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High Pressure Oxidative Induction Time Analysis By Differential Scanning Calorimetry

by

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ABSTRACT

A series of high pressure oxidative induction time measurements (HPOIT) were conducted on a polyethylene geomembrane sheet in order to investigate the interaction of the pressure and temperature variables on the induction time. The experiments consisted of determining the HPOIT at constant cell volume employing a wide operational range of pressure and temperature values. The HPOIT test results were found to be inversely related to both variables, with temperature being the predominant factor. A modified Arrhenius model was constructed from the data to account for both the temperature and pressure dependency of the HPOIT test.

INTRODUCTION

Oxidative induction time analysis (OIT, also known as oxidative stability) has found widespread use in the geosynthetic community as a quality control and fingerprinting tool. The use of the test is primarily restricted to materials composed of polyolefin resins such as VLDPE and HDPE (typically used in the production of geomembranes). The concept of oxidative stability is important to resin manufacturers and end users, since the useful lifetime of a particular product is often related to its resistance to oxidative decomposition.

The OIT measurement is an accelerated thermal-aging test and the data generated provides a qualitative assessment of the material tested. It is determined by the thermo-analytical measurement of the time interval to the onset of exothermic oxidation of a material at a specified temperature in an aerobic atmosphere. The onset of oxidation is signalled by an abrupt increase in the sample's evolved heat or temperature. The OIT is commonly used because of its relative ease and speed. OIT measurements usually require less than two hours at appropriately chosen test conditions.

Traditionally, OIT determinations have been conducted on geomembrane materials using a variation of ASTM method D-3895. Caution should be exercised in data interpretation since oxidation reaction kinetics are a function of temperature and inherent properties of the stabilization additives (volatility, solubility, diffusion) contained in the sample. Although quantitative relationships between OIT test data and the level of stabilization can be established for some additive formulations, there has been no proven and documented correlation between the OIT test result and the product's thermal stability performance in the field. Additional test data such as heat oven aging is often required to supplement the OIT data in order to improve the accuracy of predicting long-term performance.

Recently, a variation of the OIT test based on pressure has gained prominence among test users. Advocates of the HPOIT test claim that the oxidative data obtained under the combination of pressure/temperature correlates much better with traditional accelerated aging tests. The use of the HPOIT test offers two main benefits. First, high pressure decreases the volatility of the additives by elevating their boiling points, and second, high pressure increases the concentration of the reacting oxidizing gas. This allows lower test temperatures to be used or provides significantly shorter test times at equivalent temperature (1). In this report we investigate the relationship between the temperature and pressure variables of the HPOIT test and how they affect the measured induction time.

EXPERIMENTAL

The geomembrane sheet used as the test sample in this study was a commercial product obtained from the market. The sheet (approx. 2.5 mm thick) was formulated with a medium density resin which contained an approximate concentration of 2000 ppm each of a phenolic and phosphite antioxidant system. The sheet also contained 2.2% carbon black.

This particular sheet is used in our laboratory as a control sample for the conventional OIT test. The following summarized data has been generated on this sample in the last year (obtained under ASTM-D-3895 conditions: 200^{o}C and 20 psi oxygen) : an average OIT of 112.5 minutes with a relative standard deviation of 2.5% (based upon forty-five determinations). The low standard deviation obtained for this sample is an indication that it is homogenous and hence suitable for use as a test control sample.

All HPOIT measurements were performed with a TA Instruments 9900 Thermal Analyzer equipped with a 910 Differential Scanning Calorimetry (DSC) cell base and a high pressure DSC cell. The DSC was calibrated in air using indium and tin. The calibration step was performed at ambient pressure as a matter of convenience since calibration at elevated pressures would necessitate that individual calibration sequences to be performed for each different pressure setting. The DSC cell was recalibrated on a monthly basis. Ultra high purity oxygen (extra dry) was used as the oxidizing gas. Test specimens were sourced from compression molded plaques (thickness 250 ± 15 microns) obtained from randomly selected areas of the sheet. Specimen disks (6.0 mm) excised from the plaques had a weight between 5-10 mg and were contained in degreased aluminum pans.

