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Early Recognition of Oxidative Degradation in Polymers by Chemiluminescence

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SUMMARY: Most common polymers degrade readily during normal use by reaction with oxygen. Rapid screening tests are requested by industry to characterise the oxidative stability of the materials. The chemiluminescence (CL) method, which is based on the fact that oxidation reactions of most organic materials, including polymers, are accompanied by weak emission of light, has the potential for being such a test. Selected examples of CL measurements, in a commercially available instrumentation, on different kind of materials and material formulations (as used in industrial applications) clearly indicate that the CL technique is capable of determining the relative oxidative stability of polymers at very early stages of degradation.

Introduction

The major cause of degradation of most organic materials is oxidation. Oxidation occurs in the presence of oxygen under common environmental conditions during manufacturing and end use application, also at elevated temperatures and upon exposure to UV-light. Oxidation usually leads to negative changes in material properties. Oxidation stability is therefore of great importance both in processing and in the long-term application of polymeric materials. Consequently, the determination of the oxidation stability of materials is one of the most important objectives in the testing technology.

The continuously increasing lifetimes of modern, highly stabilised polymer systems brings challenges, in that real-life testing is not possible and accelerated methods are the only way of reducing test time. The commonest acceleration method is to raise the stress conditions (temperature, UV-light and others) to a point at which the lifetime is short enough to measure in a reasonable time. However, for various reasons, these measures have strong limitations. Thus there is still a great need for rapid screening tests. Chemiluminescence is one potential method for the early recognition of oxidative degradation.

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Chemiluminescence (CL) is defined as the production of light as a direct result of a chemical reaction. Although the first study of CL from polymer oxidation was already reported in 1961, this technique was not recognised as an important test method due to the low quantum yield of the CL reaction. Recent advances in detector technology have changed the situation.

It will be shown here that by means of the, in principle, simple and extremely sensitive CL-technique the oxidative degradation processes can be characterised at a very early stage under conditions approaching those in service, making it now a competitive technique for the characterisation of degradation and stabilisation of polymers and other oxidising materials. This will be demonstrated for selected examples of CL tests on polymers, especially of the application of the test method in industrial environments.

Chemiluminescence (CL) and Polymer Oxidation

Most common polymers degrade readily during normal use by reaction with oxygen. It is a generally accepted fact that oxidation reactions of most organic materials, including polymers, are accompanied by the weak emission of light.

The first degradation step in oxidation reactions is the formation of unstable alkyl radicals, which react immediately with the oxygen of the air to form peroxy radicals. These react further and are transformed into a variety of species in an accelerating degradation cycle (autooxidation). The luminescent reaction is believed to be the termination of two peroxy radicals in a "Russell mechanism" [1], which leads to an excited "triplet" carbonyl group emitting light when transition to the ground state happens. The spectral range of the emitted light varies with the polymer type but is generally in the ultraviolet and visible wavelength range (380 to 450 nm) [2].

Most recently, another theory has emerged into discussion to explain the origin of the formation and emission of photons. It is based on the concept of "Chemically Initiated Electron Exchange Luminescence (CIEEL)[3]".

Chemiluminescence of polymers was first observed in 1961 by Ashby[4]. The simplicity and extreme sensitivity of the CL technique in detecting oxidation reactions makes it a valuable tool for determining the extent and nature of thermal and photo-oxidation in polymers at very early stages and under conditions approaching those in service [2]. However, despite its sensitivity, chemiluminescence has not been widely accepted as an established method in an industrial environment. One reason is the low quantum yield of reactions evolving luminescence, which requires very sensitive and delicate photon counting instruments to measure the very low emission.

CL Instrumentation

All CL instruments used in polymer studies consist of a sensitive light sensor linked to an oven.

Recent advances in detector electronics, the development of new detector types and availability of commercial CL-instrumentation have culminated in the introduction of this technique in industrial applications as a competitive technique for the study of degradation and stabilisation of polymers and other oxidising materials.

The most common light detector is a very sensitive photomultiplier tube (PMT), used in the photon counting mode. In home-made instruments, slow scan charged coupled device cameras (CCD) have also been used recently[5,6].

Requirements for the oven are: variable and rapid heating rate, wide temperature range, good temperature stability (experiments are often carried out in isothermal mode), an automatic gas exchange facility (variable gas flow) and of course absolute light tightness of the system.

