APPLICATION**NOTE**

Investigation of the Oxidative Stability of Polyolefins and Thermoplastic Elastomers by Means of DSC

Dr. Elisabeth Kapsch, Dr. Ekkehard Füglein and Dr. Stefan Schmölzer

Oxidative-Induction Time (OIT)

Oxidative-induction time (OIT) measurements allow for characterization of the long-term stability of hydrocarbons such as oils, fats, but also of plastics like polyolefins, particularly polypropylene and polyethylene.

For determination of the oxidative stability, standardized test methods by means of DSC (Differential Scanning Calorimetry) are used. These tests can easily be carried out and provide reliable information on the stability of e.g., a polyethylene coating. The thermo-oxidative performance of a material can be predicted and failure prevention can be achieved.

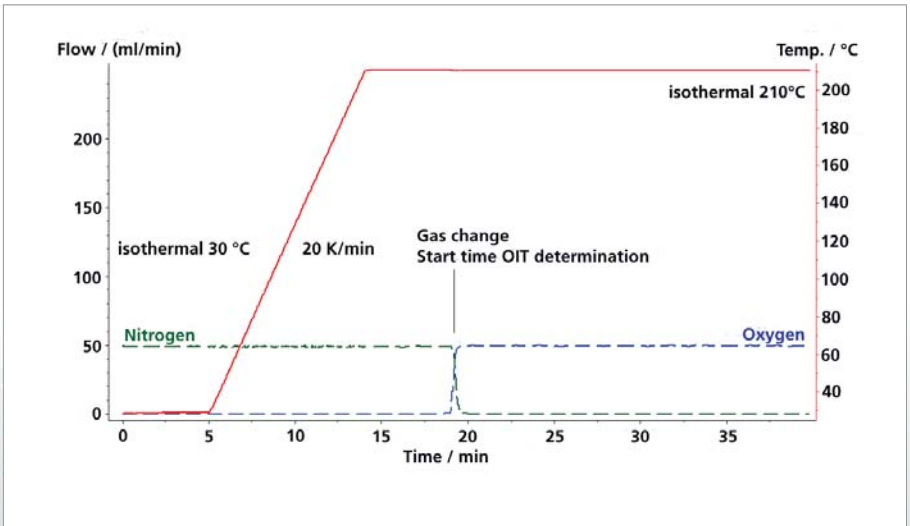
OIT tests by means of DSC are internationally recognized. Well-established standards are e.g., ASTM D3895-92, ASTM D6186, EN 728 und ISO 11357-6.

DSC systems for determination of the OIT are the DSC 204 ***F1*** *Phoenix*®, DSC 200 ***F3*** *Maia*® and DSC 404 ***F1/F3*** *Pegasus*®.

Method

The samples are heated under a protective gas to a temperature above their melting point. At a constant temperature, the sample atmosphere is switched from inert to oxidative. The amount of time elapsing until the exothermal oxidation of the sample begins is referred to as OIT.

DSC 200 ***F3*** *Maia*®



1 General method for determination of the OIT

OIT Measurement Conditions for all Examples Presented

- Crucible material: aluminum, open
- Atmosphere: O_2 / N_2
- Purge gas rate: 50 ml/min
- Isothermal temperature: 210°C, 190°C

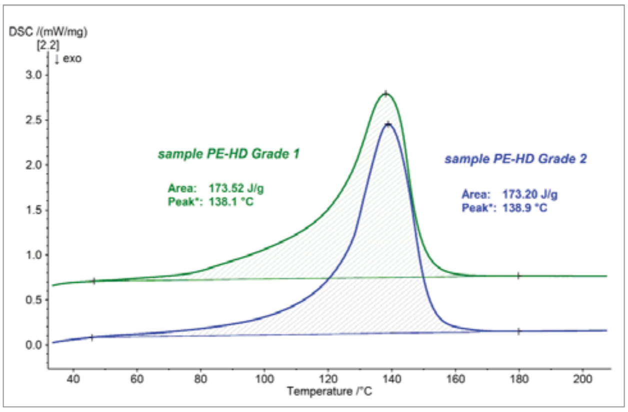
NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Tel.: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

