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Determination of the Aging Resistance of Polymers with Standardized Tests for Thermo-Oxidative Aging, OIT Determination with Differential Scanning Calorimeter (DSC)

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Agenda

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Determination of the Aging Resistance of Polymers with Standardized Tests for Thermo-Oxidative Aging, OIT Determination with Differential Scanning Calorimeter (DSC)

1. External factors influencing aging of polymers

2. Possibilities to reduce aging

3. Oxidative-InductionTime (OIT)

- Standards
- OIT determination with DSC

3. Failure analysis using OIT measurements

4. Summary

External Factors Influencing Aging of Polymers

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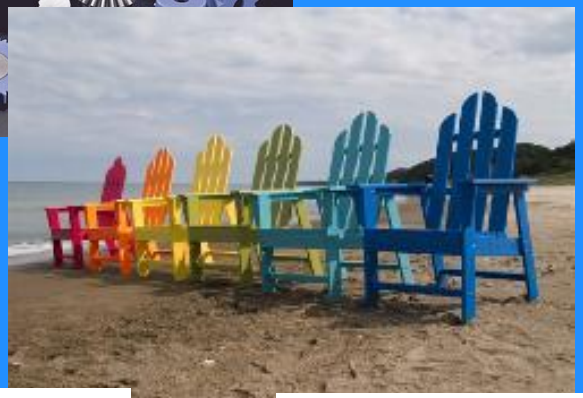
light
• UV-radiation

temperature

outdoor exposure
• air (oxygen)
• water
• soil

mechanical load
• tensile, compression , shearing, vibration



biological exposure
• bacteria
• funguses

chemical exposure
• oil, tensides
• ozon

External Factors Influencing Aging of Polymers

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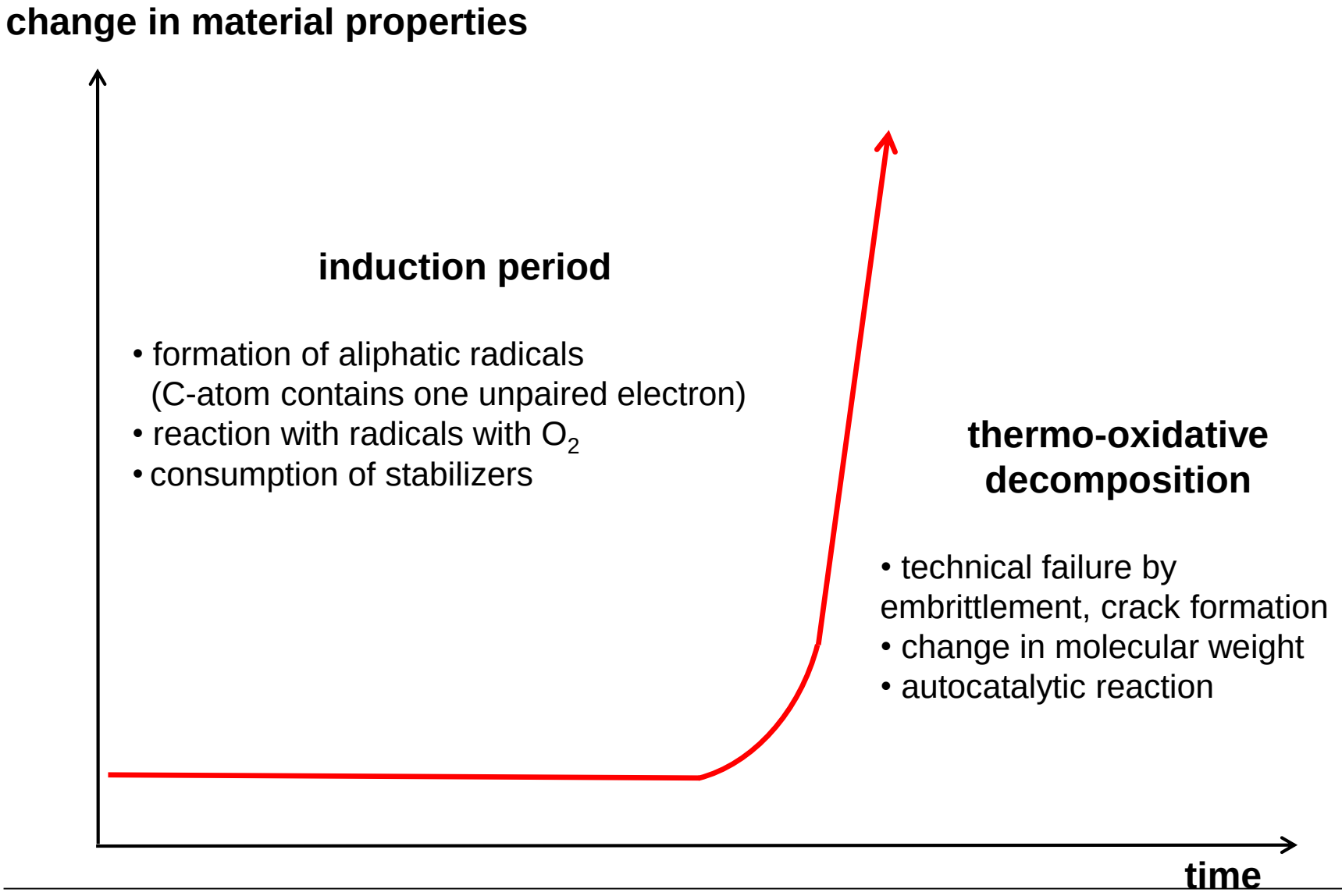
Most important stress types influencing long-term use of polymers

- **Oxidation**
  thermo-oxidative (T, O_2) and photo-oxidative aging (hf, T, O_2)
- **Influence of chemicals and simultaneous mechanical stress**
- **Biological aging**

Phases of Thermo-Oxidative Aging



Possibilities to Reduce Aging: Stabilizers

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Appropriate Stabilizers protect polymers against damage by:

- **oxygen (air)**(O_2)
- **heat** (T)
- **light** (hf)
- **shearing** (τ)
- **metal ions** (M^{n+})

Stabilizers slow down the aging process and extend the induction period

Types of Stabilizers

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- **antioxidants**

(primary antioxidants) protect the polymer during production and molding as well as from influences caused by heat and oxygen.