The commercial CL instrument [7] which was to be used here for the CL measurements is a multi-cell instrument with four completely independant test cells. Figure 1 shows the design of one measuring system (left hand: schematic view; right hand: one cell opened). The setup is kept as simple as possible. The material to be tested is placed on an aluminium sample holder in the sample cell in a laminar, weak nitrogen or oxygen flow, heated from the bottom and the cell is covered by a lens, focussing the light emitted from the sample to the PMT. The PMT is protected against to any extraneous light by an optical shutter located between the lens and the entrance of the photomultiplier. The highly sensitive water-cooled detector is sufficiently far away from the heating plate and additionally protected by a heat absorbing glass. The light and temperature signals are monitored, depending on preset testing conditions, and CL-curves may be analyzed automatically or manually during or after completion of the test.

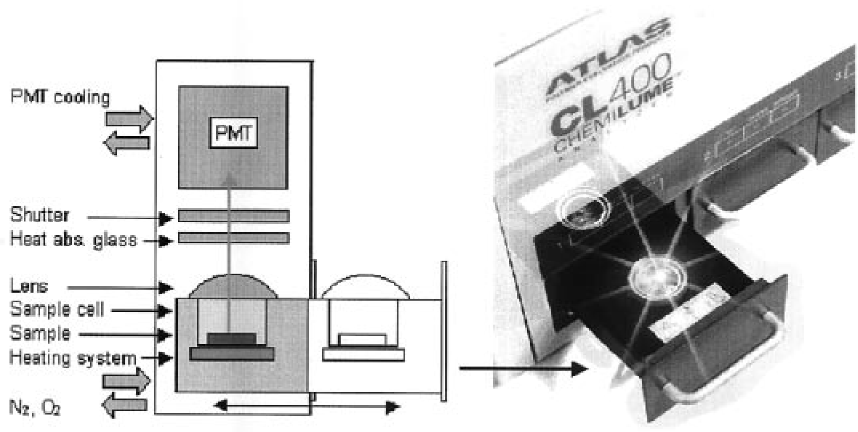

Fig. 1: Schematic view of one measuring CL system (left hand) and picture of the opened cell (right hand)

CL – Experimental Techniques

Essentially two testing procedures are used for measuring and evaluating the CL emission of samples. Most important is the measurement in an oxygen atmosphere at a given constant temperature (the sample is usually brought to the desired temperature in an inert gas before oxygen is admitted) and calculation (in most cases automatically) of the Oxidation Induction Time (OIT) – analogous to the OIT calculation of DSC measurements. The second procedure is the measurement of the Cl emission at increasing temperature in an inert gas flow (e.g. nitrogen).

In principle, the former method can both be applied to follow an oxidative degradation process in-situ by the CL experiment itself (thermooxidation) or to expose a material system to be investigated for temperature, UV light or other stresses first and then to estimate the existing degradation as "residual resistance to oxidation" afterwards, by means of CL. The second method may be used directly to measure oxidation products which have emerged from an earlier degradation reaction in the polymer. The integration of the CL signal over the time is then a measure of the amount of oxidation products that were present before the CL experiment commenced, and therefore characterises the degree of deterioration of the material.

As standardized testing procedures do not yet exist in the field of CL measurements, testing procedures must be carefully established for the various individual industrial applications. It is noted that the CL – technique is under discussion in ISO/TC 35, for paints and varnishes, to be standardized as an analytical test method in this field, and similar activities for testing of polymers have commenced at ASTM.

A typical CL-signal vs. time characteristic, as measured under isothermal conditions in oxygen, is shown in Figure 2 (polypropylene sample stabilized at 150 °C).

