Thermal Analysis Option

DSC-Chemiluminescence System

Measurement of Light and Heat Flow

Chemiluminescence (CL) is the term used to describe the emission of light as a direct result of a chemical reaction. CL originating from oxidative degradation processes in polymers was reported in the early 1960s. Technological developments have resulted in CL becoming a sensitive and well-established technique that is used for prescreening tests.

A good example is the testing of polymer additives, for instance to investigate the effect of stabilizers on the oxidative degradation of polymers. In the food and pharmaceutical industries, CL is mostly used to obtain information about the stability of various products such as oils or fats. Such studies are of importance for the conservation of food and pharmaceutical products.

CL measurements can be made using highly sensitive CCD cameras that include sample imaging possibilities. This provides images of the light emission all over the sample. Such images can, for example, be used to visualize and quantitatively evaluate possible inhomogeneous distribution of stabilizers in a material with the aim of improving the manufacturing process.

Features and benefits

- **CL is very selective** – CL occurs only as a result of the oxidative decomposition reaction of the sample
- **CL is extremely sensitive** – measurements performed at lower temperatures are of greater practical relevance
- **High-pressure CL** – high pressures dramatically accelerate oxidative degradation and suppress vaporization
- **Unique imaging possibilities** – allow the initiation and propagation of oxidative degradation to be studied
- **Simultaneous CL and DSC measurements** – DSC provides complementary information on thermal effects such as glass transitions and melting
- **Modularity** – an HP DSC 1 or an HP DSC827^e can easily be upgraded to include CL capability

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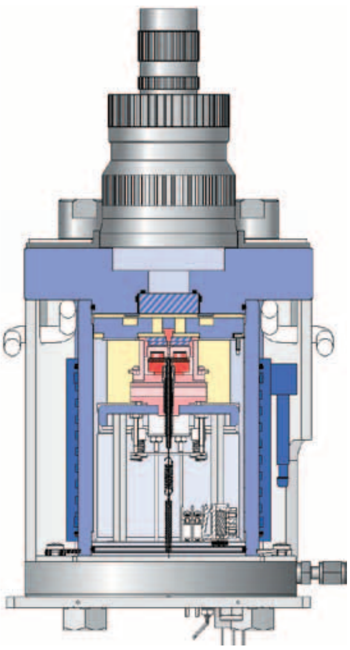
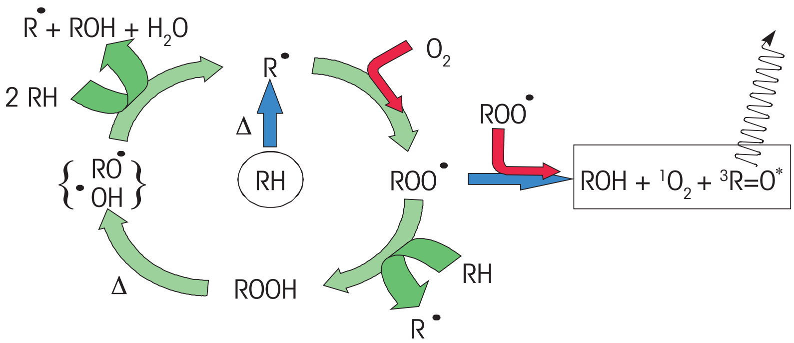
High-Pressure Measurements
Using DSC-Chemiluminescence

The high-pressure DSC-CL combination has the potential to replace the traditional time-consuming oven aging tests in the prescreening phase of novel polymer formulations. A good example is the determination of the oxidation induction time (OIT) or oxidation onset temperature (OOT), tests that are commonly performed in the petroleum industry. The major benefits of using an HP DSC for CL measurements is that oxidative degradation is accelerated as a result of increased temperature and pressure. The evaporation of volatiles is suppressed under the influence of a precisely controlled atmosphere around the sample.