- **co-stabilizer**

(secondary antioxidants) support the efficiency of the primary antioxidants

- **light stabilizer**

increase the resistance against light (UV)

- **metal deactivator**

minimize the influence of metal contact: Cu cable

International Standards: Excerpt

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ASTM D 3895	Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry
ASTM E 2009	Standard Test Method for Reaction Induction Time by Thermal Analysis
ASTM D 4565	Standard Test Method for physical and enviromental performance properties of insulations and jackets for telecommuncations wire and cable
ASTM D 525	Standard Test Method for Oxidation Stability of Aviation Fuels

International Standards: Excerpt

ASTM E 487-79	Standard Test Method for constant temperature stability of chemical materials
ISO 11357-6	Determination of oxidation induction time by DSC
EN 728	Plastics piping and ducting systems – Polyolefin pipes and fittings – Determination of oxidation induction time

Determination of Oxidative Induction Time OIT with Differential Scanning Calorimeter - DSC

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Pre-condition: **polyolefin contains antioxidants and other stabilizers**

measurant: **the time (induction period) to prevent oxidation of the material**

DSC 214 Polyma
with automatic sample changer
Temperature range: -170°C….600°C

DSC 204 F1 Phoenix
with automatic sample changer
Temperature range: -180°C….700°C

DSC (Differential Scanning Calorimetry)

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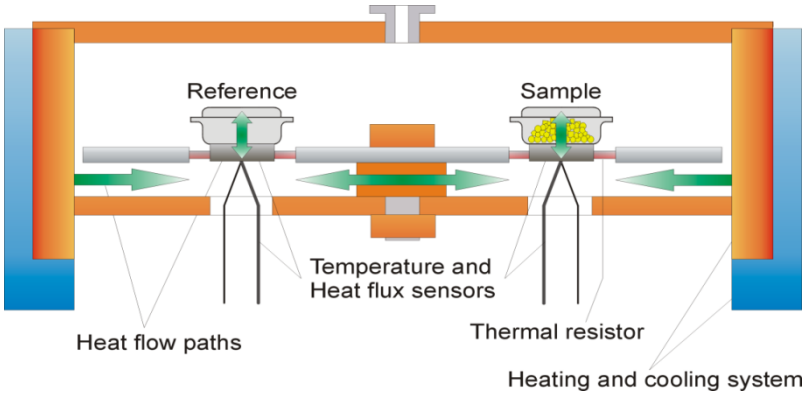
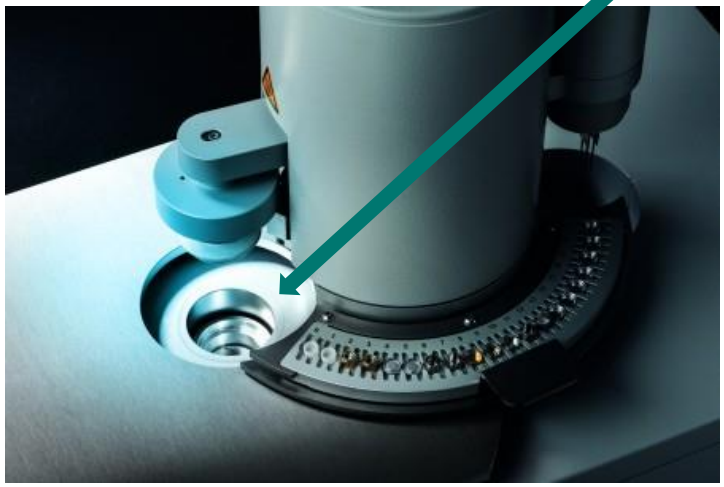
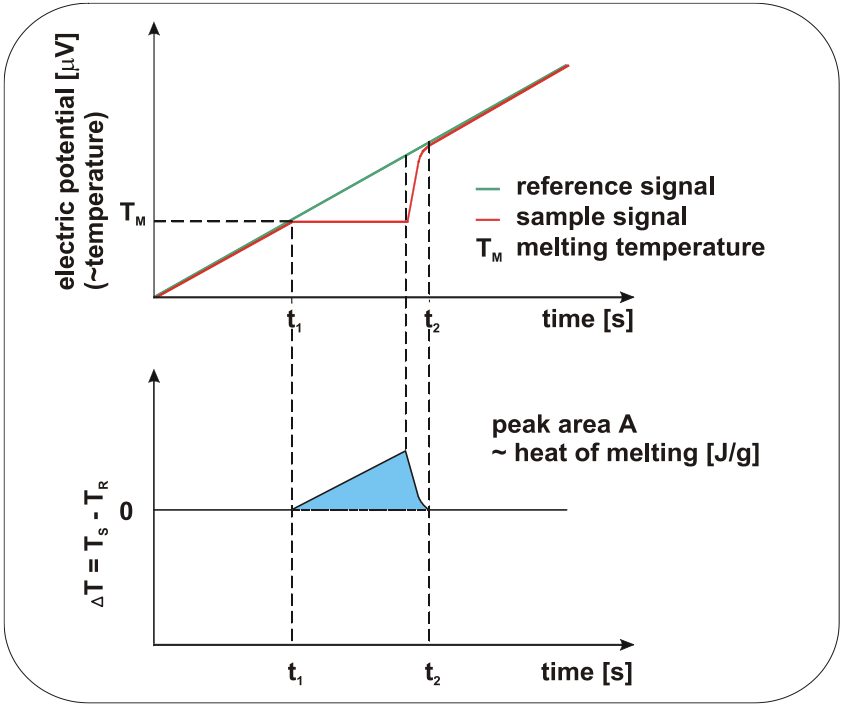
measuring cell





