Oxidative Behavior of Materials by Thermal Analytical Techniques

Alan T. Riga and
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Foreword

This publication, *Oxidative Behavior of Materials by Thermal Analytical Techniques,* contains papers presented at the symposium of the same name, held in New Orleans, Louisiana, on 21-22 Nov. 1996. The symposium was sponsored by ASTM Committee E37 on Thermal Methods. Alan Riga and Gerald Patterson served as chairpersons of the symposium and are editors of the resulting publication.

Overview

This Special Technical Publication represents a compliation of presentations from an international symposium addressing the Oxidative Behavior of Materials by Thermal Analytical Techniques which was held 20-21 Nov. 1996 in New Orleans, Louisiana. The symposium and this subsequent publication examine the new thermal analytical techniques describing the physical properties and oxidative degradative behavior of polymers, lubricants, and petrochemicals. Historical reviews, oxidation mechanisms, new test methods, unique techniques, robotic methods, new reference standards, and bias considerations form the basis of this publication.

It was generally agreed, but certainly highlighted by Roger Blaine, TAI, keynote speaker, that the factors affecting the oxidation induction time (OIT) were: the isothermal temperature; pan type, metallurgy, and shape; and pressure and oxygen flow rate. Polymer oxidation was emphasized in a number of papers. Professor Joseph Perez, Penn State University, keynote speaker, focused on the measurement of oxidation in formulated passenger car and diesel engine oils. Professor Perez discussed the evolution of oxidation systems from the complex Dornte type systems of the 1940s to the current use of microreactors, for example, DSC, TGA, and Klaus Penn State Microreactor (PSMO). He stressed the variables such as: metal surfaces that affect the rate of oxidation or thermal decomposition, temperature effects on the related thermal and oxidative processes, effects of volatility on vapor phase versus liquid phase oxidation, oxygen diffusion rate limitations, and additive effectiveness. Some of the differences in the thermal and oxidative behavior in bulk systems (engine tests) and microsystems (DSC, TGA, PSMO) were discussed.

Alan Riga, Lubrizol, reviewed the recently approved and soon to be published Standard Test Method for Determing OIT of Hydrocarbons by DSC/PDSC. An interlaboratory study using this DSC/PDSC method was reported by Blaine and Riga, with ASTM Reference C, a diluted fully formulated engine oil from Lubrizol and ASTM Reference D, a polyethylene film from TAI.

A successful robotic DSC evaluation by M. Kelsey, Mettler-Toledo, clearly differentiated References C and D at 195°C and one atmosphere of oxygen. This abbreviated OIT method without heating/cooling (from room temperature) or gas switching reduces the experimental time, avoids a nitrogen purge, and gives a slightly better reproducibility. The abbreviated OIT method suggests a possible revision to the DSC ASTM E37 test protocol. A question raised by a number of participants was ''Is it possible that some PDSC oxidative testing can be replaced with robotic DSC?''

A modified Arrehenius model was used to predict OIT of polymers. An adaptation of this model for evaluation of the oxidative stability of oils was discussed.

A new scanning DTA/TGA oxidation test was presented. This DTA method is based on air oxidation and defines an oxidation temperature. A good correlation was observed between the isothermal PDSC OIT in oxygen of eight readily available olefin reference polymers and the oxidation temperature. The DTA air oxidation method as well as the PDSC oxygen method use the melting temperatures and heat of fusion of polyethylenes and polypropylenes to verify the temperature and heat calibrations.

A unigue approach to the oxidation process was presented by Rick Seyler (Kodak). This paper considered oxidation as a negative factor in the determination of vapor pressure by

DSC in nitrogen. The observed exotherms in DSC measurements were associated with partial oxidation of the chemical specimen from residual air in the DSC specimen container. An application of this method is to study vapor phase oxidation of organics.

Other applications of DSC or PDSC oxidation tests included: radiation-damaged polyethylene, cellulose, thin film oxidation, medical poymers, and asphalts.

The attendees agreed that this symposium was rewarding and much knowledge was gained. They commented that the prsentations focused on areas that have not been previously discussed. Symposium cochairman, Alan Riga, suggested that another meeting be organized in two years at a future NATAS conference. The speakers and attendees agreed.

Rick Seyler, Kodak, summarized the symposium in the form of the following poem:

OIT BLUES

A SYMPOSIUM REVIEW

By R. J. Seyler

Don't you know its not thermodynamic?
Rather, OIT is really quite kinetic!