All HPOIT experiments were conducted employing the constant volume operational mode. The pressure cell was loaded with the sample in the same manner as a normal DSC cell. The cell was then capped and all valves with the exception of the outlet valve were closed. The cylinder regulator was then adjusted to deliver the desired test pressure. The inlet valve was then slowly opened and the oxygen gas was purged through the cell for 5 minutes to displace the ambient air. After 5 minutes both the inlet and outlet cell valves were closed.

Minor adjustments were then made with the valves as required in order to obtain the selected pressure. The temperature program used in this study consisted of a 20°C/minute ramp to the test temperature followed by an iso-track segment of sufficient length to observe the thermal transition. The OIT was determined as the elapsed time from the start of the test (heating) to the onset of the oxidative endotherm. During the heating cycle the excess cell pressure was vented with the purge valve to compensate for the increase in pressure caused by thermal expansion. The cell was cleaned (by thermal desorption) after every 3-4 measurements to remove any accumulated organic matter to ensure safe operation.

The thermal experiments that were conducted consisted of determining the HPOIT under a wide range of conditions. The pressure was varied between 100 to 800 psi (689-5516 kPa) in 100 psi increments to 10°C increments with pressure held constant.

RESULTS AND DISCUSSION

The complete set of HPOIT data that was generated is summarized in Table 1. Some data points were measured in duplicate with the recheck value given in parentheses. In all cases the recheck values are reasonably close to the original value (the average variation between the duplicate test results is only three percent.). The HPOIT values varied from as low as 15 minutes under extreme conditions to well over 1000 minutes (approx. 17 hours) under mild conditions. A sample HPOIT thermal curve is shown in Figure 1.

Isothermal and isobaric plots of the data are shown in Figures 2 and 3 respectively. At constant temperature, HPOIT decreases as pressure increases. Similarly, at constant pressure, HPOIT also decreases with increasing temperature. The data shown in Figures 2 and 3 indicate that increases in both temperature and pressure accelerate the OIT value. The difference between the HPOIT becomes more significant at the lower temperature or pressure. In order to study the influence of temperature and pressure on the OIT and to gain a better insight into the fundamental aspects of the HPOIT test, a simple mathematical model was developed to interpret the test results.

To develop the analytical model, two assumptions were made for the OIT-temperature-pressure relationships, namely; (1) the correlation of OIT with temperature follows an Arrhenius equation and (2) the Arrhenius parameters obtained in the first assumption can be expressed in terms of oxygen pressure. Based on these two assumptions, the HPOIT test can be simply described by the following modified Arrhenius Equation:

Table 1

HIGH PRESSURE OIT DATA (min.)

Temperature (°C)						
Pressure (psi)	**150**	**160**	**170**	**180**	**190**	**200**
100	1030	488	221	100	49.6	26.2
200	813	355	158 (151)	79.3	38.8	22.3
300	660	291	133	64.2 (63.1)	33.9 (32.2)	20.1 (20.8)
400	562	246 (240)*	119	56.6	29.7	18.8 (18.9)
500	485 (510)	225	100	51.6	26.4	17.5
600	452	188	89.3	46.9 (46.1)	24.7 (24.9)	15.9
700	409 (408)	169	86.7 (80.5)	44.8	24.1	15.8
800	386	147	70.0	42.1	23.2	15.7