signal generation



OIT – Measurement
Isothermal Measurement According to DIN-EN 728

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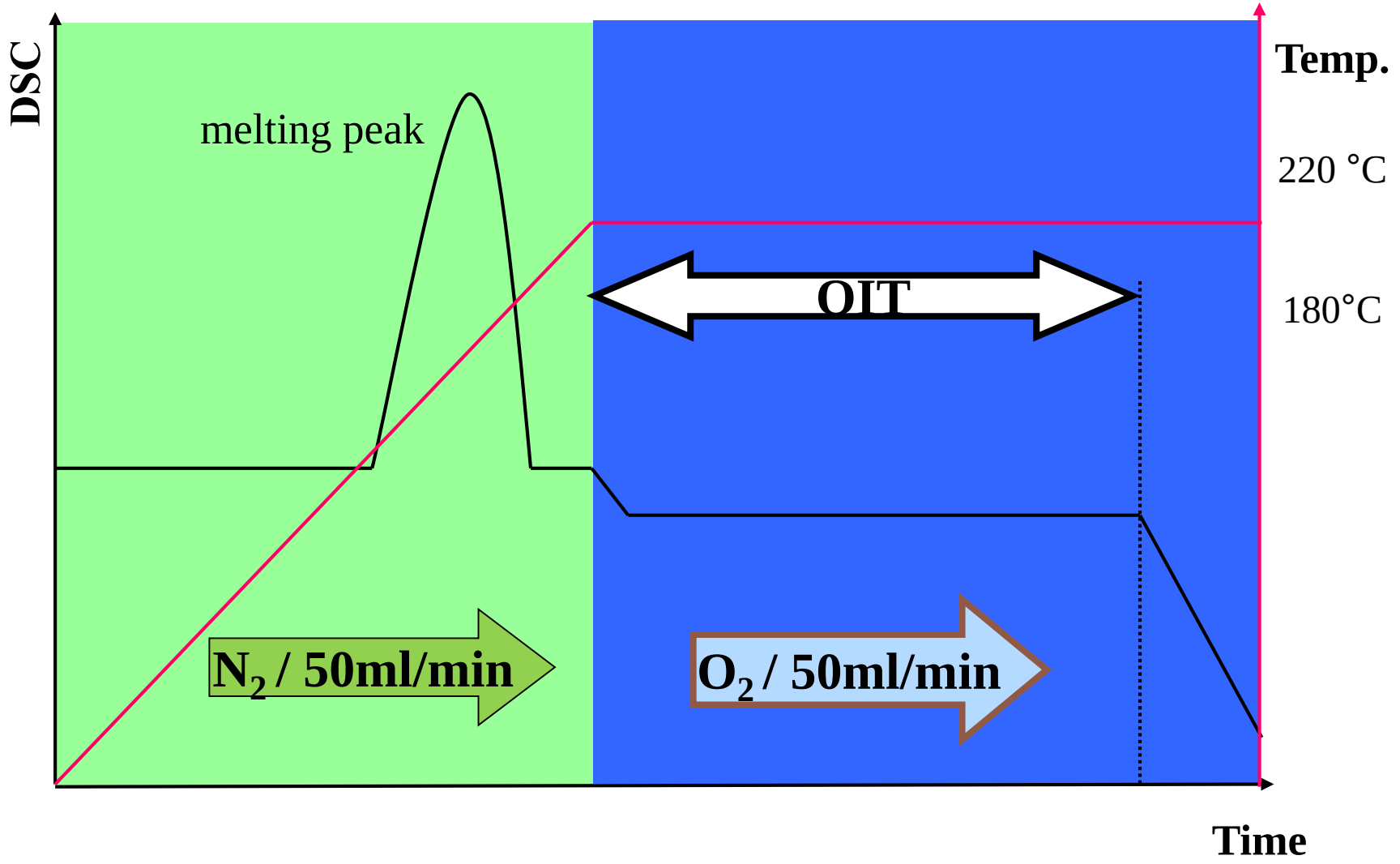
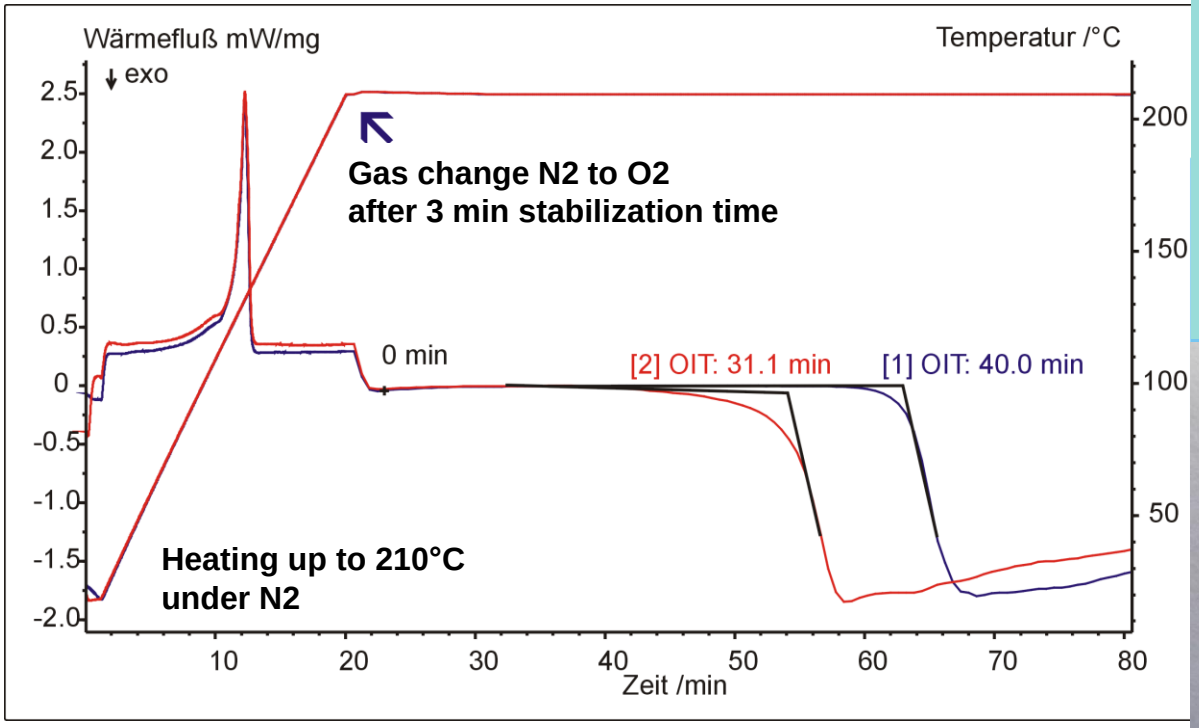
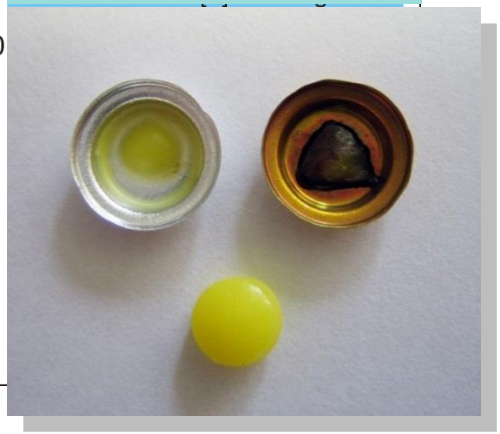


