Measurement of Oxidative Induction Times (OIT) by DSC

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Oxidative induction time (OIT) measurements provide a valuable characterization parameter associated with the long term stabilities of polyolefins, particularly polyethylene. Cables utilized for telecommunication purposes are generally encased in a coating comprised of polyethylene. In order to ensure that the cable coatings will exhibit acceptable, long-term stability, and to prevent failure of the cable, a simple test needs to be performed which will provide a reliable indication of the stability of the polyethylene coating. The OIT test is an internationally recognized means of characterizing the thermo-oxidative stabilities of polyolefins (ASTM D3895 and DIN EN 728).

Differential scanning calorimetry (DSC) provides an easy-to-use, and sensitive means of characterizing the thermal and thermo-oxidative properties of polyethylene materials. The technique measures heat flow into or out of a sample as the sample is heated, cooled or held isothermally. For polyolefin materials, DSC can be used to measure the following important parameters:

- Melting points
- Heats of melting
- Percent crystallinities
- Glass transition temperatures (Tg)
- Crystallization times and temperatures

Figure 1. PerkinElmer Pyris 6 DSC with Autosampler.

- Thermo-oxidative stabilities
- Processing conditions
- Thermal histories
- Effect of recyclates
- Effectiveness of anti-oxidantant agents
- Quality assurance

The PerkinElmer Pyris 6 DSC provides an excellent means of characterizing the thermal and physical properties of polyolefins, including oxidative induction time measurements. The heat flux Pyris 6 DSC offers the following desirable features:

- Stable baseline performance
- High sensitivity
- Ease of use for both hardware and software
- 45-position reliable autosampler for unattended operation
- Comprehensive validation
- Tolerance software (e.g., automatic ‘pass/fail’ assessment)
- Compact design
- Attractive pricing

PerkinElmer™ instruments.

Figure 2. DSC OIT results on high density polyethylene materials.

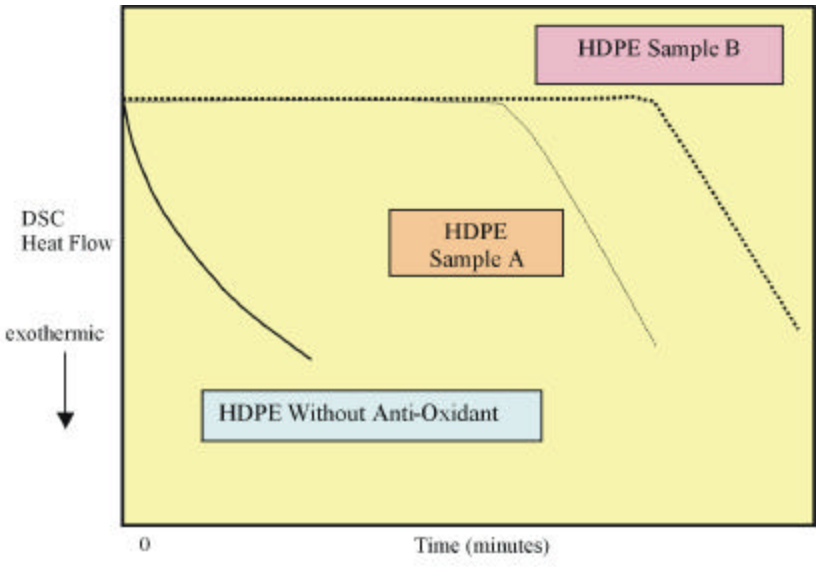
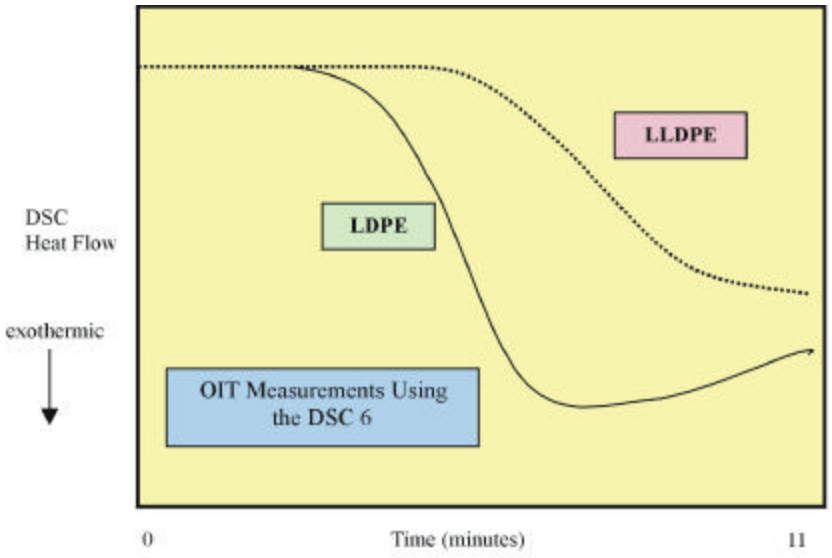


Figure 3. DSC OIT results on LDPE and LLDPE resins.