Cross-section of the high-pressure DSC cell

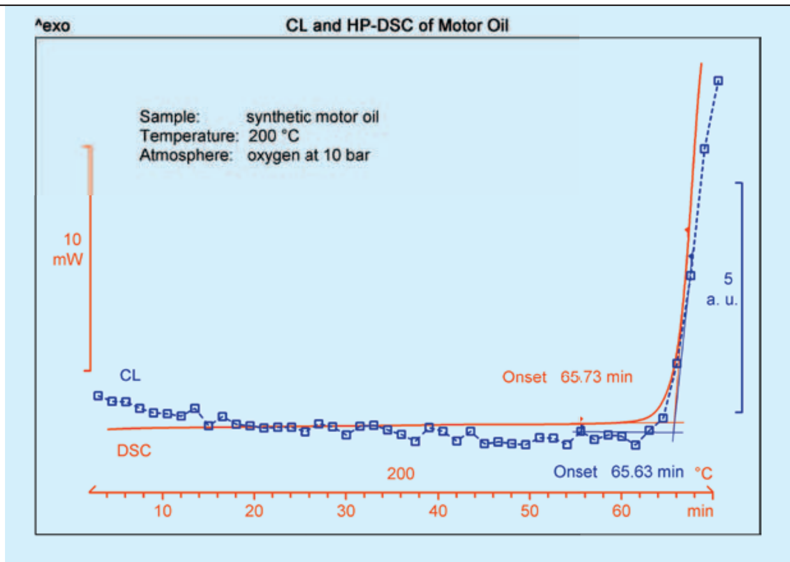
Background / Theory
A reaction scheme for autooxidation of hydrocarbon polymers is highlighted below. Oxidative degradation of hydrocarbon polymers occurs via a radical chain reaction that proceeds in the presence of oxygen. Key intermediates are hydroperoxides, which are always present as a result of oxidation during processing, or the influence of heat, light or mechanical stress on the material. Chemiluminescence is believed to arise from the phosphorescent relaxation of a carbonyl entity formed in a bimolecular termination reaction or by direct hydroperoxide decomposition.

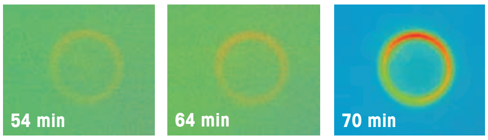


A simplified scheme for the autooxidation of an organic material involving a chemiluminescent termination reaction.

Industry	**Applications**
Plastics (elastomers, thermosets, thermoplastics)	• OIT and OOT, influence of additives on thermal stability
Food	• Stability of oils and fats • Conservation treatment of food products
Paints, lacquers, adhesives, coatings	• Stability • Determination of the gel point
Inorganic materials	• Age determination of sediments (thermoluminescence)
Petrochemistry	• Stability (OIT, OOT)
Pharmaceutical	• Stability