**Values in parenthesis denote duplicate test results.*

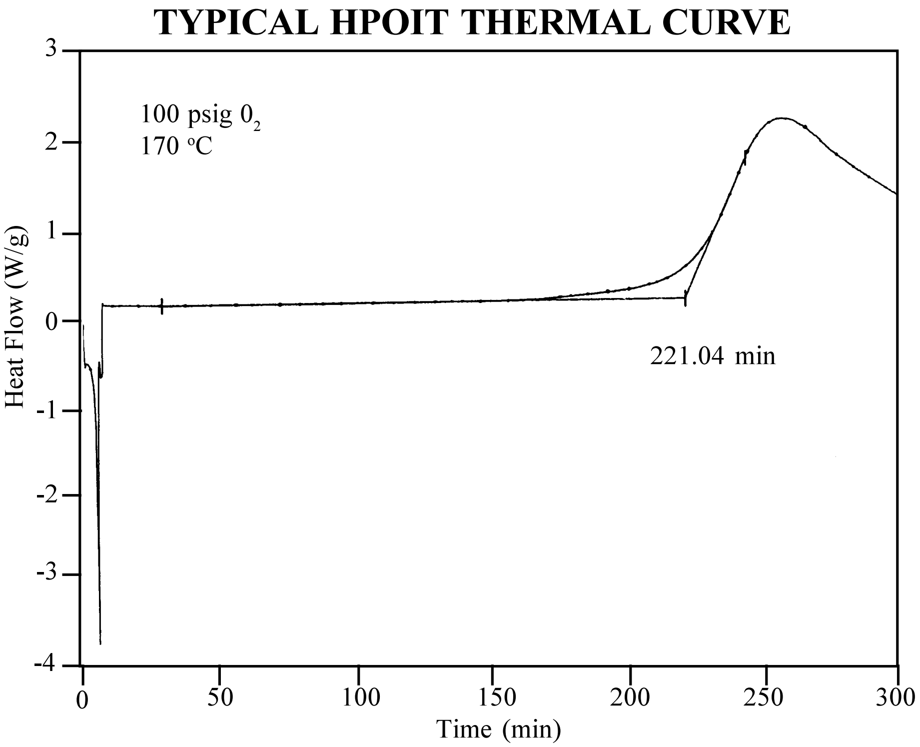

Figure 1

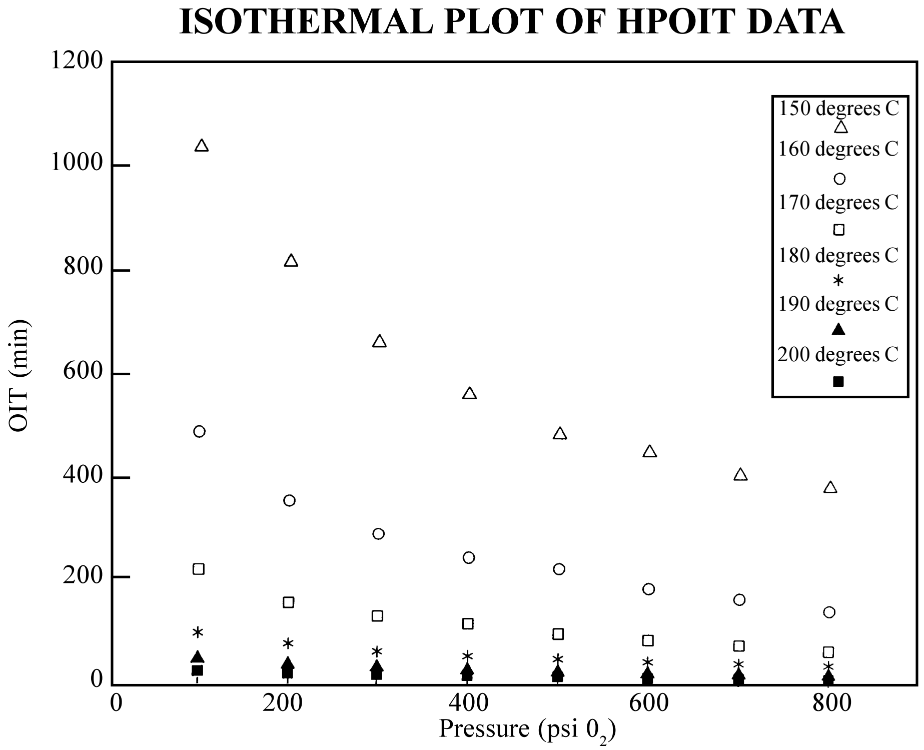

Figure 2

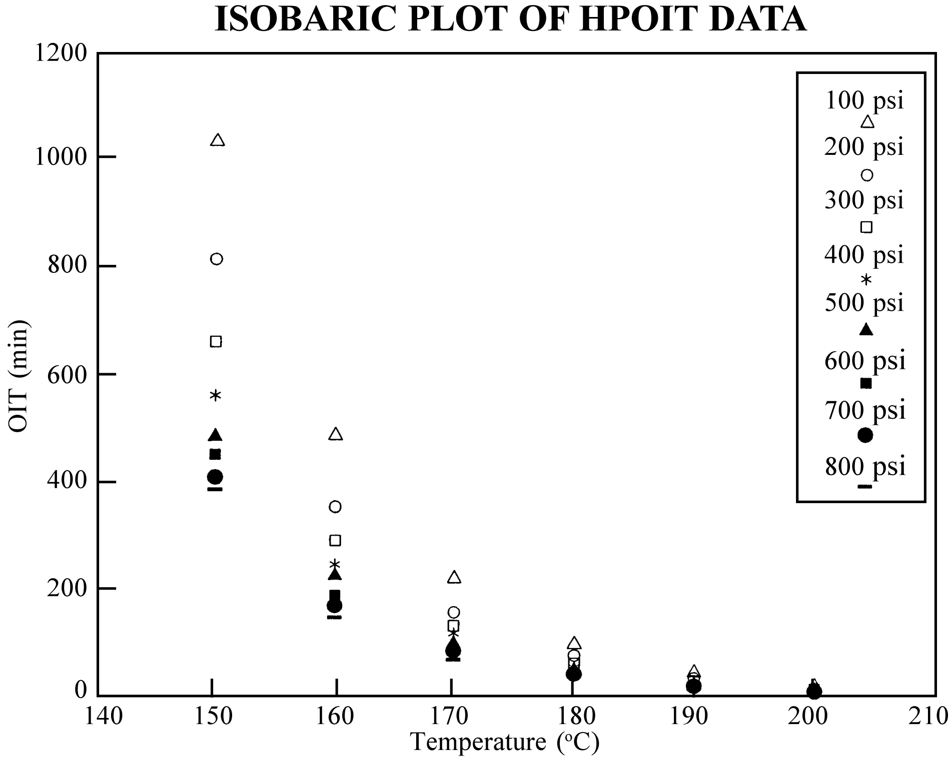

Figure 3

$$t = A\,EXP\,\left[\frac{E}{RT} + \left(B + \frac{C}{T}\right)P\right] \qquad (1)$$

where:
t = HPOIT (minutes)
T = temperature (K)
P = pressure (psi)
E = activation energy (KJ/mol)
R = gas constant (8.3144 J/K.mol)
A,B,C = material constants

The model consists of four adjustable parameters, where A and E account for the temperature dependency, B is responsible for the pressure effect; and C takes care of the combined effects due to temperature and pressure. It is important to note that the four adjustable parameters are independent of temperature or pressure. The four material constants in the model were determined using the least square minimization technique on the basis of the forty-eight HPOIT data points provided.

The four adjustable parameters in the modified Arrhenius model (i.e., Equation (1)) were estimated to be: A = 3.73 x 10^{-13}; E = 125.41; B = 5.37 x 10^{-3} and C = -2.95. Although the four constants are temperature and pressure independent, they are thought to be the characteristic values for a given antioxidant system of a polymer. In other words, the values of A, E, B or C are expected to vary from one polymer to another, as well as from one antioxidant package to another.

To illustrate the consistency of the mathematical model, the modelling results were compared with the experimental data. The symbols in Figure 4 represent the test results, while the solid lines are the data. There are small deviations for the data at the higher pressures (at 700 - 800 psi). Interestingly, the HPOIT data follows an Arrhenius type of equation (i.e. 1n t vs. 1/T) in spite of the oxygen pressure. The extent of this linear correlation is consistent with the first assumption in the model. The modified Arrhenius model appears to explain the temperature and pressure dependency of OIT.

