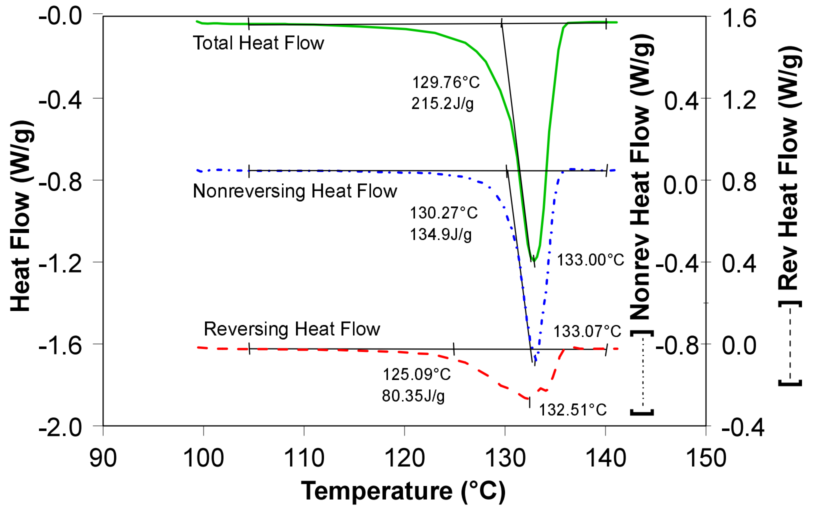

Figure 4

Figure 5 contains the results for the standard variable cooling rate experiments. This figure is a plot of the measured heat of fusion of the materials from the total and nonreversing heat flow, versus the sample's thermal history. It is evident that MDSC is sensitive to subtle changes in crystallinity by examination of the slopes of the lines. As the crystallization cooling rate is increased, the crystallinity of the sample decreases. This is manifested as a decrease in the measured heat of fusion in both the total heat flow and the nonreversing heat flow signal. However, the slope of the nonreversing heat flow data is twice that of the total heat flow data. This suggests that the nonreversing heat flow is twice as sensitive to subtle changes in crystallinity as the total heat flow.

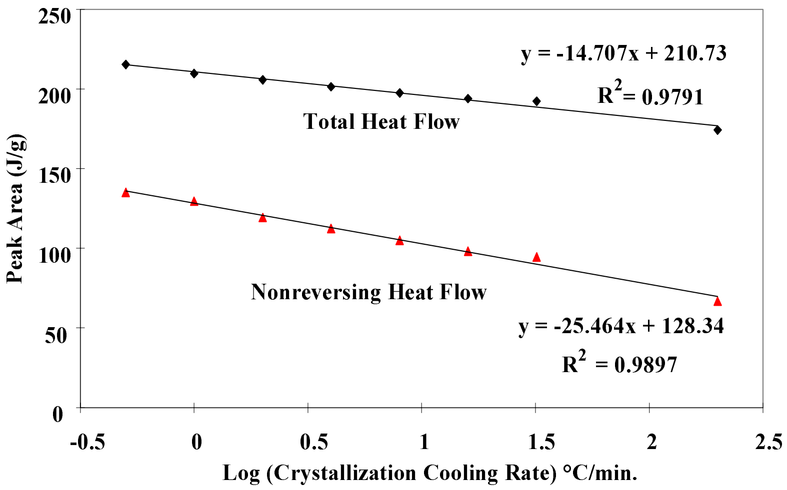

Figure 5

In order to normalize the dual effect of both the total heat flow and the nonreversing heat flow peak areas sensitivity to thermal history, the ratio of the two areas can be calculated. This ratio is referred to as the *Nonreversing Quotient*, and is proportional to the relative crystallinity of the sample. Figure 6 contains a plot of the nonreversing quotient versus thermal history. Note that the nonreversing quotient is extremely sensitive to subtle changes in thermal history, as its value nearly doubles over two decades of difference in crystallization cooling rate.