Isothermal OIT

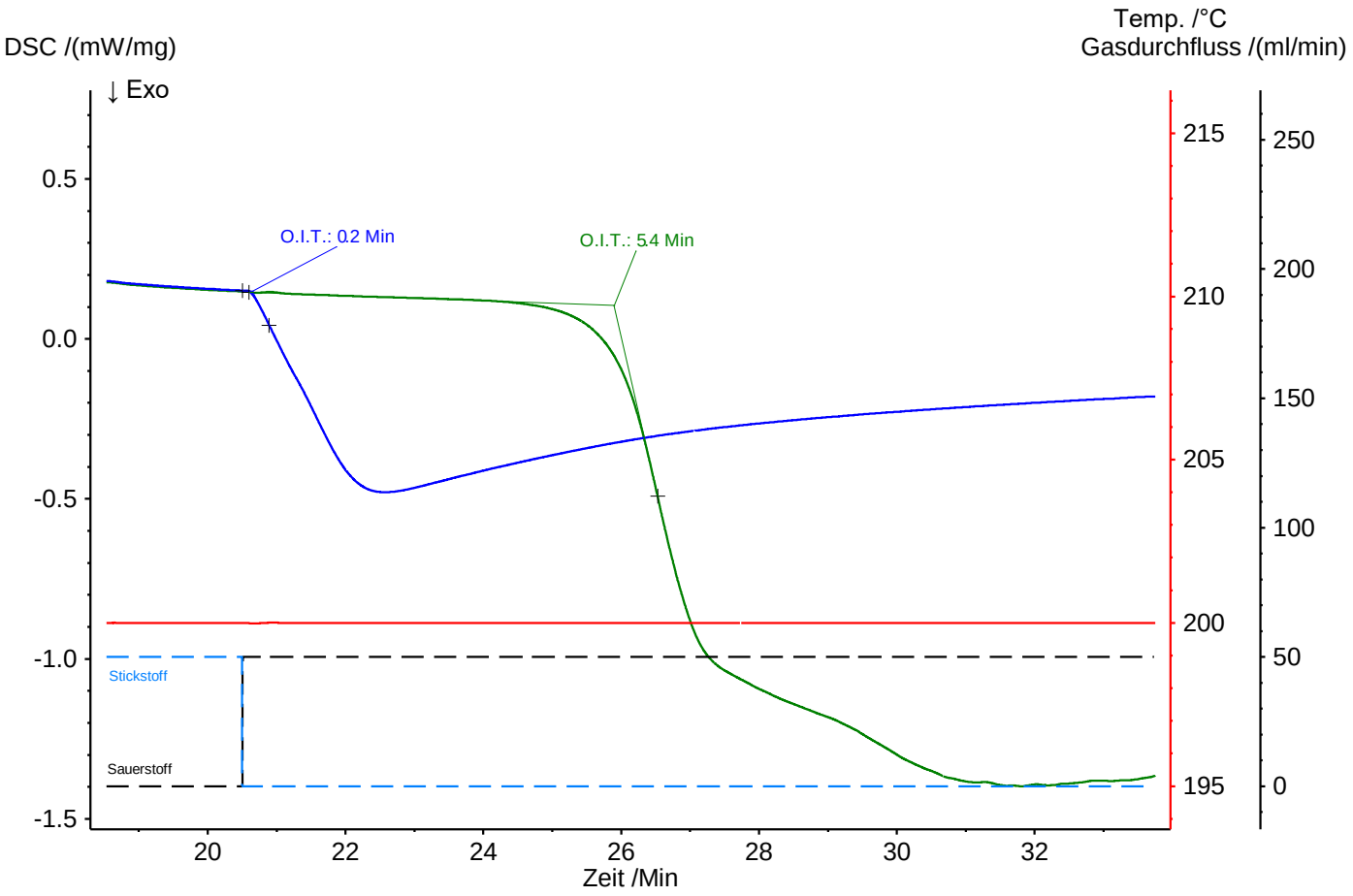


Sample: (1) PE tube
smooth surface
(2) PE tube
rough surface
Mass: (1) 7.2 mg
(2) 7.67 mg
Crucible: Al, pierced lid
Heat. rate: 20 K/min
isothermal
Atmosphere: N2/O2



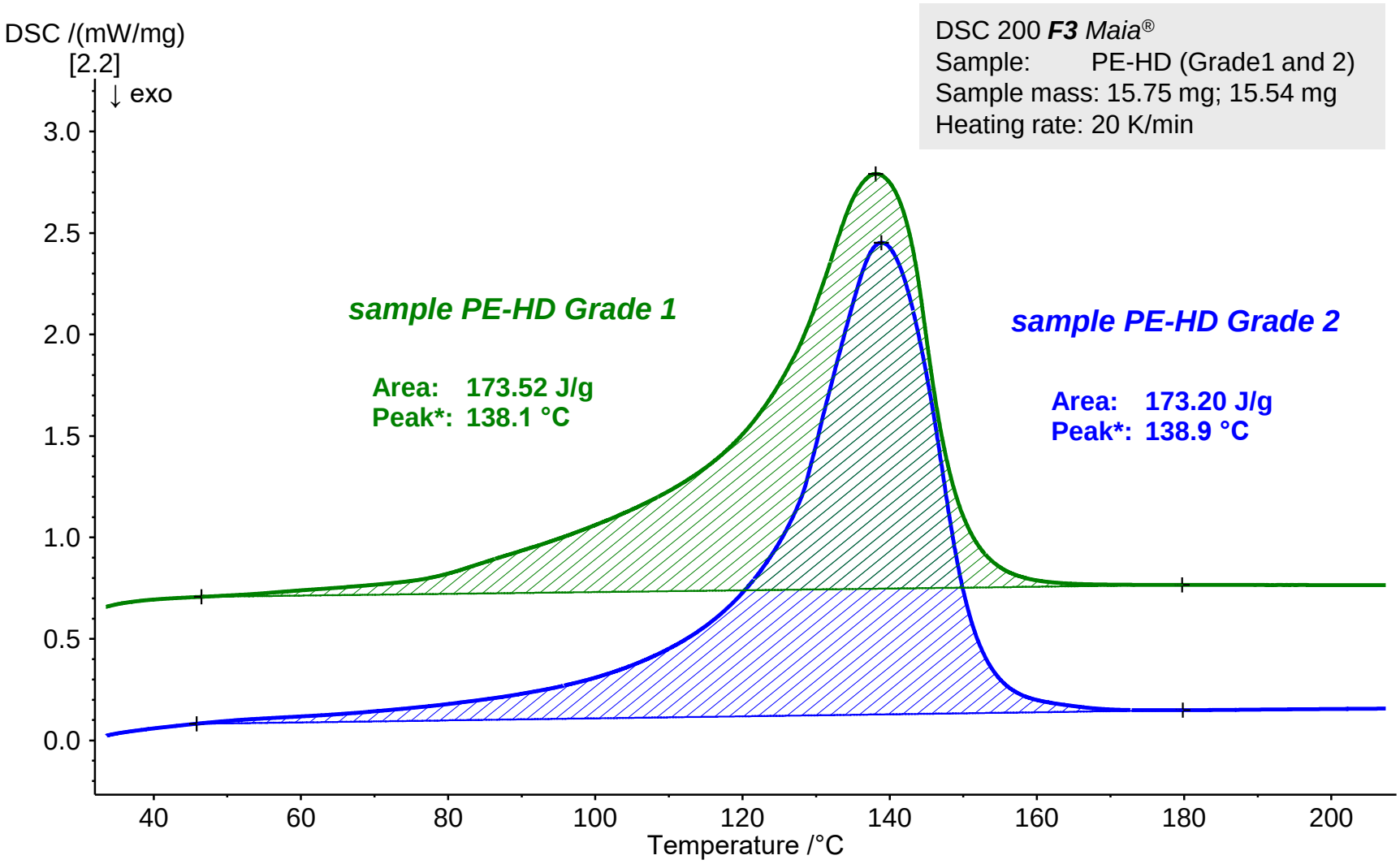
O.I.T. measurement according to DIN EN 728, ISO 11357-6, ASTM D 3895 (normally with open Al-or Cu-pans, Cu-pans for cables).
Isothermal temperature depends on standard.