So when you do your OIT
It most likely won't be like me!

With so many ways to do the test
Precision within-lab will be the best.

When finally on a protocol we agreed
Eaxct control of temperature we'll need.

So now proceed as best we can
Just make sure its an aluminum pan.

Beware when other metal is present
Copper catalysis is a serious contaminant.

Other conditions like area, weight, and flow
Their influence we will need to know.

To switch the purge gas it was shown
One need not, for the BIAS is now known.

A last condition we yet must know
What point in time do we declare zero?

When all our tests we run one way
Which value of OIT do we report today?

Extrapolated onset, threshold, or the peak
'Tis a single number of value that we seek.

We need to realize that induction time
May have different significance for yours and mine.

Unless our sample is without formulation
OIT will address the type of stabilization!

We have tried our best to listen well
To learn all the messages you had to tell.

But when all is said and done
We should yet be troubled by just this one.

That from accelerated aging over which we toiled
The egg we hatched may have been Hard Boiled!

Alan T. Riga
The Lubrizol Corporation
Wickliffe, OH; Symposium
cochairman and coeditor

Gerald H. Patterson
The Lubrizol Corporation
Wickliffe, OH; Symposium
cochairman and coeditor

Contents

Oxidative Behavior of Polymers and Petrochemicals

Roger L. Blaine[1,2], C. Jay Lundgren[1] and Mary B. Harris[1]

OXIDATIVE INDUCTION TIME - A REVIEW OF DSC EXPERIMENTAL EFFECTS

REFERENCE: Blaine, R. L., Lundgren, C. J., and Harris, M. B., **"Oxidative Induction Time - A Review of DSC Experimental Effects,"** 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.

ABSTRACT: Over the past several years, a number of ASTM committees have explored a wide variety of experimental parameters affecting the oxidative induction time (OIT) test method in an attempt to improve its intra- and inter-laboratory precision. These studies have identified test temperature precision as a key parameter affecting OIT precision. Other parameters of importance are oxygen flow rate, specimen size, specimen pan type, oxygen pressure and catalyst effects. The work of Kuck, Bowmer, Riga, Tikuisis and Thomas are reviewed as well as the collective work of ASTM Committees E37, D2, D9 and D35.

KEYWORDS: differential scanning calorimetry, oxidation, oxidative induction time, oxidative stability, polyethylene, polyolefins, thermal analysis

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Oxidative Induction Time (OIT) is an accelerated aging test. It provides an index useful in comparing the relative resistance to oxidation of a variety of hydrocarbon materials. The test consists of heating a specimen to an elevated temperature (often 200 ^{o}C) in a differential scanning calorimeter (DSC). Once temperature equilibrium is established, the specimen atmosphere is changed from inert nitrogen to oxidizing air or oxygen. The time from first oxygen exposure until the onset of oxidation is taken as the OIT value. This general procedure is applied, for example, to polyethylene wire insulation [1, 2], geosynthetic barriers [3], edible oils [4], lubricating oils and greases [5, 6]. Table 1 shows a few of the currently used application areas for OIT.

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[1] Applications development manager, and applications chemists, respectively, TA Instruments, Inc., 109 Lukens Drive, New Castle DE 19720.

[2] Corresponding author.

Table 1 -- Applications

Material	Applications
Polyolefins	Wire and Cable Insulation
Polyethylenes	Pipe
Polyolefins	Geosynthetic Materials
Greases	Lubricants
Peanut Oil	Confections
Oils	Lubricants
Hydrocarbons	Fuels
Oils	Automatic Transmission Fluids

Most materials are tested to measure the effectiveness of the antioxidant package added to improve lifetime, although a few materials (e.g., edible oils) are tested in their natural, non-fortified state.

Background

The OIT procedure was first developed by Gilroy and coworkers at Bell Laboratory as a test procedure to screen polyethylene insulation used in telephone wire and cable for its oxidation resistance in pedestals [7]. The method first became available as a Western Electric specification [8] and later as ASTM Test Method for Copper Induced Oxidative Induction Time of Polyolefins [1]. Polyolefin manufacturers quickly embraced the procedure and began to apply it to other applications including raw resins, finished pipe [9], as well as to wire and cable insulation [2], and, most recently, geosynthetic waste pit liners [3].