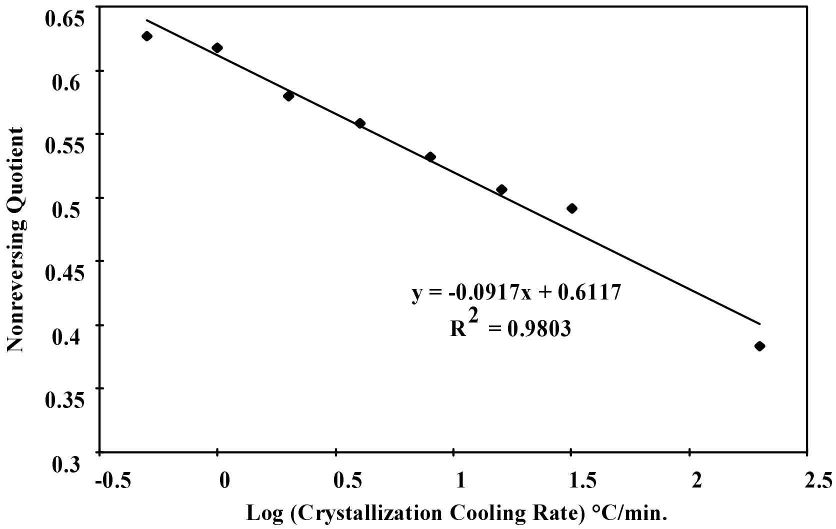

Figure 6

As nonreversing quotient is sensitive to changes in thermal history and thus changes in crystallinity, it was theorized that MDSC would be a suitable alternative to the expensive and time-consuming tensile-breaking test. Thus, it was necessary to draw a correlation between the two testing modes.

Six HDPE feedstock specimens were initially tested by tensile breaking, and then by MDSC. (*Note: Nonreversing quotient will be sensitive to changes in experimental conditions including underlying heating rate, modulation amplitude, modulation period and sample mass. It is therefore necessary to standardize all conditions prior to making any correlations.*) The MDSC samples were prepared by cutting a thin wafer from the tensile test-bar. The correlation plot between the two techniques is given in Figure 7.

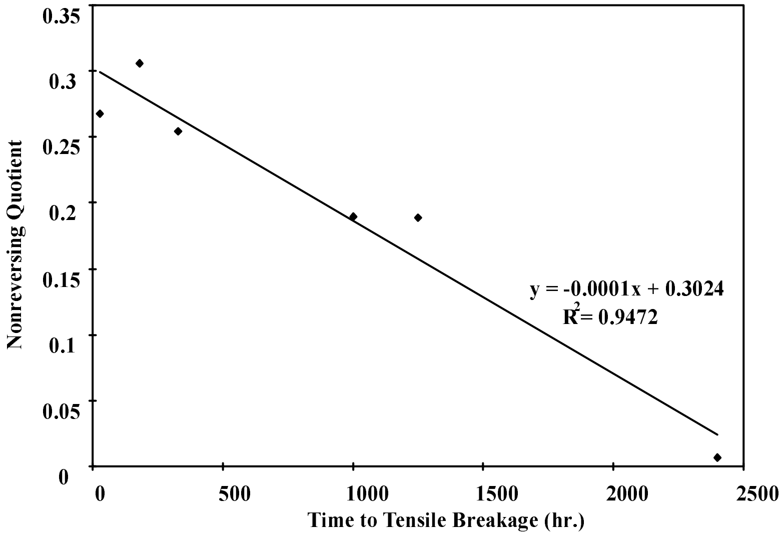

Figure 7

The data in this plot suggests a good correlation between the nonreversing quotient and the time to tensile breakage. In HDPE, nonreversing quotient increases with relative crystallinity. This corresponds to shorter breakage times, due to relative brittleness of the sample. The equation of the line fit to the data in Figure 7 approximates a linear correlation, with an R^2 value of 0.9472. From the equation of the line, the nonreversing quotient corresponding to a particular breakage time tolerance can easily be calculated. For the manufacturer of the underground storage tanks, the tolerance of 300 hours corresponds to a nonreversing quotient of 0.27. If a particular specimen exceeds this quotient, it can be assumed that this material will fail the tensile test. The broad distribution of the data points in Figure 7 suggests that individual samples will exhibit nonreversing quotients which vary sufficiently as to accurately predict tensile failure in a series of specimens.

As the MDSC experiment requires very little sample and takes only about 1 hour to complete, the manufacturer considered the technique a highly desirable alternative to the more cumbersome tensile breaking test.

