

Combining Artificial Weathering With Chemiluminescence For Lifetime Predictions Of Polymeric Materials

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Summary: While artificial weathering is a long established tool to investigate long-term behaviour of polymers at outdoor conditions the use of chemiluminescence as a highly sensitive and broadly applicable sensor for the effected change is a recent addition. This combination of artificial weathering with chemiluminescence could already be successfully applied to differentiate and evaluate long-term stability of various real use polymeric building materials relatively to each other and promises to be a useful tool for a variety of other polymeric materials as well.

Keywords. Chemiluminescence, lifetime assessment, weathering, polymer.

1 INTRODUCTION

Artificial weathering testing aims at simulating natural weathering at accelerating conditions. To achieve this acceleration either weathering parameters like temperature or UV irradiance are increased above the mean or time compressed cycling is applied in order to repeat stressing periods more frequently than less stressing ones. For a comparison of different materials artificial weathering typically is conducted until a change in a macroscopic parameter like tensile strength, colour, or gloss is observed. The dilemma consists in the goal to achieve information on weathering stability in ever shorter exposure periods on the one hand and still to achieve scalable results to the conditions to be described on the other, with the danger to activate completely different reaction paths and resulting completely different product rankings always at stake.

One way out of this dilemma are more sensitive sensors to detect the changes caused by the weathering, hence allowing a shortening of the preceding weathering duration. A detection mechanism on molecular level will allow accessing changes at the earliest stages of the degradation. Established techniques such as FTIR or NMR also already access this level, but additionally a higher sensitivity of the probing technique is required to detect very few molecules. These requirements are met by chemiluminescence. Compared to for instance FTIR at least two to three orders of magnitude in sensitivity can be gained by using chemiluminescence as the detector for change.

Coming back to the material to be investigated, polymers, in order to explain the molecular detection mechanisms, the question pursued for most outdoor applications is the long-term stability at outdoor conditions.

1.1 Degradation mechanism in polymers

Most polymers are liable to oxidation, both photo- and thermo-oxidation principally, but photo-oxidation at least is more damaging for temperatures within the solid state of the polymer. UV radiation can cause the polymeric backbone to be broken up; an initial bond is opened and radicals form on both sides of the fracture. These can either react with themselves or with oxygen. Once initiated the auto-catalytic oxidation process can start to infect the whole material, chains are broken down in ever smaller pieces (or, depending on conditions, also crosslinks can be formed), with ever higher oxidation states; the final state would be carbon dioxide and water. Macroscopically the material loses its toughness and becomes brittle.

As polymers with sufficiently high photo-oxidative stability from an intrinsic protecting chemistry would be extremely expensive, mostly the approach to blend photo-absorbers and stabilizers in sub-percent weight ratios into the polymeric material is been taken. To investigate the long-term outdoor performance of a polymer on molecular level is the question of its stabilisation against this exposure. This stabilisation finally is the result of the interaction of the polymer-stabilizer system

1.2 Detection of degradation with chemiluminescence

Chemiluminescence links the rate of the molecular oxidation reaction with a macroscopically detectable emission of light (Ashby (1961), Schard & Russel (1964a), George (1981), Billingham et al. (1988), Matisová-Rychlá. & Rychlý (2000)).

The macroscopically detectable flux of photons, I , is linked to the oxidation reaction with a rate Φ that is going on at molecular level by the following equation

$$I = G \Phi n$$

which uses G ($0 \leq G \leq 1$) as a constant that incorporates all factors influencing the detection efficiency for photons being emitted, and F ($0 \leq F \leq 1$), which is the overall quantum efficiency of the reaction, defined as the ratio of actually emitted photons per number of potentially reacting particles. This quantum efficiency for chemiluminescence typically is very low, 10^{-3} up to 10^{-8} . It still is possible to detect the weak emission of light through the sensitive detection by single photon counting (G close to a value of 1) and the fact that the photon flux increases linearly with the number of reactive particles. The difficulty to determine the respective quantum yield of a system under evaluation (every slight change in the composition spells a new system) means that chemiluminescence results are not absolute but usually are used relative to rank the performance in residual stabilisation of different materials.