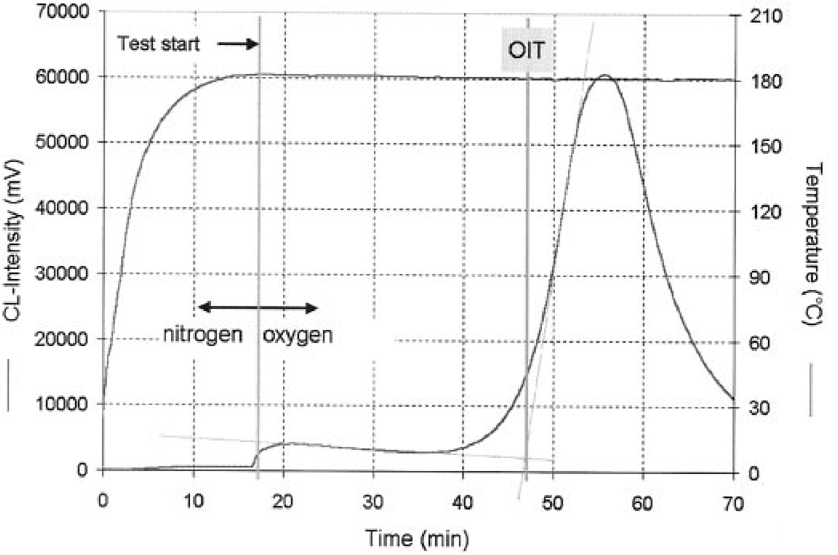

Fig. 2: CL intensity of a polypropylene film as a function of test time (stabilised, isothermal mode - 180 °C); determination of Oxidation Induction Time (OIT); OIT = 30,5 min

The test, carried out under isothermal conditions starts with a „pretest phase“ during which the sample is brought to temperature, usually under an inert atmosphere (e.g. nitrogen). After reaching the preset temperature the gas flow is automatically switched to oxygen. Regarding the case of a stabilised sample, peroxy radicals are efficiently trapped by the antioxidant in the induction period and the CL signal is on a low level.

Once the antioxidant is consumed, the autoacceleration of the oxidation causes the radical concentration to increase, resulting in an increased rate of termination and a rapidly increasing CL intensity. Besides various theoretically available analysis data, the "Oxidation Induction Time (OIT)", especially can easily be determined from this characteristic. The OIT characterises the relative oxidative stability of the material formulation tested.

Specific experimental factors have been taken into account when running CL-measurements [7]. The above described "isothermal mode" of CL experiments is the strategy that will be followed in this paper.

Determination of Thermal Oxidative Stability by CL

The emission rate of most polymers at near ambient temperature is generally too low to be detected and therefore samples are tested at elevated temperatures to increase the emission. But care has to be taken that this measurement does not lead to effects that may cause degradation processes not occuring in end-use environments.

Figure 3 shows typical isothermal CL curves of a PP film (low content of sterically-hindered phenolic antioxidant), oxidised at different temperatures in the molten and

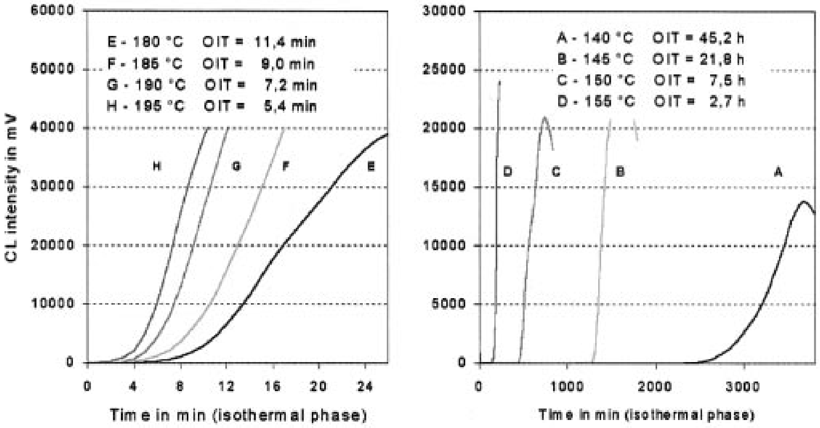

Fig. 3: Isothermal CL tests on a PP film at different temperatures; molten state - examples (left hand), solid state – examples (right hand)

solid state of the material. The rise in temperature systematically shortens the OIT (Figure 4, left hand). The Arrhenius diagram (Figure 4, right hand) clearly indicates the different oxidation mechanisms in the molten and solid state of the material. CL measurements in the molten state may be used to evaluate the processing oxidative stability but, since both the degradation kinetics and the distribution of the additives in the molten polymer are completely different from those of the solid material, conclusions regarding the thermooxidative stability of polymers drawn from measurements above the melting point (usually performed with the DSC method) are often misleading with respect to their long term performance in end use environments.

Nevertheless, because of the high sensitivity of the CL method it is possible to make measurements in the solid state at lower temperatures, closer to real degradation conditions. The approximately linear relationship in the Arrhenius diagram of the PP sample in solid state indicates that the OIT data can be used to predict the inherent stability of the material, with the potential of limited extrapolation to still lower temperatures.

