APPLICATION NOTE

Polymers – DSC / Kinetics Analysis / OIT Tests

KINETICS NEO

Kinetics Analysis on the Oxidative Stability of HDPE Black Pipes by Means of OIT Tests

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Introduction

High-density polyethylene (HDPE) pipes are widely used in various industries, including water distribution, gas transportation, and industrial applications, due to their excellent mechanical properties, chemical resistance, and long-term durability. However, their service life is highly dependent on their resistance to oxidative degradation, which can lead to embrittlement, loss of mechanical strength, and ultimately, failure of the material.

The evaluation of oxidative stability is crucial for predicting the long-term performance of HDPE pipes, particularly those exposed to challenging environmental conditions, such as temperatures. One of the most effective methods for assessing the oxidation resistance of polymers is the Oxidation Induction Time (OIT) test, which is performed using a differential scanning calorimeter (DSC). This method is standardized by international protocols, including ASTM D3895-19 and ASTM D6186-19 [1,2].

This study aims to determine the activation energy of HDPE black pipes through kinetic analysis derived from OIT tests.

Measurement Conditions

To ensure the reproducibility of the OIT tests, the HDPE samples were prepared in the same manner, and three measurements were obtained [3]. The test involves several stages:

- The sample is heated to a temperature above its melting point under a dynamic nitrogen flow;
- An isothermal segment is held for 3 minutes under a nitrogen atmosphere;
- The atmosphere gas is changed from nitrogen to oxygen.

The termination of the test is marked by the onset of degradation. This is automatically identified through utilization of the *Proteus*® measurement software. The measurement conditions are summarized in table 1.

Table 1 Test parameters of the OIT test

Instrument	NETZSCH DSC, low-temperature version
Crucible	*Concavus*® Al, open
Sample Mass	9.90 to 10.10 mg
Isothermal temperature	200, 205, 210, 215, 220 and 225°C
Purge gas rate (N_2)	50 ml/min
Atmosphere	O_2/N_2

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Measurement Results

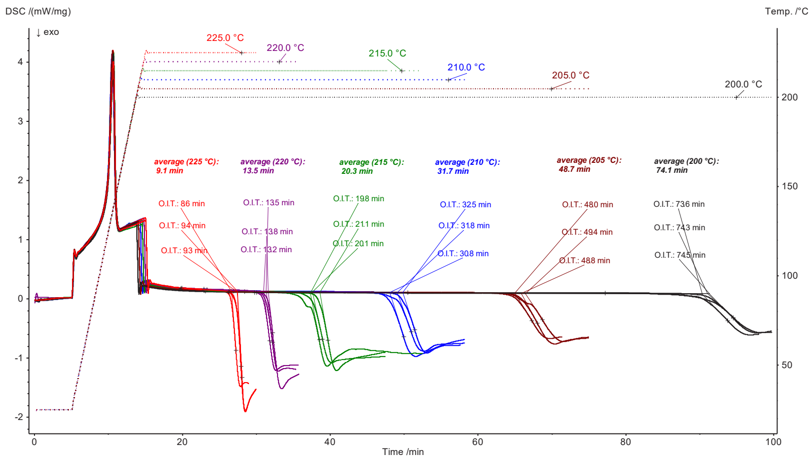
Figure 1 depicts the test results. The endothermal peak detected during heating is due to melting of the high-density polyethylene black pipe. The oxidation induction time (OIT) was determined by evaluating the extrapolated onset of oxidation in measurements with different isothermal segments. A clear increase in OIT was observed with decreasing temperatures of the isothermal segment: 9.1 min at 225°C, 13.5 min at 220°C, 20.3 min at 215°C, 31.7 min at 210°C, 48.7 min at 205°C, and 74.1 min at 200°C. This trend exhibits slower oxidation at lower temperatures.