Most undesired irreversible ageing processes in polymers are connected to oxidation. At least for polyolefins this is via the so-called free radical autooxidation mechanism (Scott (1965); Ranby & Rabek (1975); Kamiya and Niki (1978); Stivala et al. (1983); Al-Malalaika (1993)). It allows chemiluminescence to be very widely applied for lifetime assessments (Ashby (1962), Schard & Russel (1964b), Kron 1996, Kohler & Kröhnke (1999), Schartel et al. (1999)). Also, as it is directly linked to the oxidation reaction, it gives a more direct evaluation of the residual stabilization of the polymer than other techniques that often only allow to access a value as result (such as molecular weight, carbonyl index...) the functional relationship of which to the stabilization first having to be assessed.

While the degradative changes effected by the weathering in the polymer mostly are photochemical or photo-oxidative in nature, the investigation of residual stabilisation with chemiluminescence is thermo-oxidative. However, this procedure can be justified, as radicals are the common intermediate for these mechanisms and because radicals are the particular species dealt with by the stabilizer.

The chemiluminescence assessment following the weathering exposure is applied to determine the amount of effective stabilization still active in the polymer. The experiment also could be carried out combining exposure and determination of residual stabilisation in just one chemiluminescence run but this bears various severe disadvantages. Therefore, the first variant was applied.

Examples are presented of relative lifetime assessments for polyethylene films used as greenhouse coverings that were exposed to outdoor weathering conditions under the influence of different stabilizers and of varied weathering conditions.

1.3 The material investigated

Agricultural films for greenhouses mostly consist of LDPE films stabilized with HALS (*Hindered Amine Light Stabilizer*). The main purpose is to protect the growing crop in the greenhouse against pests and fungi and to ensure environmental parameters for optimal growing conditions. While at usual outdoor conditions the HALS stabilizer would provide sufficient protection against degradation caused by UV irradiation, in the case of greenhouse films lifetimes are remarkably reduced and far below demands. With hundreds of thousands of tons of greenhouse films being used all over the world, a majority of these only survive one vegetation period before it is likely to fail and is dumped. The degradation mainly consists in an embrittlement of the material at the exposure conditions that causes the material to structurally fail, which then means to the crops in the greenhouse that they are no longer protected. The shortening of lifetimes compared to other uses of the polymer mainly is due to an additional chemical exposure, that has to be taken into account in the form of agrochemicals being used within the greenhouse, as functionalising chemical agents within the film material itself, or as acid rain from external emittents. The widespread heavy use of agrochemicals comprises the burning of sulphur leading up to the formation of sulphur dioxide, which readily oxidises to sulphuric acid, H_2SO_4 . At the conditions prevailing within the greenhouse the initially diluted acid that forms within condensation dew droplets can concentrate (H_2SO_4 only has negligible vapour pressure) to result in highly damaging acid. In this concentrated form, the acid can both attack the polymer itself and the stabilizer system.

1.4 The actual measurement program

In this study a specially modified artificial weathering test, the 'Acid Dew and Fog Test' (Schulz et al. (1999)), ADF test, was applied to simulate the climatic conditions of greenhouse films at accelerated conditions and with special consideration of the acid deposition. Subsequently chemiluminescence was used to characterise changes effected by this exposure and to rank different polymer / stabilizer systems according to their residual stability.

2 EXPERIMENTAL

All measurements were done in BAM, the Federal Institute for Materials Research and Testing, Berlin, Germany.

2.1 Weathering

2.1.1 Equipment

Artificial weathering was carried out in a commercially available weathering device, which is equipped with fluorescent lamps (Weiss Umwelttechnik, Germany; type 'Global UV Test'). Spectral irradiance was according to ISO 4892-3: 1994 (with no UV output below the normal solar cut-off of 290 nm). The set of UV lamps used to simulate the desired shape of the spectral distribution provides an UV irradiance of 45 W / m^2 in the range 290 to 400 nm. The 'Global UV Test' device allows running the test at defined, reproducible weathering conditions. Temperature is held constant within $\pm 1 \text{ K}$ and relative humidity within $\pm 5 \text{ \%RH}$.