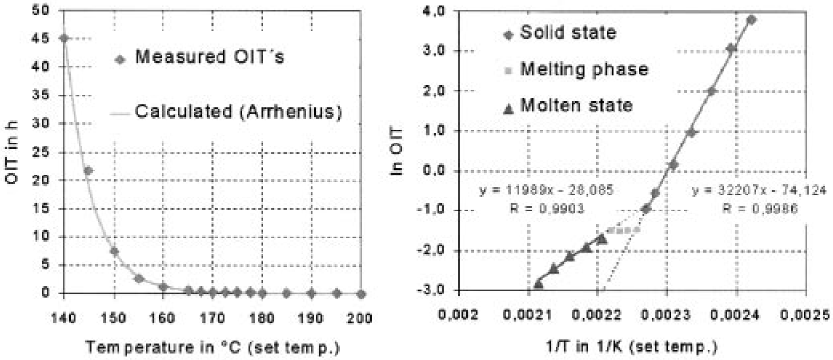

Fig. 4: CL isothermal tests (see Figure 3) - OITs vs. temperature; Arrhenius diagram (right hand)

The OIT data from CL measurements can also be used to assess the efficiency of stabilisers in material formulations[8]. One example of isothermal measurements on four differently stabilised (details unknown) rubber materials (EPDM), where DSC measurements failed in accurately evaluating the material stability at 200 °C, is shown in Figure 5. The CL measurements (OIT data) clearly characterise in a short term test the different relative thermooxidative stabilities of the investigated material formulations resulting in the same ranking as experienced in practice.

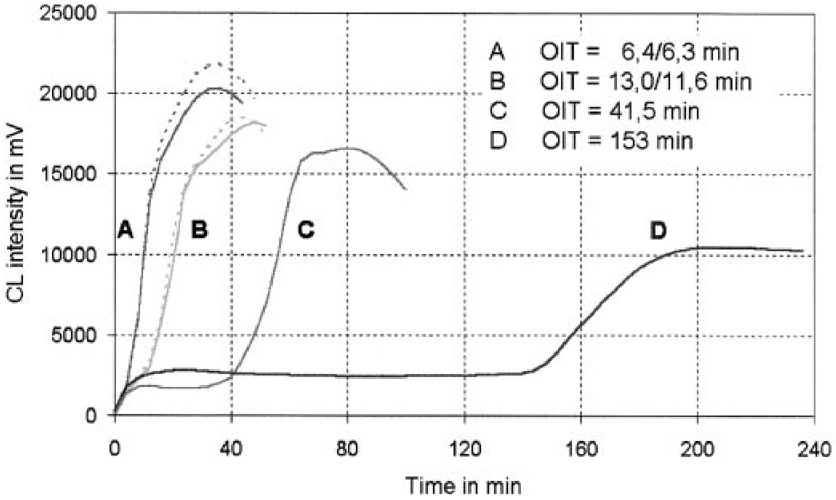

Fig. 5: CL tests (200 °C, isothermal phase, oxygen) on rubber materials (EPDM), differently stabilised (A to D)

Traditionally the study of antioxidant stability on long-term heat aging is usually performed in air ovens at elevated temperature. Oven aging is considered as standard method but it suffers on many drawbacks. Such tests are very time consuming and the results can be affected by interactions between different material formulations exposed simultaneously in the same oven environment [9]. Alternative test methods which especially provide information on the relative oxidative stability in a short time space are therefore of great interest.

Results of a comparitive study of CL – OIT vs. oven ageing time on PP with different additive concentrations have shown good correlation, for phenolic additive systems, in shorter test times (using the CL technique) [10].

Oven aging tests, especially on polymer fibers, are generally difficult to perform. The CL measurement is one method with the potential for determining the oxidative stability of fiber materials. An example hereof is as follows:

CL measurements on three differently stabilised PP fiber types (details unknown) in isothermal mode (150 °C) were compared to oven aging (130 °C, 50 % residual tensile strength – tests conducted by the supplier of the fibers). Results are shown in Table 1.

Table 1: CL isothermal tests (150 °C, oxygen) on PP fibers, differently stabilised (A to C); OITs compared to results of oven ageing (130 °C); influence of spin preparation (SPP) on OIT

Method	Oven ageing (hours)	CL – OIT (hours)	
Temperature	130 °C [a)]	150 °C	
PP Fiber	With SPP	With SPP	Without SPP
A	750 ± 150	6,7/7,1	27,4/28,2
B	1300	18,9/19,6	39,8/42,5
C	3250	48,2/46,6	71,5/74,2

[a)] 50 % residual tensile strength

The ranking of the materials based on the OITs determined from tests in isothermal mode at 150 °C equals the ranking of the samples from the oven tests at 130°C, thus confirming the already existing experiences, but reducing the test time to a fraction of that needed for the latter (Table 1).