NETZSCH

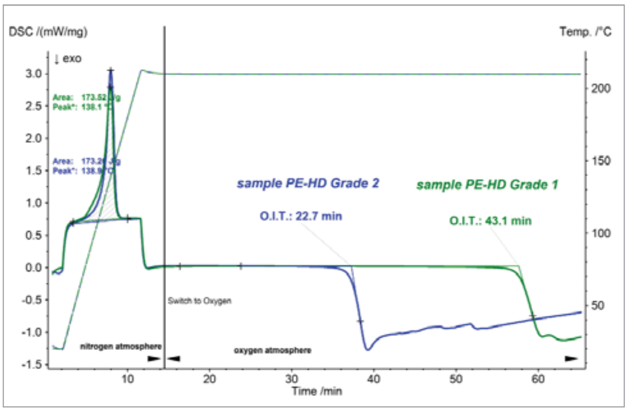
OIT Tests on PE-HD Samples Differing in Grade

Only very small differences were determined for the melting behavior (melting enthalpy and peak temperature) of two PE-HD samples differing in grade (figure 2a). However, clear differences between the two samples can be observed in the OIT. Sample Grade 1 is stable 43 min before oxidation starts (figure 2b). Sample Grade 2 yields a much lower stability; the OIT is reached after 23 min.

This example already shows that more detailed information can be obtained from DSC curves just by varying the temperature program.



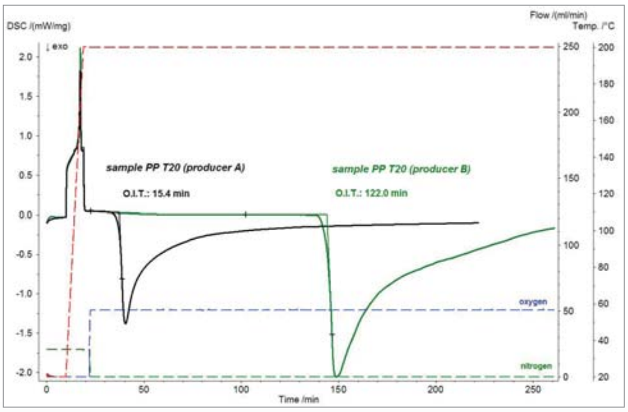
2a Samples PE-HD Grade 1 and Grade 2, melting



2b Oxidation behavior of PE-HD at 210°C

PP T20 from Different Producers

Two highly heat-resistant polypropylene samples from different producers were investigated regarding their oxidative stability. Again, the melting behavior of the two materials is nearly identical. Only the OIT tests reveal the difference. The oxidative stability of sample "Producer A" is determined at 15 min whereas the second sample "Producer B" shows a very high stability. Here, degradation starts after 122 min (figure 3).



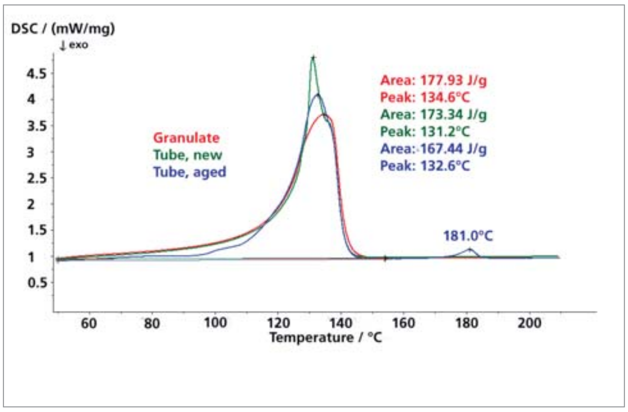
3 OIT tests on PP from different producers

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Tel.: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