It has long been known that the effectiveness of antioxidants, as measured by the OIT at high temperatures, may differ as a function of temperature [7, 10]. This may be due to a number of causes including changing mechanisms, loss of antioxidant due to volatilization at high test temperatures, etc. Many users would like to move the OIT test temperature closer to the actual use temperature to avoid some of these difficulties. Further, as additive packages have improved, OIT values have become progressively longer. In order to shorten the analysis time and to reduce test temperatures, increasing use is being made of Pressure DSC to accelerate the measurement at lower test temperatures.

The expanding applications for the OIT test method, the widespread use of Pressure DSC and improvements in apparatus electronics have combined to create increased interest in re-examination of the parameters of the OIT test method aimed at improving its precision. This interest has largely focus on improving inter- (between) laboratory reproducibility since intra- (within) laboratory repeatability is generally quite good. A general rule-of-

thumb is that interlaboratory reproducibility should be about twice the within laboratory repeatability. For much OIT work, the reproducibility is much poorer than this rule-of-thumb. This indicates that within a single laboratory, the same thing is done the same way every time but that there are differences in procedure in going from one laboratory to another.

Several authors, and groups of workers have (re)examined the effects of a number of experimental parameters on OIT values and their precision. It is the purpose of this paper, then to review and report on the efforts of ourselves and others in there efforts to improve the OIT test method.

Endpoint Selection

The onset of oxidation is taken as the endpoint for the OIT measurement. Two means of determining the oxidation onset are in use. The most common is the "extrapolated onset" in which tangents are drawn at the point of maximum rate of oxidation and the baseline prior to the oxidation. Their intersection is taken as the endpoint for the OIT measurement.

The second method for establishment of the endpoint for the OIT determination is the point of "first-deviation-from-baseline". In this approach, some "threshold" is set above the baseline prior to oxidation (say 0.05 W/g). The endpoint for the OIT determination is taken at the point where the exothermic event crosses that threshold.

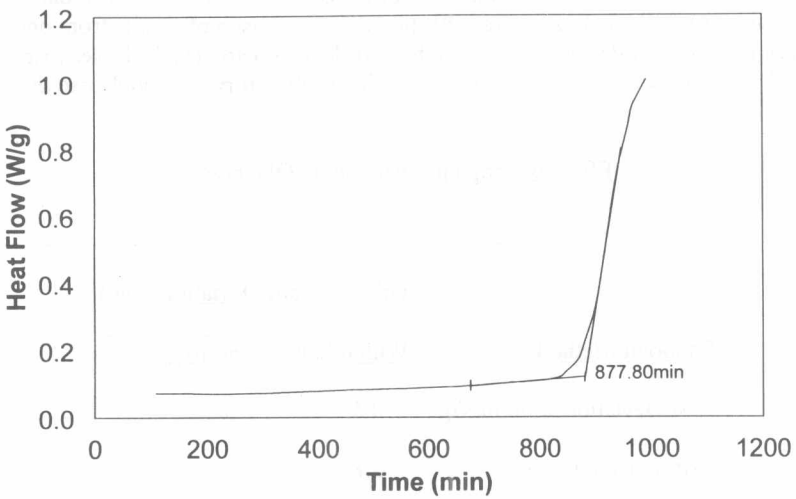

FIG. 1 -- Single stage oxidation endpoint determination.

If the oxidation exotherm is sharp, these two endpoint indicators produce similar results as seen in Figure 1 where the two values differ by only a few percent. Some materials, however, seem to have a multi-staged oxidation and the endpoint established by the two experimental procedures may be quite different as shown in Figure 2.