Instrument requirements for DSC: Example PP

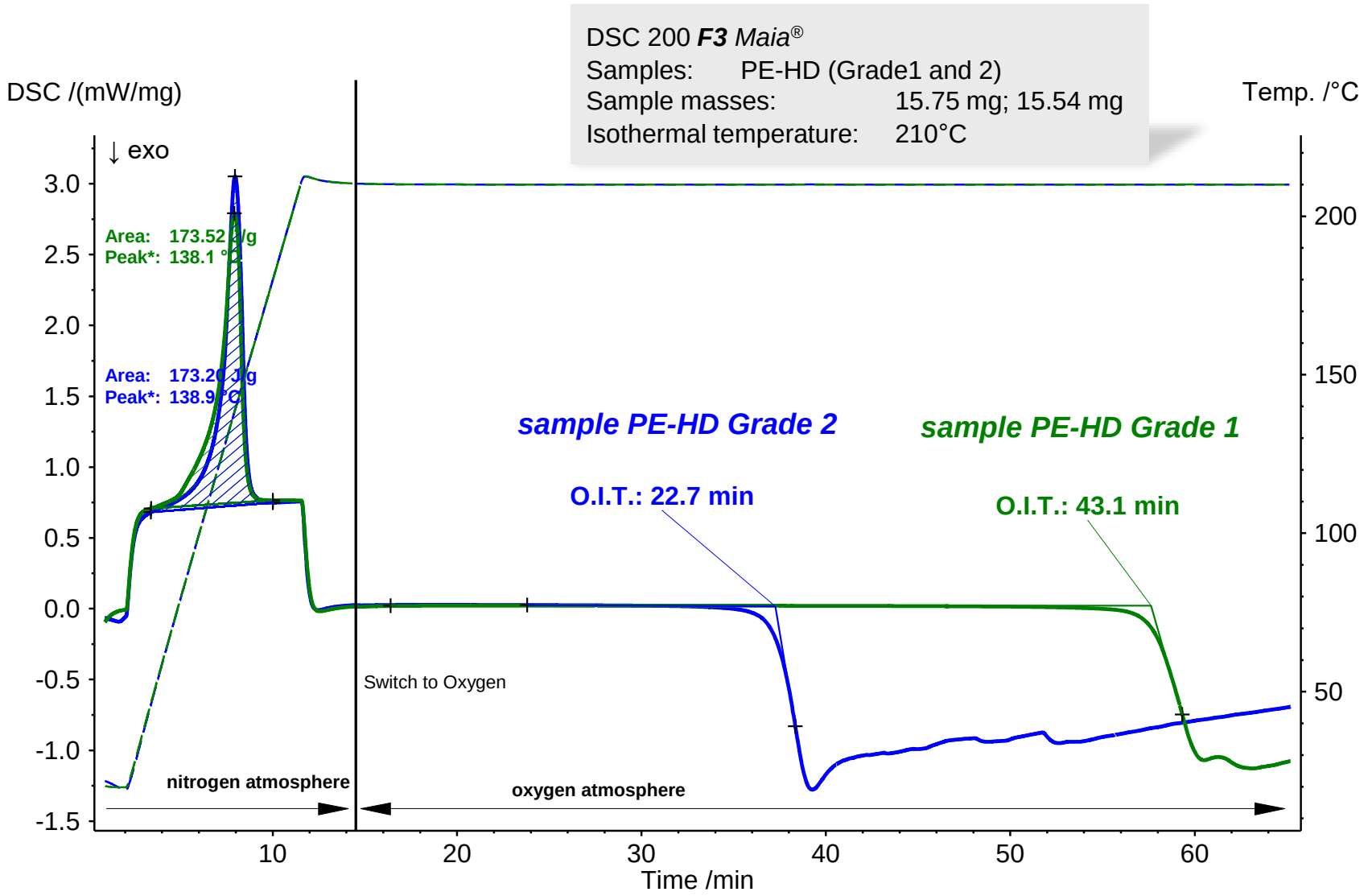


As soon as the change from nitrogen to oxygen happens oxidation occurs. Following the standard unstabilized polymers should show oxidation in less than one minute. See blue curve (isothermal segment only for both measurements).