MTGA

The utility of the modulated TGA experiment is demonstrated in the calculation of kinetic constants for the thermal decomposition reaction of the high-density polyethylene. The actual decomposition of the polymer is somewhat unremarkable in that it decomposes in one solitary, rapid step centered near 450 °C. The decomposition is complete, leaving no residue or char. The MTGA plot for the decomposition of the polyethylene is given in Figure 8. The dashed line in this figure is the derivative of the weight signal, or the rate of weight loss. Note how the rate of weight loss oscillates significantly in the decomposition region, due to the modulation of the temperature and heating rate of the experiment. From the kinetic equations discussed previously, the kinetic constants for the decomposition of HDPE can be calculated and compared to those value derived from ASTM E1641. The results are given in Table 1.

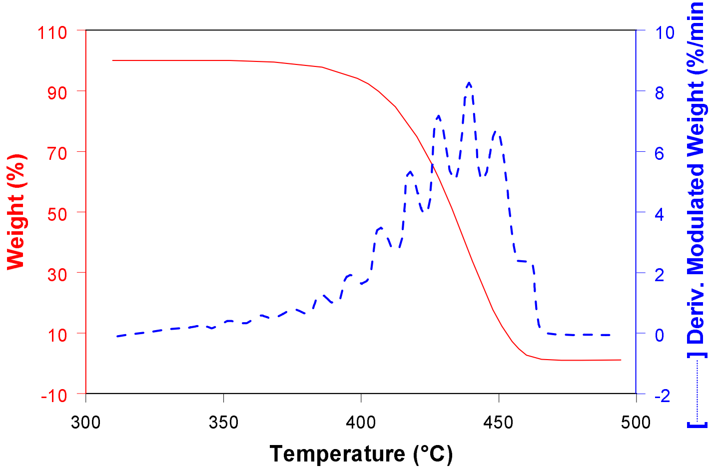

Figure 8

The data in Table 1 demonstrates that MTGA can generate kinetic constants which match the values from classical standard techniques. In the case of HDPE decomposition, the precision of MTGA actually is better than ASTM E1641. However, the real benefit of MTGA is found in the relative time required for generation of kinetic constants. The standard ASTM E1641 decomposition kinetics requires at least four experimental determinations on the same material at different heating rates. MTGA can accomplish the same results in one experiment. When coupled with Hi-Res™ TGA, the heating rate can be accelerated in baseline regions where no decomposition is occurring, and automatically slowed through the decomposition region, to further expedite the data collection. Modulated TGA is seen as a viable alternative to the traditional decomposition kinetics technique, when applied to the decomposition of the polyolefin, HDPE.

Kinetic Constant	MTGA	E1641
Activation Energy (E)	190 ± 3.2 kJ/mol	190 ± 9.5 kJ/mol
Pre-exponential factor (log Z)	12.8 ± 0.2 min^{-1}	12.9 ± 0.6 min^{-1}

Table 1

Conclusions

Modulated DSC and Modulated TGA are shown to be extremely valuable techniques in the characterization of the polyolefin, high-density polyethylene. MDSC has been used to determine the relative crystallinity of HDPE through the use of the nonreversing quotient. This value has shown good correlation to the traditional yet time-consuming tensile breaking test. MTGA has been shown as a viable alternative to ASTM E1641 in the generation of decomposition kinetic constants.

References

1) Modulated DSC® and MDSC® are terms which describe technology invented by Dr. Mike Reading of ICI Paints (Slough, UK) and patented by TA Instruments (U.S. Patent Nos. B1 5,224,775; 5,248,199; 5,335,993; 5,346,306; 5,439,291; 5,474,385) (European Patent No. 0559362) (Canadian Patent No. 2,089,225).

2) For a list of literature publications involving MDSC, see TA Instruments publication TN-33

3) a) R. L. Blaine, *Proc. 25th NATAS Conf.*, 485-492, **1997**., R. L. Blaine, *J. Therm. Anal.*, (submitted for publication) **1997**.

4) a) S. Sauerbrunn, B. Crowe & M. Reading, *Amer. Lab.*, 24, 44-47, **1992.** b) S. R. Sauerbrunn, B. S. Crowe & M. Reading, *Proc. 21st NATAS Conf.*, 137-144, **1992**. c) M. Reading, A. Luget & R. Wilson, *Thermochim. Acta*, 238, 295-307, **1994**.

5) J. H. Flynn, L. A. Wall, *Polym. Lett.*, 4, 323-328, **1966**.

6) E1641, *Test Method for Decomposition Kinetics by Thermogravimetry*, American Society for Testing and Materials, Philadelphia, PA.

7) E1877, *Calculating Thermal Endurance of Materials from Thermogravimetric Decomposition Data*, American Society for Testing and Materials, Philadelphia, PA.

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