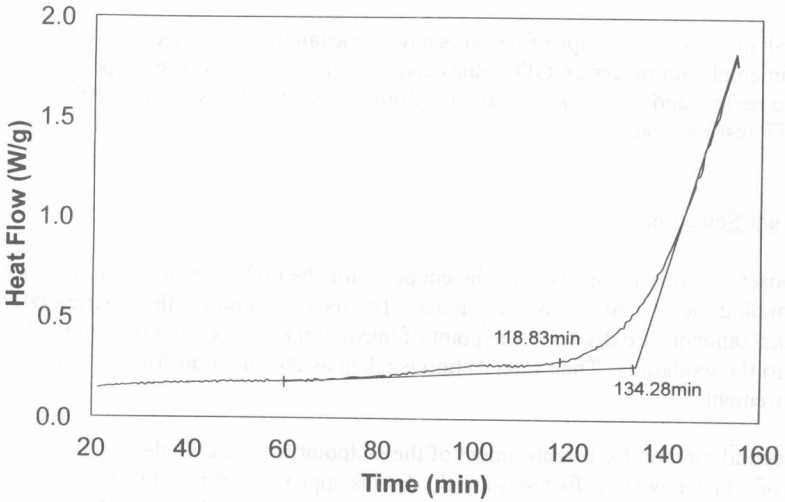

FIG. 2 -- Multistage oxidation endpoint determination

The selection of the method of determination of the OIT endpoint (i.e., extrapolated onset or first deviation) is the first parameter affecting the comparison of results from one laboratory to another. OIT values obtained by first deviation are usually lower than those obtained by extrapolated onset. Operators in a single laboratory commonly use the same

TABLE 2 -- Effect of endpoint selection on OIT precision.

	OIT Standard Deviation (min)	
Endpoint Method	Within Lab	Lab-to-Lab
First Deviation at 50 mW/g	4.5	7.3
Extrapolated Onset	2.8	7.2

approach, but workers in other laboratories may choose differing endpoint detectors. OIT results should identify the end point detector used to avoid this potential discrepancy.

Selection of the endpoint also affects the precision of the measurement. OIT precision, using extrapolated onset, usually has better precision than that using the first deviation from baseline. This is seen both in intralaboratory repeatability data and interlaboratory reproducibility values. ASTM's task group D9.18, working on an upgrade to ASTM D4565, obtained the OIT values for high density polyethylene insulation stripped from wire presented in Table 2. The OIT mean values for these tests were 122 and 126 min, respectively.

The within laboratory OIT precision values derived from the extrapolated onset is commonly two times better than that for the first deviation from baseline. For this reason, the extrapolated onset should be taken, wherever possible, as the endpoint indicator. The first deviation from baseline approach should be used only where this point on the oxidation profile provides specific information of interest to the researcher.

Effect of Temperature

The single most important influence in comparing OIT values from one laboratory to another is the test temperature of the method. Table 3 shows the effect slight changes in temperature can have on the OIT value for a high density polyethylene sample.

TABLE 3 -- Effect of temperature.

Temperature (°C)	OIT (min)
198.0	40.8
200.0	35.7
202.0	29.2

For this polyethylene sample, the effect of temperature on the OIT value is 2.9 min / ^{o}C or about 8.1 % / ^{o}C at the 200 °C test temperature. If the test temperature is not exactly the same in two laboratories or is not that called for in the test method, a serious discrepancy

is likely to result in comparing the results. This strong effect of test temperature is well known by those designing a test method [7] but may be ignored by the technologist who run the experiments because it requires instrument recalibration under conditions (i.e., isothermal operation) different than those used for most DSC experiments (e.g., 10 ^{o}C/min heating rate).

Precise temperature calibration along with the direct measurement and recording of sample temperature during the test are keys to overcoming lab-to-lab variability in OIT measurements. Some thermal analyzers have a strong temperature dependence on heating rate [11]. For this reason, temperature calibration must be carried out using a very low heating rate, usually 1 ^{o}C/min, to better simulate isothermal conditions.

Effect of Oxygen Flow Rate

A third experimental parameter which can effect the OIT value and its precision is the availability of the oxygen reactant. One of the factors affecting oxygen availability is flow rate.

OIT values are not strongly dependent upon reactant gas flow rates provided a necessary minimum flow rate is available. Unfortunately, this minimum level is quite close to the 50 mL/min commonly used [12]. Table 4 provides information on the effect of oxygen flow rate on the absolute value for OIT and on its precision, respectively, for a high density polyethylene sample.

TABLE 4 --Effect of oxygen flow rate on OIT.

Flow Rate (mL/min)	OIT (min)	Precision (%)
20	64	---
50	45	4.5
100	34	2.3

These results, and those of Ashby [12], indicate that around 50 mL/min flow rate, the OIT value may change 3.5 minutes (ca. 8%) for each 10 mL/min change in purge gas flow rate.

Further information presented in Table 4 shows that precision improves with higher flow rates. Unfortunately, not all DSC instruments are capable of flow rates as high as 100 mL/min so most standard methods have settled on the 50 mL/min rate for instrument compatibility purposes. The flow rate must be limited, however, to a very narrow range of ± 5 mL/min, to improve both repeatability and reproducibility.