It is known that CL is capable of detecting the impact of the spin temperature on the long term thermooxidative stability of PP fibers [8]. Polymer fibers are normally treated with a spin preparation agent for material processing. The supposed influence of this spin preparation on the thermooxidative stability of polypropylene fibers can also be investigated by CL. Results of tests on fibers where the spin preparation was removed (by cold extraction in isopropanol and desiccation at 40°C under vacuum) show that the

OITs of the fibers without spin preparation are evenly extended, compared to the values with spin preparation (Table 1 and Figure 6). This indicates that the spin preparation significantly reduces the oxidative stability of the PP-fibers.

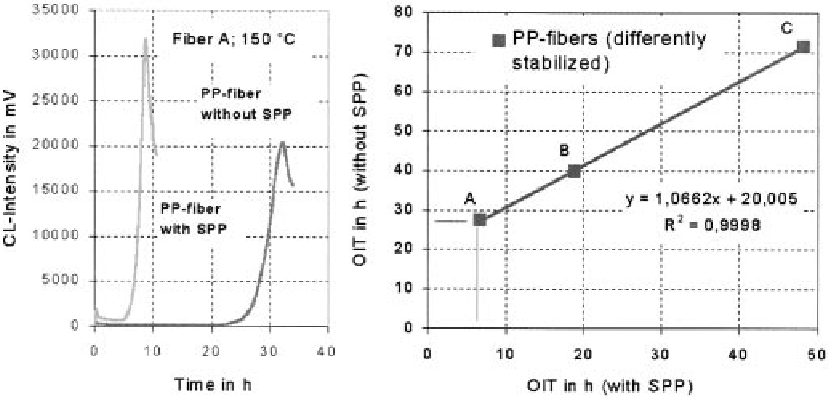

Fig. 6: PP fibers (A, B and C) – influence of spin preparation on the OIT (left hand: example fiber A)

Based on the results of these CL short-term tests, the treatment of the PP-fibers may be optimized to ensure industrial processing on the one hand, and long term thermooxidative stability on the other hand.

Determination of Photo-oxidative Stability by CL

Polymer oxidation takes place not only at elevated temperatures but also upon exposure to UV light (e.g. sunlight outdoors). Required lifetimes of polymers may be between some days or weeks (e.g. packaging films) up to decades (e.g. roofing films).

Lifetime investigations of packaging films which may only temporarily be stored outdoors are not really time consuming but very often a quick answer as to whether the quality of a delivered material is adequate or not is needed. In those cases, specific analytical test methods should have the potential to give an answer. CL measurements may have this capability, as shown in the following example.

Specific extruded tubular polyethylene films are used e.g. for packaging polymeric granulates. Usually the material is composed of 80% LDPE and 20% LLDPE with white masterbatch (TiO_2). Normally the material is sufficiently resistant to oxidation without UV-stabilizer. But sometimes it may happen that some percentage of regenerated LDPE is added which may reduce the oxidative stability of the material, resulting in material failure.

Tests on three different delivered new films have shown that material failures (e.g. embrittlement) occuring in practice (storage of packed granulates outdoors) could not be predicted by IR-spectroscopy but a clear effect was detected after storage of the films outdoors until macroscopic failure occured (Table 2).

Table 2: Oxidative stability of PE packing films, as determined by IR spectroscopy and CL tests

Method	IR spectroscopy		CL – OIT in hours	
	Carbonyl peak (1736,45 cm^{-1})		120 °C	150 °C
Material	New	Exposed	New	
1	none	high	85	6,8
2	none	mean	148	8,9
3	none	mean	> 160	10,4

Respective CL-tests were carried out on the above three new PE-films under isothermal conditions at 120°C. The calculated OITs (Table 2) clearly indicate differences in the resistances to the tested films oxidation (especially film 1). The CL-test results correspond to the results from IR-spectroscopy after exposure of the films to sunlight and to the respective experiences in practice.

The already considerable CL testing time at 120 °C can significantly be reduced by increasing the test temperature e.g. to 150 °C (Table 1 and Figure 7) without changing the ranking of the materials.