The influence of temperature and pressure on OIT can be easily visualized in a three dimensional response surface shown in Figure 5 which was obtained from the modelling results. Different regions in the response surface correspond to different levels of OIT. HPOIT decreases with increasing either the temperature or the pressure. However temperature has the predominant effect on the OIT was compared to pressure since OIT decreases more rapidly with temperature than with pressure. This is due to the fact that the order of magnitude of the activation energy (i.e. E) in Equation (1) is much greater than that of the material constants B or C.

The linear Arrhenius relationships shown in Figure 4 reveal the temperature dependency of HPOIT to be mainly associated with the kinetic effect (i.e., the reaction rate

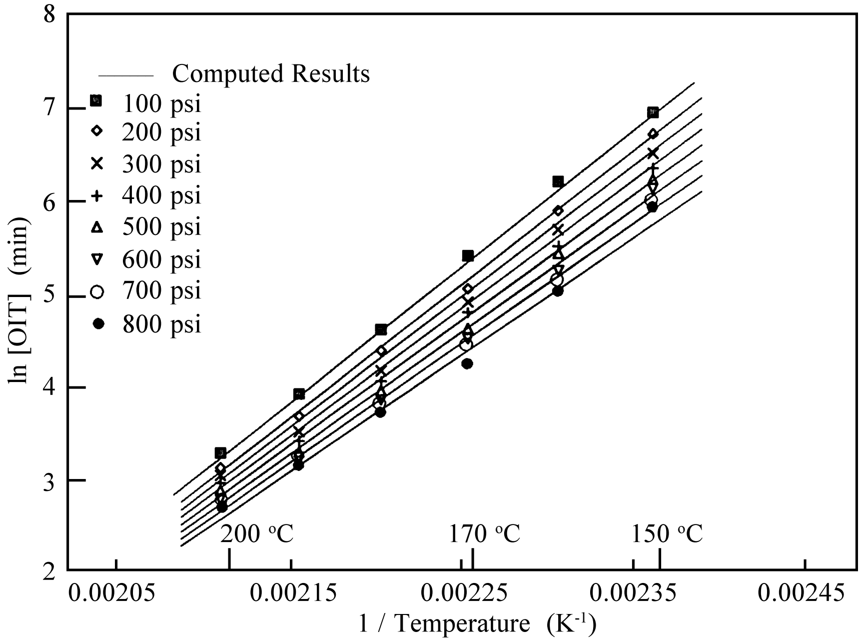
MODIFIED ARRHENIUS PLOT OF HPOIT DATA

Figure 4

increases with temperature). The concentration effect of oxygen. For instance, increasing the oxygen pressure increases the local oxygen concentration, as well as the diffusion rate of oxygen as the number of moles of oxygen per unit volume increases. Thus, the OIT decreases as the oxygen concentration increases. This is similar to the fact that the measured OIT determined in a pure oxygen environment is usually lower than that obtained in air, provided other experimental conditions remain the same.

For simplicity, the response surface shown in Figure 5 can be converted to a two dimensional contour plot. As indicated in Figure 6 the same level of OIT can be obtained in a multitude of temperature/pressure combinations. Based on this type of relationship it may be possible to correlate HPOIT data with conventional OIT data (i.e. ASTM D-3895 conditions) if additional HPOIT data is generated and modelled at the lower pressure region (i.e. between 20-100 psi).

CONCLUSIONS

Oxidative induction time is inversely related to both temperature and pressure with temperature being the dominant factor. HPOIT test data can be described by a modified four-parameter Arrhenius model. In conjuction with the mathematical model, the HPOIT test procedure offers the following advantages over the conventional OIT test: minimization of polymer degradation and suppressed antioxidant volatility can be achieved by measuring the OIT at lower temperatures and higher pressures, and the OIT determination can be accelerated by employing appropriately selected pressure/temperature conditions in order to shorten analysis time.