Kinetic Analysis OIT Measurements

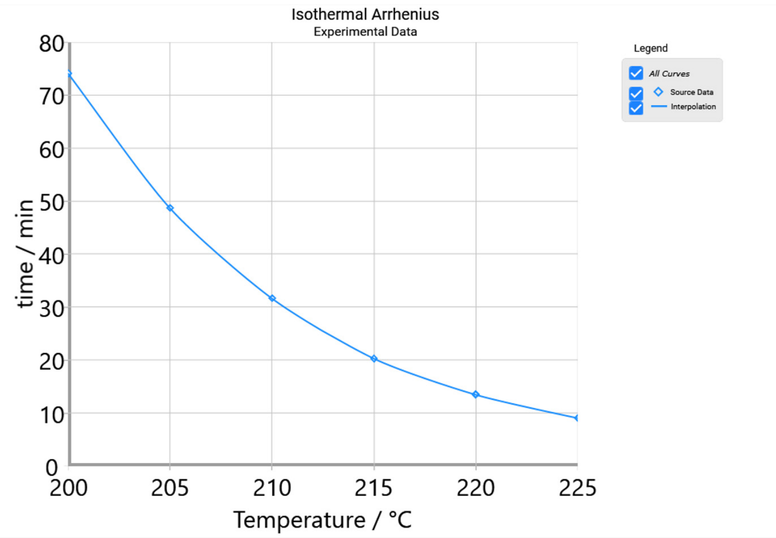
The Kinetics Neo software is used for determination of the kinetic parameters for predicting the isothermal lifetime.

The kinetic analysis measurements are conducted at various isothermal temperatures, as illustrated in figure 1.

Figure 2 presents a Time-to-Event chart illustrating the Oxidative Induction Time (OIT) of a black HDPE pipe as a function of temperature. The OIT values are typically derived from Differential Scanning Calorimetry (DSC) tests (figure 1).



1 Oxidation Induction Time (OIT) measurements on HDPE black pipe samples during different isothermal segments.



2 Oxidation Induction Time (OIT): Time-to-event data for an HDPE black pipe

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A kinetic analysis of OIT measurements on HDPE black pipe samples for molten polymers under different isothermal conditions was performed using the model-free Isothermal Arrhenius according to method E from ASTM E 2070-23 [4] (figure 3). The analysis produced a plot of Log(time-to-event) versus the inverse of the temperature with a linear fit curve.

For the determination of kinetic parameters, the activation energy and pre-exponential factor were derived from the slope and intercept of the linear fit. The calculation of the pre-exponential factor assumes a first-order reaction and that the event occurs at a conversion of 5%. Kinetic parameters were determined by the Kinetics Neo software for the Oxidation Induction Time (OIT).

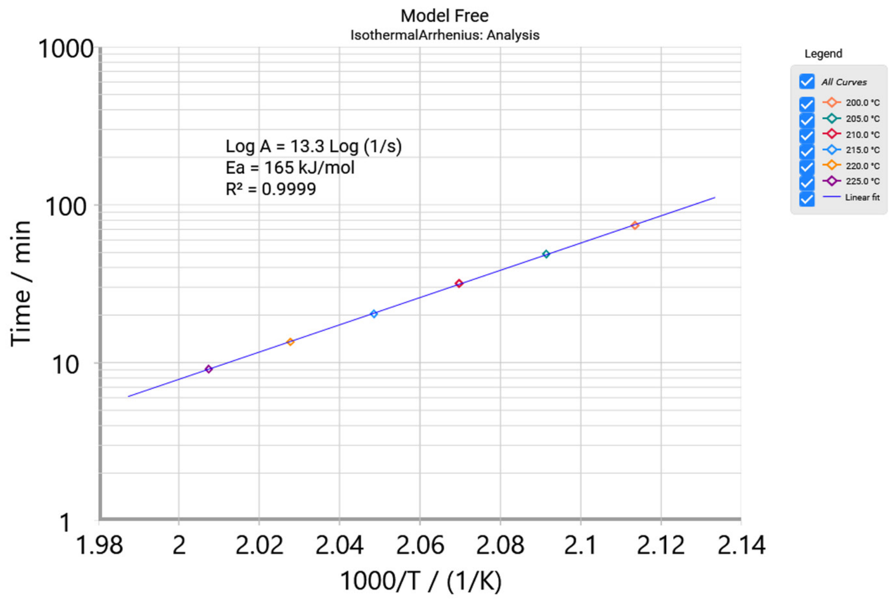
Kinetic parameters (table 2) were determined by the Kinetics Neo software for the Oxidation Induction Time (OIT).