2.1.2 Test conditions

The 24h ADF weathering cycle comprises:

- a 14 h dry period at varying climatic conditions (9 h at $35 \text{ }^\circ\text{C}$ and 30 \% RH followed by 5 h at $60 \text{ }^\circ\text{C}$ and 5 \%RH),
- a 4 h rain period (demineralized water at $35 \text{ }^\circ\text{C}$) at $60 \text{ }^\circ\text{C}$ and 5 \%RH , and
- a second 6 h dry period at $35 \text{ }^\circ\text{C}$ and 30 \% RH .

Five out of seven cycles per week are started with a short-term spraying of a dilute (pH1,5) acid mixture of H_2SO_4 , HNO_3 and HCl in the weight ratio 1 : 0,3 : 0,17 and a pH of 1,5 (resulting in about 3 mg acid solution per cm^2 of exposed specimen surface).

To assess the contribution of the acid deposition to the extent of photo-ageing acid free weathering was performed additionally. The cycles of the acid free weathering only differ from the ADF cycles described above in that the acid spraying was dropped.

2.2 Chemiluminescence measurements

2.2.1 Equipment

The Chemiluminescence set-up used consists of a own-build heating sample chamber and commercial equipment for the single photon counting detection of emitted photons.

Heating is done electrically, controlled by a Lake Shore (Westerville, OH, USA) 340 temperature controller. This is done within an own-build sample chamber that has a gas inlet and outlet, the sample in its middle, and a quartz window on its top connecting it to a photomultiplier.

An outer, gas tight, stainless steel chamber contains a gas inlet in its bottom. From there the gas from outside first is fed through a chamber filled with steel wool that is situated below a heater and serves to pre-heat inflowing gas. Within the outer chamber, a ceramic inner part is placed, which is thermally insulated from the outer stainless steel part but is connected with it via the gas inlet. Within this inner chamber a pack of resistors is used to heat (room temperature up to 490 K) a removable aluminium pan of 25 mm in diameter from below. Also a PT100 resistor is placed on the bottom of the aluminium pan to measure the temperature that is further processed by the temperature controller and read out from there by a PC. The cover of the inner ceramic chamber consists of a ceramic cover, which can be screwed onto the body of the inner chamber and which incorporates a quartz window in its middle. The quartz window has a hole in its middle to allow the gas to flow outwards. A spring, which is squeezed by the quartz window cover from above, presses the sample close to the aluminium pan. The outer chamber is covered by a removable stainless steel plate that contains another quartz window in its centre (no hole). The gas outlet is below the cover. The cover again is connected as shortly as possible to the housing of a side-on low-noise photomultiplier tube (HAMAMATSU, Herrsching, Germany, Type R1527P select) which is to ensure a maximum in geometrical detection efficiency.

All materials used for the chamber (especially those in 'view' of the photomultiplier) were tested before to be as low emissive in terms of photons released at the temperatures applied as possible.

The signal of the photomultiplier tube is processed by an Perkin Elmer / EG&G/ ORTEC (Oak Ridge, TN, USA) single photon counting device consisting of pre-amplifier VT120C, discriminator 935 and counter 994.

The ORTEC counter and the Lake Shore temperature controller are connected via an IEEE bus to a PC that uses an own programmed Turbo Pascal software to read out and to control.

2.2.2 Measurement Parameters

Before each measurement of a sample, a blank measurement was carried out with all parameters and the entire set-up as in the actual measurement only without sample on the aluminium pan. The obtained background intensities never exceeded limits that would make it necessary to use them to correct the actual sample measurement. However, this procedure mainly was used to ensure that inner part of the cell did not show any contamination from preceding measurements.

The heating program for all measurements presented consisted of 5 min at room temperature to determine the dark rate, then under constant flow of nitrogen heat-up to 172°C (445 K) at a rate of 5 K /min. After the maximum temperature was reached the gas flow was switched to compressed air and temperature was held constant within less than ± 0.1 K error. The investigation temperature is above the melting point of the PE-LD.