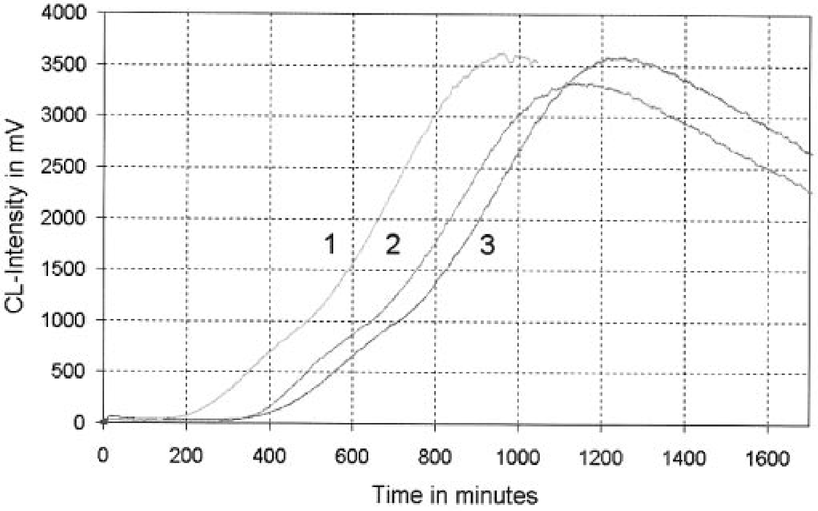

Fig. 7: Results of CL tests (150°C, isothermal phase, oxygen) of three different PE packing films

The useful life of highly stabilised polymeric materials which are used for sealing purposes on roofs has continuously increased in recent years. This means that using conventional accelerated test methods (e.g. testing in weathering instruments), long testing periods of at least several thousand hours may be necessary for detecting changes in application-relevant material properties and for predicting the lifetimes of these materials.

Based on those long term stabilities even CL-measurements may need considerable but still „short“ testing times, compared to the experimental approach mentioned above. Cl-tests on a special highly-stabilised polyolefin material system (detailed data are not available) may serve as an example. The results of tests carried out under isothermal conditions (Figure 8) show a high OIT even at 160 °C for the new material. The significantly reduced OIT measured after 10 years outdoor exposure clearly signifies an ageing effect caused by the environmental conditions but the still high OIT-value indicates a remarkable residual oxidative stability of this material system, thus confirming the fact that the foil is still in practical use without any failure.

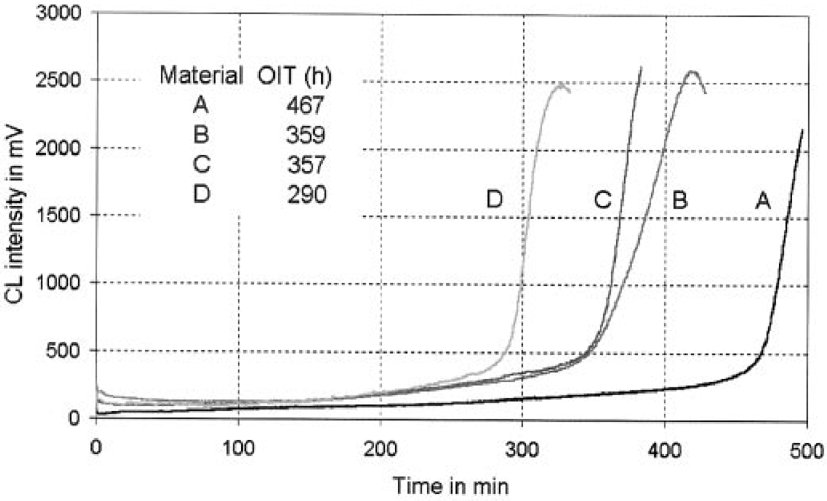

Fig. 8: CL tests (160 °C, isothermal, oxygen) of polyolefin sealing material (A – new, B/C - <10 years outdoor exposure, D – 10 years outdoor exposure)

Conclusions

The recent advances in detector electronics, development of new detector types and availability of commercial instrumentation formed the basis for an, in principle, simple but extremely sensitive technique for measuring the low amounts of light emitted from oxidising polymeric materials.

Selected examples of CL measurements under isothermal conditions on different kind of materials and material formulations clearly indicate the potential of the CL technique to be a valuable tool

- for determining the extent and nature of thermal- and photoinduced oxidation processes in polymers at very early stages and under conditions approaching those in service, and

- to provide valuable informations on where other conventional test methods may fail and/or suffer from various drawbacks.

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