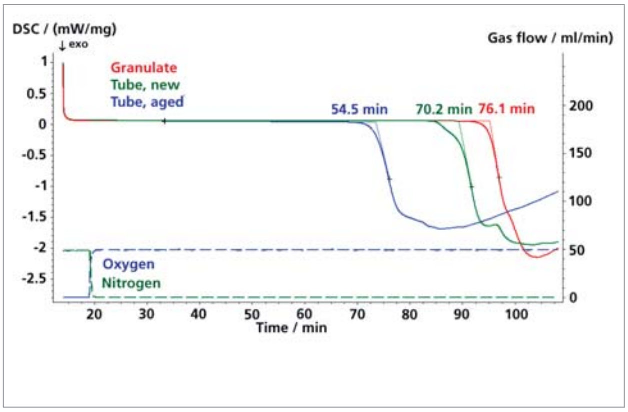
Results of OIT Tests on PE Granulate, Extruded Tube and Aged Tube

Materials PE-HD, PE-RT Type 1 and PE-RT Type 2 were investigated, each as a granulate, an extruded tube and an aged tube. All were subjected to a temperature change treatment. The melting behavior and behavior in an oxidizing atmosphere for sample series PE-HD and PE-RT Type 1 are depicted in figures 4a, 4b and 5a, 5b.

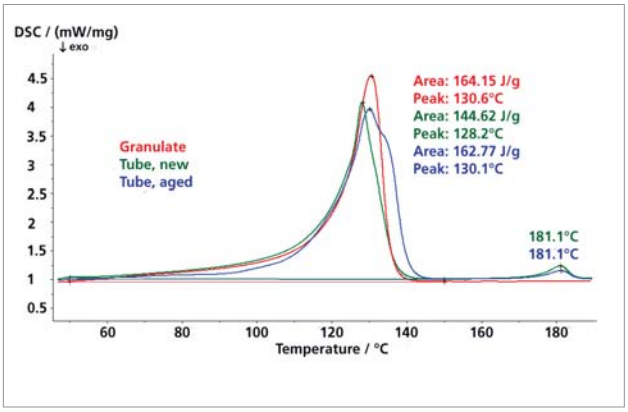
In addition, figure 5b demonstrates that occasionally, the OIT cannot be evaluated due to a very low oxidative stability. When the atmosphere is switched from nitrogen to oxygen, the aged material (blue curve) starts to degrade with an insignificant time delay. In cases like these, a dynamic temperature program is helpful to show the differences of apparently same materials.



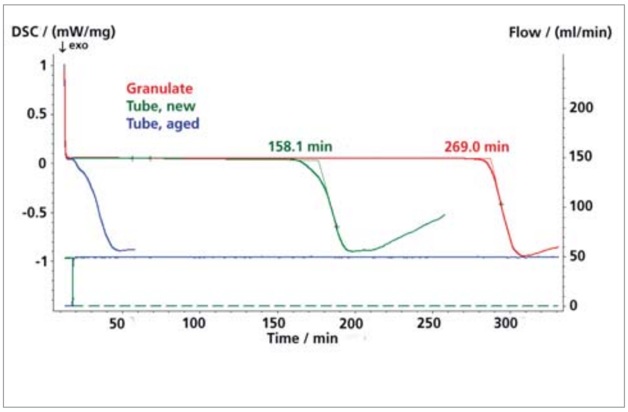
4a PE-HD, melting



4b PE-HD, oxidation behavior at 210°C



5a PE-RT Type 1, melting



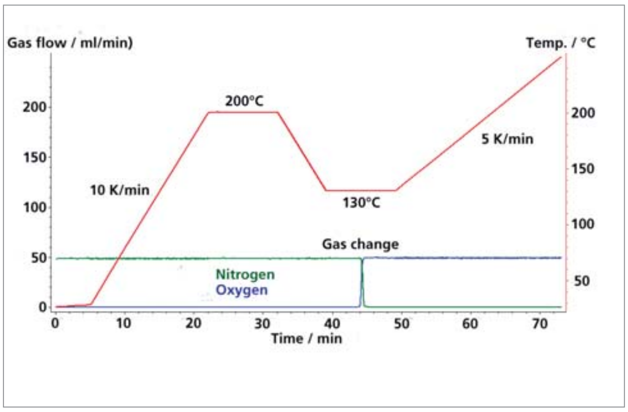
5b PE-RT Type 1, oxidation behavior at 190°C