Registration of photons is done as integral emission without spectral resolution. The spectral characteristics exclusively are determined by the photomultiplier (within the UV/VIS range of concern to this discussion). The two quartz windows in the light path only show a negligible influence on the spectral transmission behaviour. A postulated emission of singlet oxygen in the NIR region in the course of the oxidation would already be beyond the spectral sensitivity of the PMT used.

Registration of photon rates was carried out continuously (gate time 1 s); count rates were accumulated to a constant integration time of 4 min for each measurement point.

2.3 Other Measurements

2.3.1 Tensile Tests

These tests were carried out using a Monsanto T2000 tensometer. Tests were carried out in adaptation of the DIN 53504 standard; tension speed was 100 mm/min. For each measurement five samples were tested. Only the orientation parallel to the direction of extrusion was tested.

2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

A Nicolet FTIR spectrometer, NICOLET NEXUS FTIR, (Nicolet, Madison WI, USA) was used. Measurements were done in direct transmission mode. Spectral resolution was 4 cm^{-1} . For background and sample measurements always 32 scans were recorded. The baseline was smoothed and CO_2 and H_2O bands removed by subtraction of the blank spectrum.

A FTIR spectrum of Hostavin N30 shown in 'Fig. 3' was measured in Tetrachloro methane. To match it with the actual peak position of the stabilizer in polyethylene a comparison of unexposed polyethylene with high stabilizer concentration showed that it had to be shifted by 7 cm^{-1} .

2.4 Materials

The material used as an example to compare traditional detectors of the change with chemiluminescence is a polymer, PE-LD, that is stabilized against photo-oxidation with a HALS. Different of these stabilizers blended into the same polymer are to be compared in terms of their protective effect to the polymer. It is to be used as protective cover of greenhouses, typically in Mediterranean countries.

A PE-LD (low density polyethylene) film of $200\text{ }\mu\text{m}$ thickness ($\pm 10\%$) for use as agricultural films was investigated, containing 0,2% and 0,4% of stabilizers, respectively. Two different HALS materials were compared within the PE: Hostavin N30 and Chimasorb 119. The film was especially prepared not to contain other additives.

The material was characterised using differential scanning calorimetry (DSC), UV/VIS and FTIR spectroscopy.

Material exposed to the ADF weathering without acid will be labelled 'w', that one exposed to the ADF test including acid will be labelled 'a', unexposed material 'u'.

3 RESULTS AND DISCUSSION

In order to show why a sophisticated technique as chemiluminescence could be useful firstly it shall be explained what shortcomings the traditional techniques, like tensile test of FTIR spectroscopy, suffer from. Therefore, in the following a preceding weathering on the same samples was to be compared with different detection techniques.

3.1 Detection through Tensile Tests

The property of practical importance is the toughness of the polyethylene greenhouse films. The technical property to test for changes effected by the weathering exposure therefore used to be the elongation at break tested in a tensometer after the weathering.

Examples of tensile tests of the material are depicted in 'Fig. 1' for different concentrations of the stabilizer Hostavin N30 in PE-LD and in 'Fig. 2' as comparison of the performance of Hostavin N30 with Chimasorb 119.

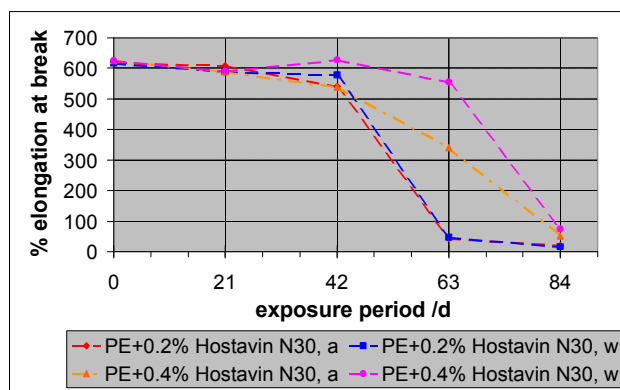


Figure 1. Tensile test of LDPE with 0,2 and 0,4 % Hostavin N30 stabilizer after 0, 21, 42, 63, and 84 days of artificial weathering without ('w') and with ('a') acid precipitation