Melting of PE-HD (Two Grades)



OIT Measurement on PE-HD (Two Grades)



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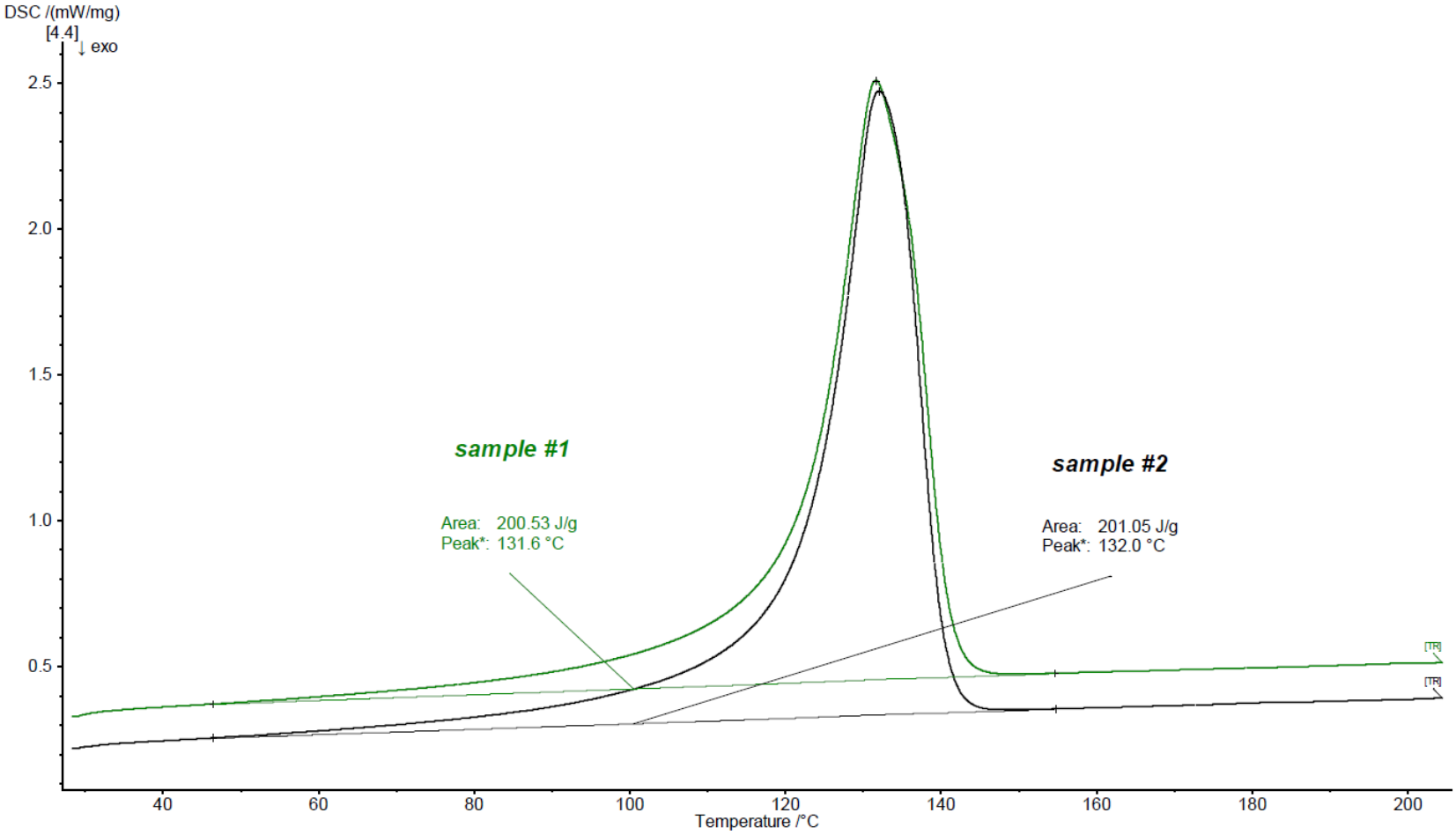
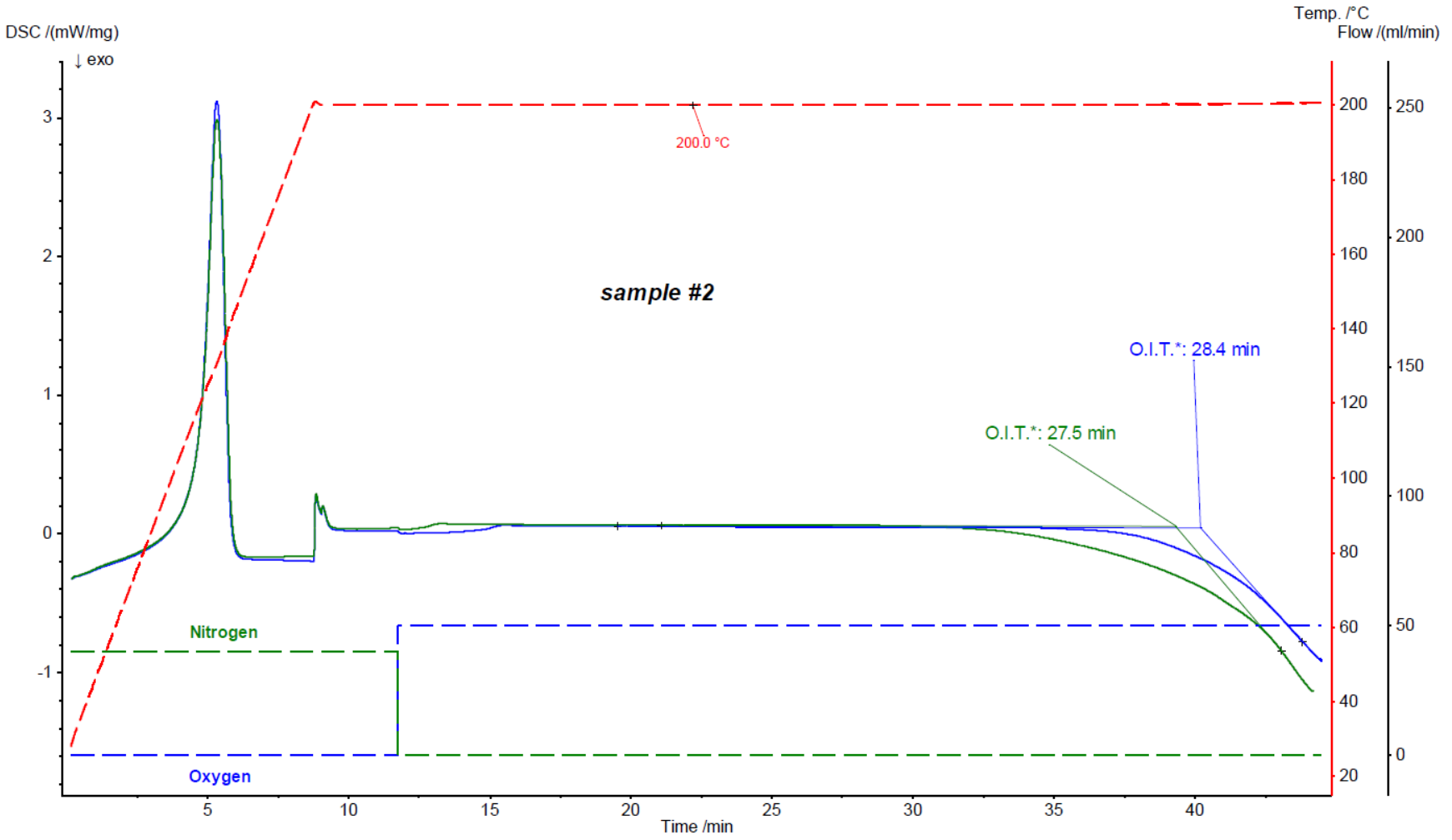
Containers from HDPE