The application of these kinetic results facilitates the prediction of the lifetime for a liquid phase at different temperatures.

This prediction is based on the extrapolation of the Arrhenius plot (figure 3), where the straight line is extended to lower temperatures, corresponding to an increase in the 1/T value.

Table 2 Kinetic parameters

Log (Pre-exponential factor)	13.3 Log (1/s)
E_a (Activation energy)	165 kJ/mol
Coefficient of determination (R^2)	0.9999



3 Kinetic analysis of OIT measurements on HDPE black pipe samples during different isothermal segments

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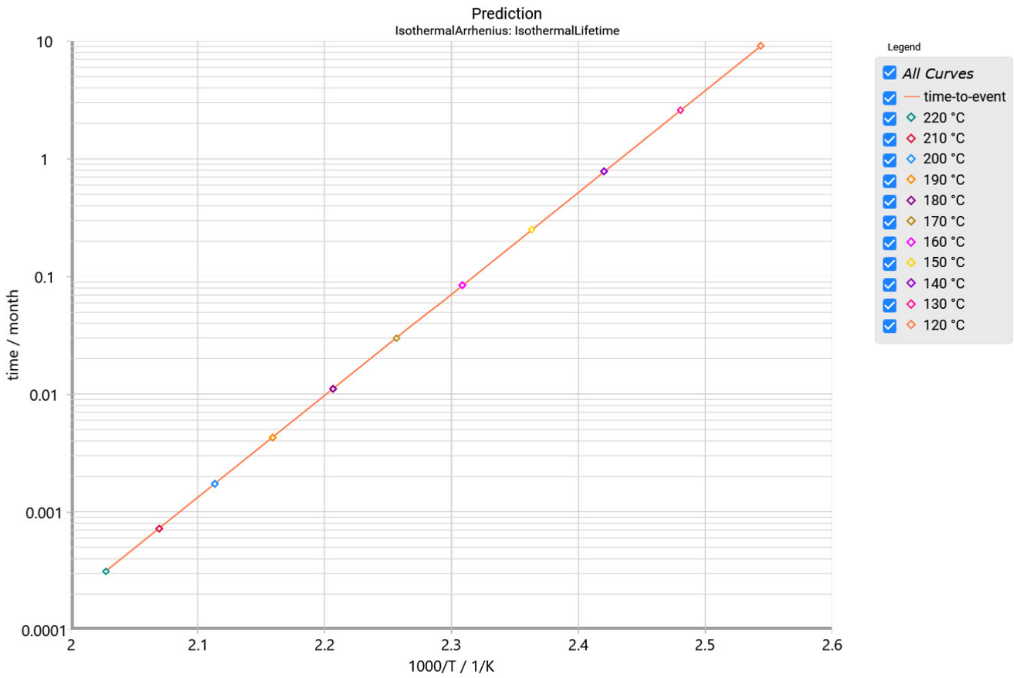

4 Arrhenius plot for HDPE black pipe samples based on OIT measurements using the Kinetics Neo software

Simulation Prediction of the Isothermal Lifetime

Figure 4 depicts the Arrhenius plot results. This curve is an extrapolated plot for different isothermal temperatures for HDPE black pipe samples. The measurements were conducted at temperatures above the polymer melting temperature. Consequently, the prediction was calculated for molten polymers. However, an extrapolation of the Arrhenius plot to lower temperatures can facilitate a comparison of the polymer's behavior, based on the estimation of the thermal stability, when the same stabilizer system is utilized [5].

Conclusion

The OIT test provides a quick and effective method for characterizing the oxidative stability of polymers and comparing their thermo-oxidative performance. A comprehensive kinetic analysis is achieved through the combination of NETZSCH DSC measurements with the NETZSCH Kinetics Neo software for the determination of kinetic parameters using the isothermal Arrhenius.

Furthermore, a comparison of the Arrhenius plots of various polymers that contain the same stabilizer can facilitate determination of the polymer that exhibits high stability under the same conditions.

Literature

[1] Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry. (2019). ASTM International. https://doi.org/10.1520/D3895-19
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[5] Ehrenstein, G. W., Riedel, G., & Trawiel, P. (2004). Thermal Analysis of Plastics - Theory and Practice. In Journal of Chemical Education (Vol. 85, Issue 3).

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