The autosampler featured with the Pyris 6 DSC utilizes high technology, shape memory alloy for the grippers, which provides reliable long-term performance. The use of the shape memory alloy grippers eliminates many mechanical components in the most critical part of the autosampler.

The following conditions are used to determine the OIT values of polyolefin materials using DSC:

- Pre-check the DSC cell to ensure that the instrument has been accurately calibrated for temperature using high purity indium (M.P. = 156.6 C)
- Ensure that the DSC cell will achieve an isothermal temperature of 200.0 C
- Ensure that nitrogen and oxygen purge gases are connected to the DSC purge gas entry port using the TAGS gas switching accessory
- Use a sample mass of approximately 10 to 15 mg
- Use open aluminum pans
- Most consistent OIT results are obtained using a single piece disk test specimen
- Better sample uniformity can be obtained by extracting the sample from the coating film test specimen using a cork borer which has a diameter matching that of the DSC sample pan
- Heat the sample under a nitrogen purge from room temperature to 200.0 C at a rate of 10 C/min
- Hold the sample under the nitrogen purge at 200.0 C for a 5 minute period to allow the sample and DSC cell to thermally equilibrate at the target temperature
- Switch from the nitrogen to an oxygen purge using the TAGS (automated gas switching accessory) after the 5 minute hold period
- The sample should be maintained under isothermal

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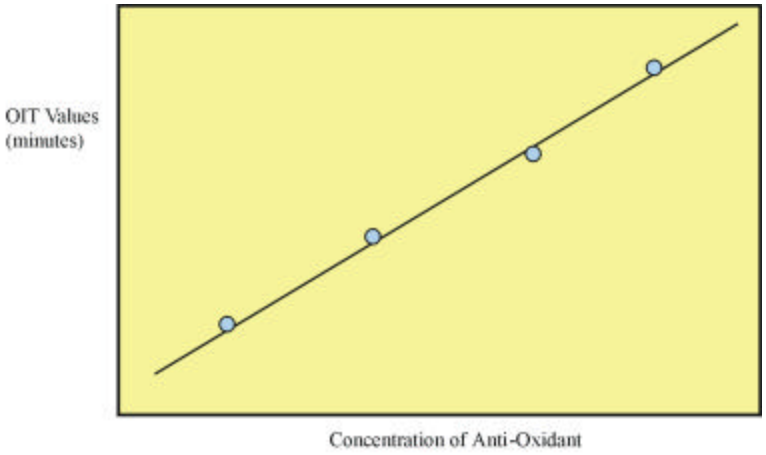
Figure 4. Increase in OIT values with regards to increasing concentration of anti-oxidant.



conditions with the oxygen purge until a significant oxidative exothermic response is obtained. The time that is required for this to occur is dependent upon the relative stability of the polyolefin material being tested. Once a significant exothermic onset has been obtained, the experiment can be terminated

- Plot the resulting heat flow data as a function of time
- The OIT value is defined as the onset time established by using the onset option in the DSC data analysis software.

Displayed in the Figure 2 are OIT measurements obtained on three different polyethylene samples.

Without the presence of an anti-oxidant, the polyethylene immediately undergoes thermo-oxidative degradation. Sample A contains an anti-oxidant and its OIT is significantly increased. Sample B contains the same anti-oxidant as Sample A at a higher concentration. As a result, the OIT of Sample B is longer than that of Sample A.

Figure 3 shows the OIT results on two different polyethylenes (LDPE and LLDPE) with the LLDPE material exhibiting the better thermo-oxidative stability.

The OIT values can be to establish the level of an anti-oxidant in a polyolefin resin, provided that a calibration curve has first been established for the given anti-oxidant. This is very useful for quality assurance purposes and is shown in the Figure 4.

Summary

The measurement of oxidative induction times (OIT) is a valuable characterization test for assessing the long-term stabilities of polyolefin materials. Longer OIT values generally translate to improved long-term performance. The test is useful for the following types of applications:

- Telecommunication cables
- Geomembranes
- Vapor barrier films
- Tubes or pipes
- Injection molding of polyethylene containers

The PerkinElmer heat flux Pyris 6 DSC with 45-position autosampler provides an easy-to-use means of measuring OIT values.

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