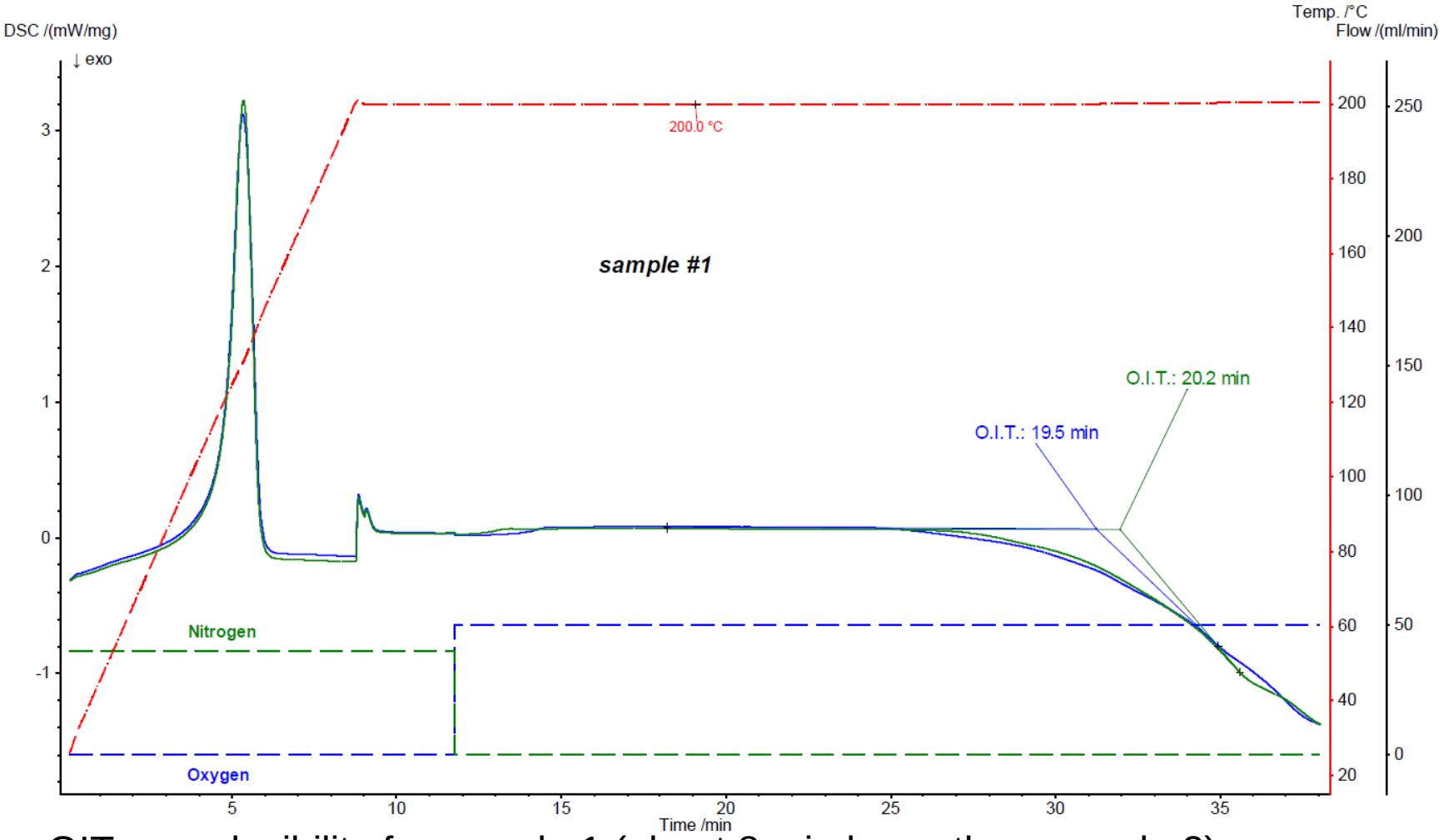
- No difference during melting

Containers from HDPE



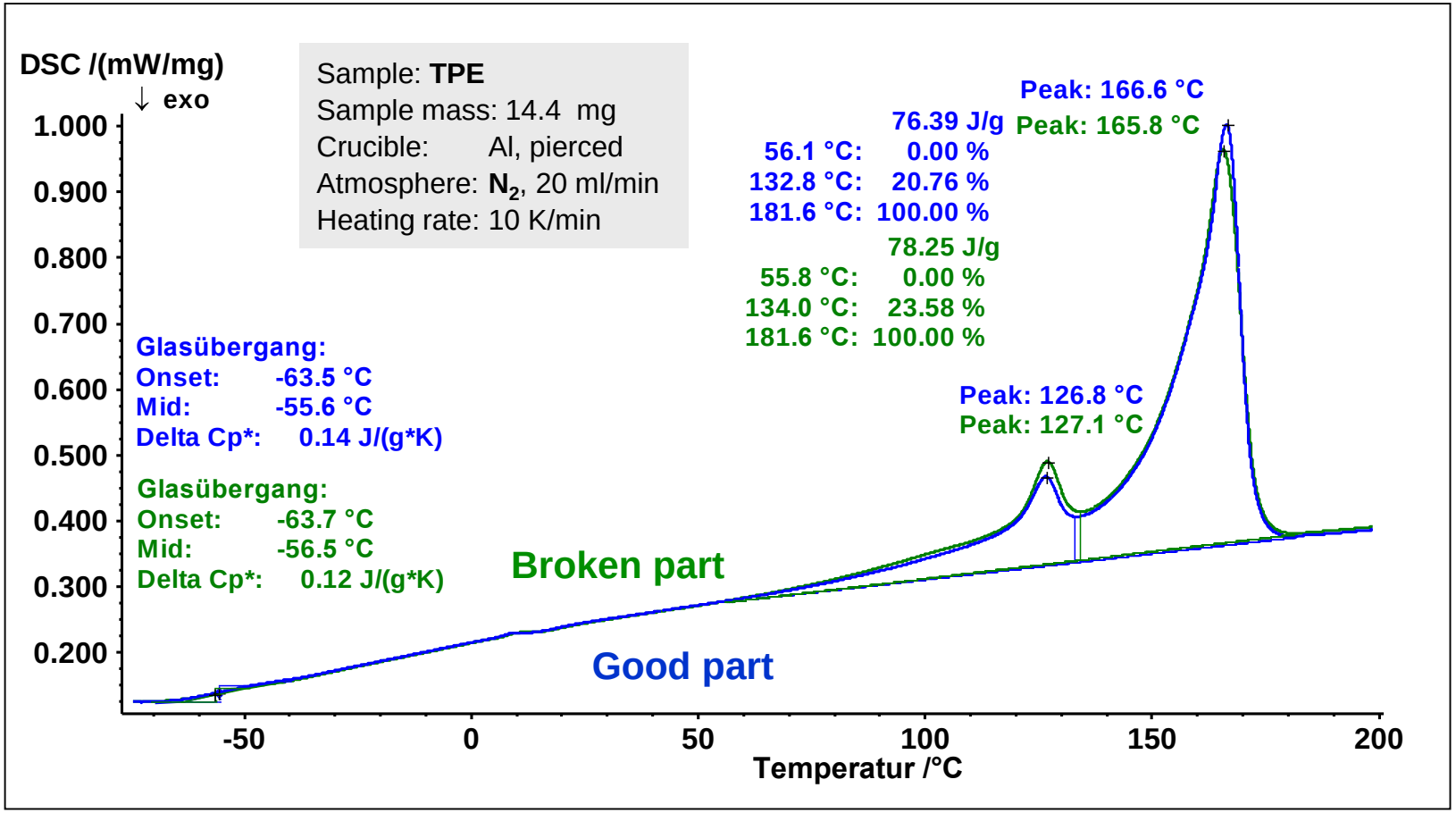
- OIT reproducibility for sample 2

Containers from HDPE



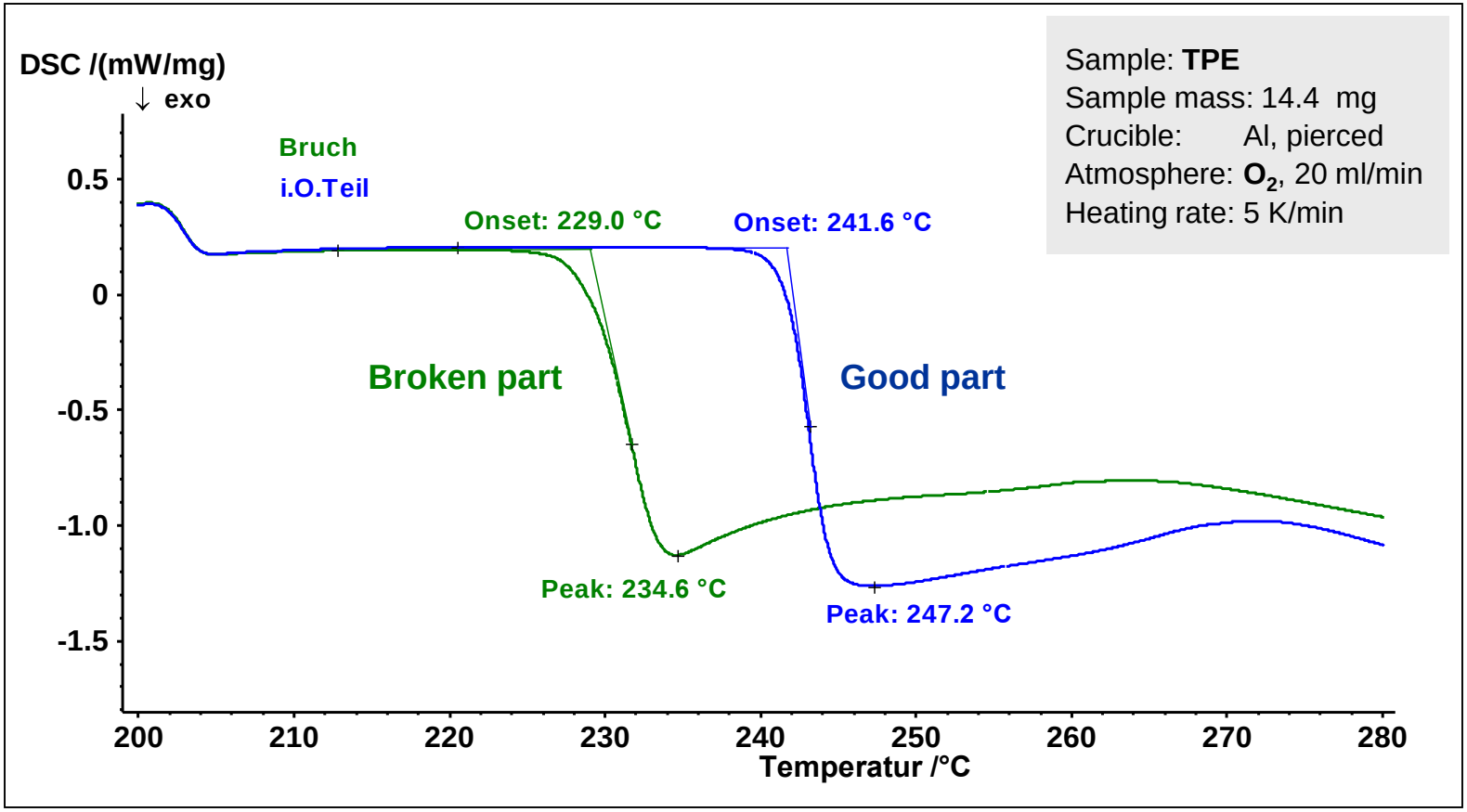
- OIT reproducibility for sample 1 (about 8 min lower than sample 2)
- Sample 1 has a lower stability against oxidation.

Heating of 2 TPE parts *Failure Analysis*



1. No significant differences between **good** and **broken** part with normal heating in nitrogen.

Dynamic OIT on the TPE parts *Failure Analysis*



2. Change to oxygen: excellent separation of material properties by dynamic OIT

Summary

O.I.T. determination is a very easy and relatively fast method for quality control and failure analysis.

The method (isotherm) corresponds to international standards applicable for polyolefin. With modifications it can also be used for other polymer types.

Long-term predictions over several years based on OIT only, however, should be rated as critical.

Some standards require high pressure DSC tests for geopolymers (3.4 MPa, ASTM D5885) or lubricants.