NGB · Application Note 023 · E · 11/12 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Tel.: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

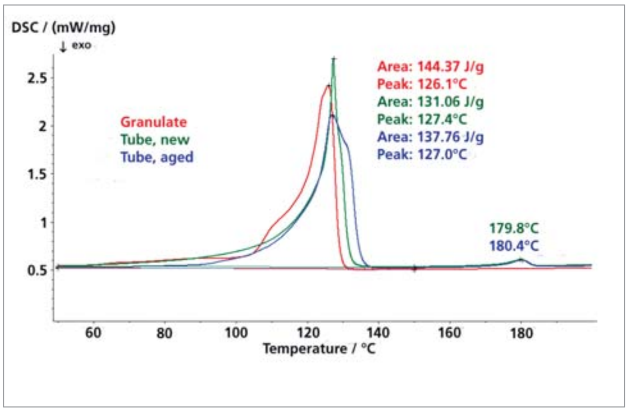
Dynamic Temperature Program for the Determination of the Oxidative Stability of PE Granulate, Extruded Tube and Aged Tube

If the samples to be compared are very different regarding their resistance to oxygen, it will not be possible to present a comparison at an identical isothermal temperature. Figure 6 shows an alternative temperature program ensuring that the samples are entirely molten and enabling a change of atmosphere at a temperature at which the most reactive sample does not react immediately after the gas change (see figure 6).

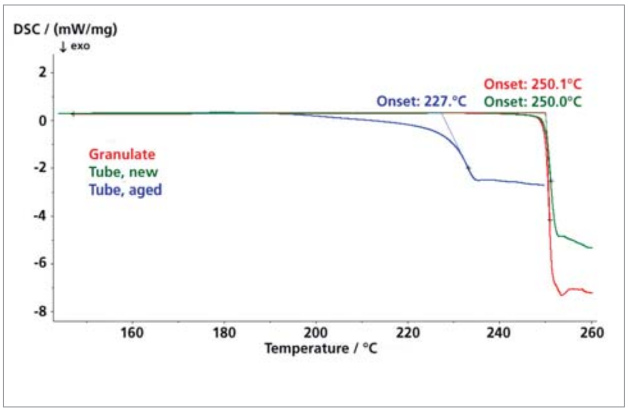


6 Dynamic temperature program for an improved comparison of the OIT

The melting behavior and oxidation behavior of sample series PE-RT Type 2 are presented in figures 7a and 7b. The isothermal temperature cannot be selected lower than 180°C since one component melts at approximately 180°C. One can now significantly distinguish between strongly differing oxidation behaviors by using a dynamic temperature program



7a PE-RT Type 2, melting; second phase at 180°C, deteced in the new and aged tube



7b PE-RT Type 2, oxidation bahavior,dynamic OIT determination

NGB · Application Note 023 · E · 11/12 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Tel.: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

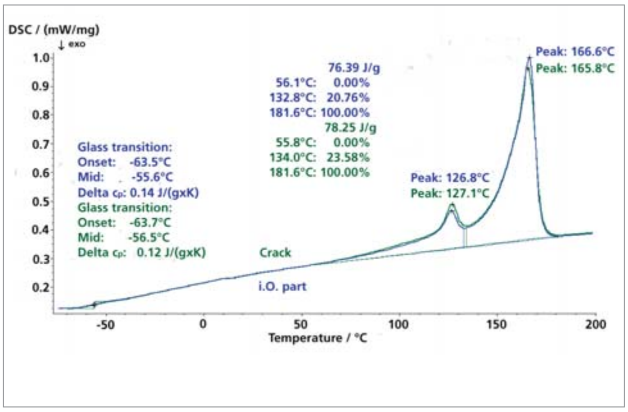
Failure Analysis of TPE Parts Via Dynamic OIT, the So-called OOT (Oxidative Onset Temperature)

In ASTM E2009-08, the oxidative onset temperature is described as a relative measure of the degree of oxidative stability of the material evaluated at a given heating rate and oxidative environment, for example, oxygen; the higher the OOT value, the more stable is the material.