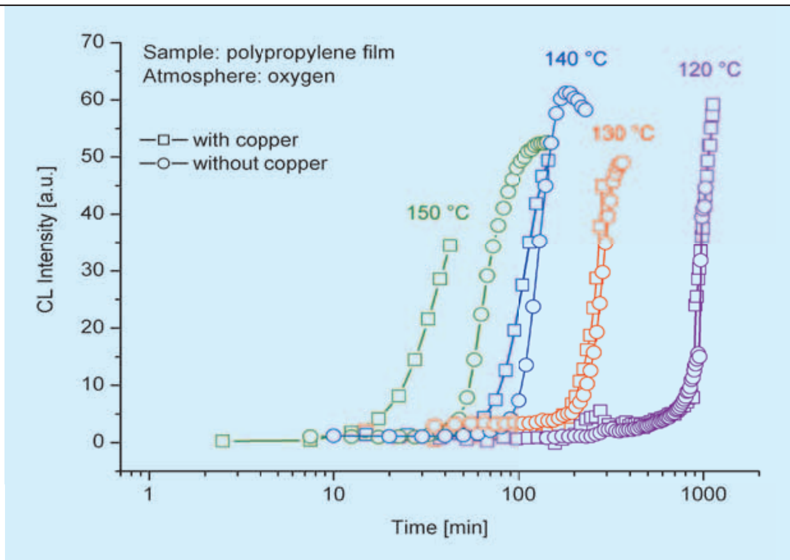
Application Examples

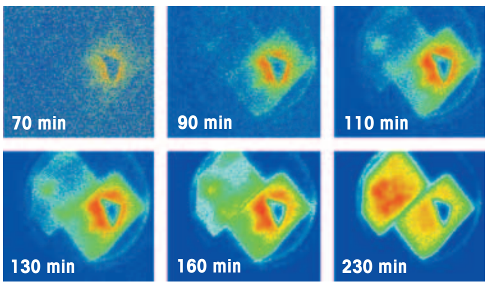




Isothermal OIT of a synthetic motor oil by chemiluminescence

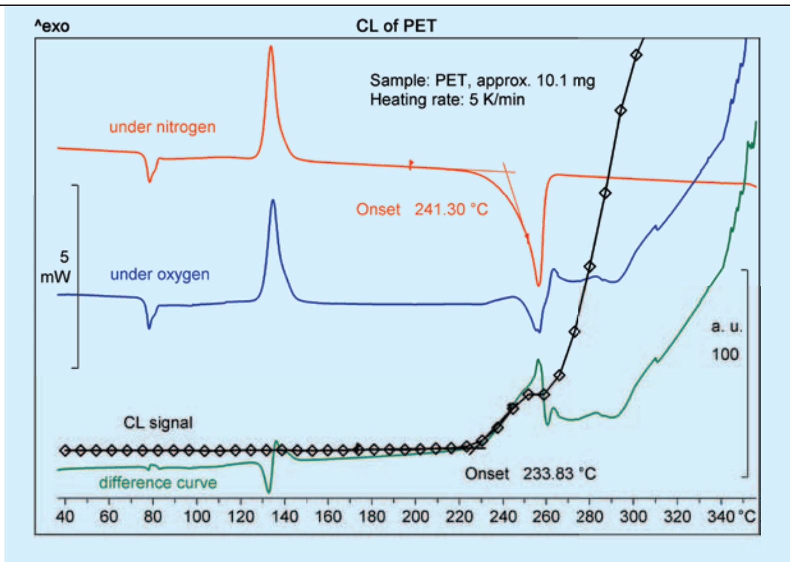
The determination of the oxidation stability of oils is an important test used in the petrochemical industry. It enables the behavior of an oil to be predicted under actual operating conditions such as in a motor vehicle engine. The diagram shows the DSC and CL measurement curves of a synthetic motor oil recorded simultaneously at a temperature of 200 °C at a pressure of 10 bar (1 MPa). Both curves show a steep increase after an induction time of about 66 minutes due to oxidation of the oil.
A DSC signal could not be detected prior to the induction time. However, the CL data shows that weak CL does in fact occur before the induction time, and can be easily detected from the beginning of the measurement. The presence of weak CL most likely indicates that the stabilizers are oxidatively degraded. Once the stabilizers have been fully consumed (after 66 min), the CL curve begins to increase in the same way as the DSC curve.
Due to surface tension effects, the oil and hence the CL are concentrated around the circumference of the crucible.

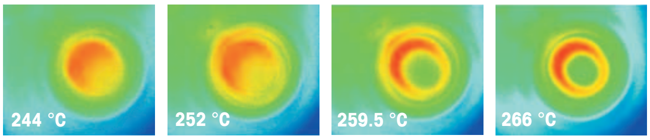




Chemiluminescence imaging of PP

The imaging properties of a CCD camera enable you to measure the chemilumiscence (CL) of several different samples simultaneously under the same conditions. This means that two samples, one considered to be "good", and the other "bad", can be compared at the same time in the same experiment.
In the example, the influence of copper on a polypropylene film (PP) at 140 °C under oxygen (50 mL/min) was investigated. The sample crucible contained two pieces of PP film of the same material. A small triangular piece of copper was placed on one of the films. The CL measurements show that the copper acts as a nucleus for decomposition: initially CL is observed only around the copper triangle. The second piece of film without copper only begins to decompose and exhibit CL after about 110 minutes. Quantitative evaluation of the images allows the CL intensity of both samples to be displayed as a function of time.





Dynamic OIT by chemiluminescence and DSC of PET

PET measured under nitrogen exhibits a glass transition, cold crystallization and finally melting. In oxygen, oxidation of the sample also occurs. The precise onset of oxidation is however difficult to determine because the DSC curve is the sum of several different effects. CL is however only observed when the sample oxidizes.

The CL intensity curve shows that the onset of oxidation is at about 234 °C, which is well before the sample has melted. The shoulder at about 250 °C in the CL curve is caused by the sample melting and "flowing", which affects the CL emission. This can be clearly seen in the CL images taken during the experiment. Before "flowing" occurs, the CL emission originates from all over the base area of the crucible. After melting, the sample, and hence the CL emission, are concentrated around the circumference of the crucible.

Image capture

The images shown in these examples were captured using analySIS® software from Olympus Soft Imaging Solutions GmbH. Packages including analySIS® software, a high aperture lens and a highly sensitive CCD camera are available from METTLER TOLEDO.

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