RESPONSE SURFACE PLOT OF HPOIT DATA

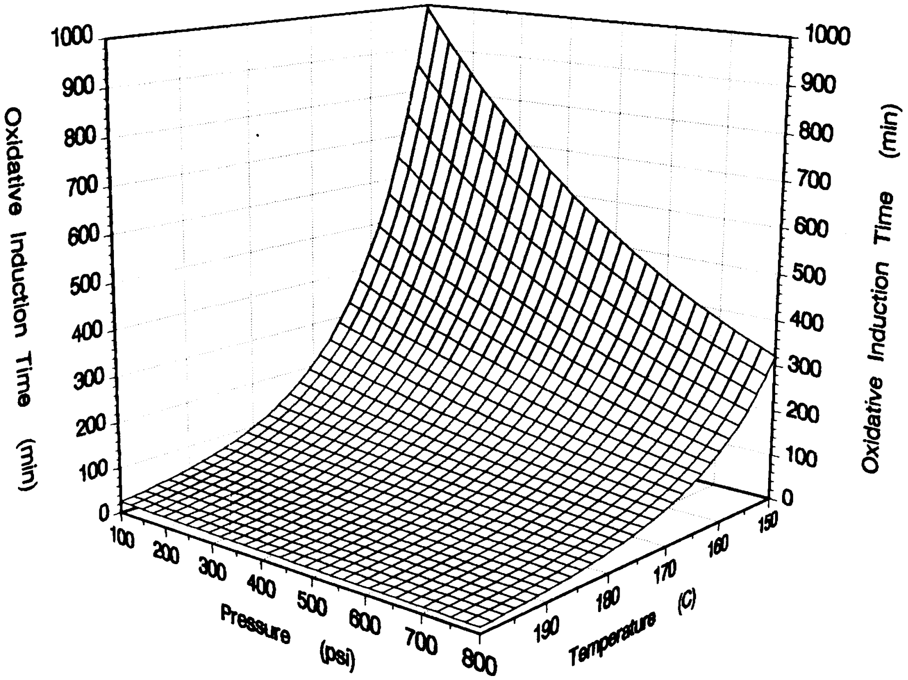

Figure 5

CONTOUR PLOT OF HPOIT DATA

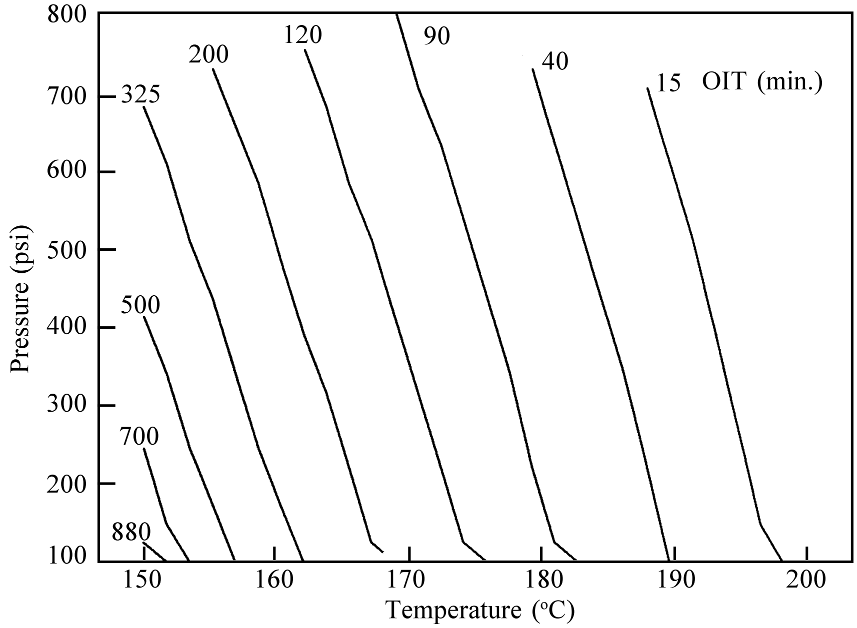

Figure 6

REFERENCES

Thomas, L.C., American Laboratory, 1987.