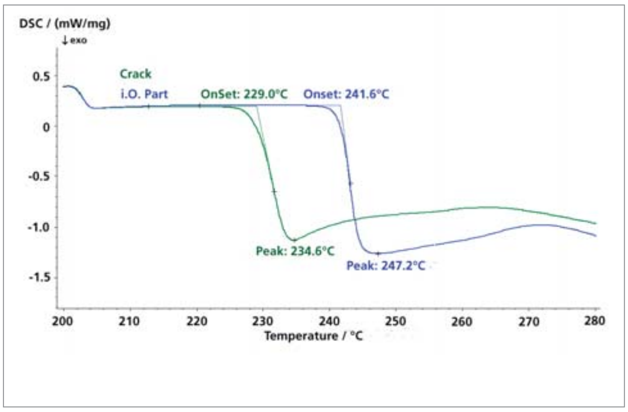
The OOT can be used for comparative purposes; it is not an absolute measurement technique like the oxidative-induction time (OIT) at a constant temperature (ASTM E1858). The presence or effectiveness of antioxidants may be determined by this test method.

DSC measurements were carried out on two TPE parts (poor and good) with a sample mass of approx. 14 mg. For the measurements, closed aluminum crucibles with pierced lid and an N_2 atmosphere were chosen. The heating rate amounted to 10 K/min (figure 8). At 210°C, the atmosphere was switched to oxygen and the heating rate was lowered to 5 K/min (figure 9).

During the 1st heating, the good (blue curve) and poor sample (green curve) show the same thermal behavior. The glass transition and peak temperatures, but also the melting enthalpy are almost identical (figure 8). However, after changing the atmosphere but still increasing the temperature, the DSC curves demonstrate differences which can be seen in a deviating oxidation behavior of the two samples (figure 9). The oxidative onset temperature (OOT) of the poor sample (green curve) is determined to 229°C whereas that of the good part only occurs above 241°C.



8 First heating curves of two TPE parts



9 OOT determination of a good and a poor part

NGB · Application Note 023 · E · 11/12 · Technical specifications are subject to change.

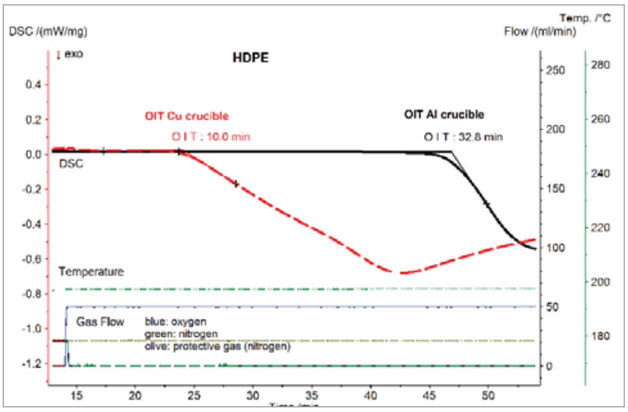
NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Tel.: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com

Influence of Crucibles on the Oxidative-Induction Time

The oxidative-induction time (OIT) can be determined in standard aluminum or open copper crucibles in accordance with ASTM D3895.

This plot represents an OIT measurement on HDPE carried out in an open copper (red) and Al (black) crucible, respectively (figure 10). It can clearly be seen that under isothermal conditions, oxidation of HDPE begins approximately 23 min earlier in the copper crucible than in the Al crucible.

Besides copper crucibles, aluminum crucibles the bottom of which can be shaped with the stamping tool kit of the sealing press are available (figure 11). These crucibles are especially designed for determination of the OIT of lubricants and grease in accordance with ASTM D5483-5.



10 Comparison of the oxidative-induction time in open copper and aluminum crucibles

11 Copper (left) and aluminum crucibles (right), especially for determination of the OIT

NGB · Application Note 023 · E · 11/12 · Technical specifications are subject to change.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42 · 95100 Selb · Germany
Tel.: +49 9287/881-0 · Fax: +49 9287/881505
at@netzsch.com · www.netzsch.com