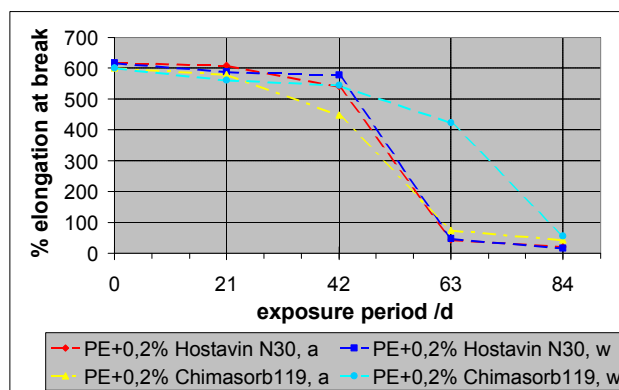


Figure 2. Tensile test of LDPE with 0,2 % Hostavin N30 and Chimasorb 119 stabilizer after 0, 21, 42, 63, and 84 days of artificial weathering with-out ('w') and with ('a') acid pre-cipitation

The results can be summarised as follows:

- The results of tensile measurements show a comparatively high measurement uncertainty.
- In terms of exposure with and without acid precipitation ('Fig.1') 0,2 % Hostavin N30 does not show a difference, while the difference for 0,4 % becomes quite remarkable. Acid precipitation causes a deterioration of the tensile behaviour.
- A differentiation between the two stabilizers ('Fig. 2) grows after 21 days of weathering, reaches a maximum after 63 days and is gone again at 84 days.
- The performance of Chimasorb 119 already is at 0,2 % about the same as that one of Hostavin N30 at 0,4 % ('Fig. 2').

This allows the following conclusions to be drawn:

- In terms of testing: Samples have to be taken and tested after 21, 42, 63 and 84 days if tensile tests are to be used as sensor for the effect of weathering on polyethylene. In this case, only the measurement window between 42 and 63 days could be used to make a differentiation. The bad signal/noise ratio for the measurement of low values of elongation at break as occurring for high duration of weathering give tensile tests a high degree of uncertainty in the evaluation of different samples.

In terms of degradation mechanism:

- Degradation starts to show macroscopic effects after an induction period of about 21 days, increases and reaches saturation and an end value after 84 days of weathering.
- The fact that for Hostavin N30 a differentiation in response to acid precipitation compared to weathering without acid only shows for the higher stabilizer concentration could mean that 0,2 % of the stabilizer are not enough to leave effective stabilizer protecting the polymer after 21 days. If there is enough stabilizer remaining in the polymer (as for the case 0,4 %) it is liable to acid attack. Also, the occurrence of differentiation for 0,4% might be a hint to an increased stabilizer liability to acid attack.

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3.2 FTIR detection

'Figure 3' summarises the results of weathering with ('a') and without ('w') acid precipitation for 21 and 42 days for the system PE-LD and Hostavin N30 as detected by FTIR.

The results of the FTIR analysis can be characterised as follows:

- Oxidation can be detected as an increase of the broad carbonyl band in the region $1680 - 1820 \text{ cm}^{-1}$.
- A competing, neighbouring band $1680 - 1720 \text{ cm}^{-1}$ owing to the stabilizer 100% 'Hostavin N30' curve compared to 0% for PE unexposed without stabilizer ('unstab., 0d_u') is so much dominated by the PE oxidation band that it can not be used to determine the concentration of the stabilizer.
- The increase in the carbonyl band is not linear with duration of weathering. It rather exhibits an induction time of between 16 days (still stabilizer, hardly carbonyl) and 21 days (first carbonyl). From then on it rises and shows a considerable differentiation between much more deteriorating acid exposure compared to weathering without acid precipitation.
- A broad range of different oxidised species produces a varying distribution of the resulting peak in the carbonyl region ('Fig.3', 42d_a curve compared to 42d_w curve), which makes comparisons difficult.

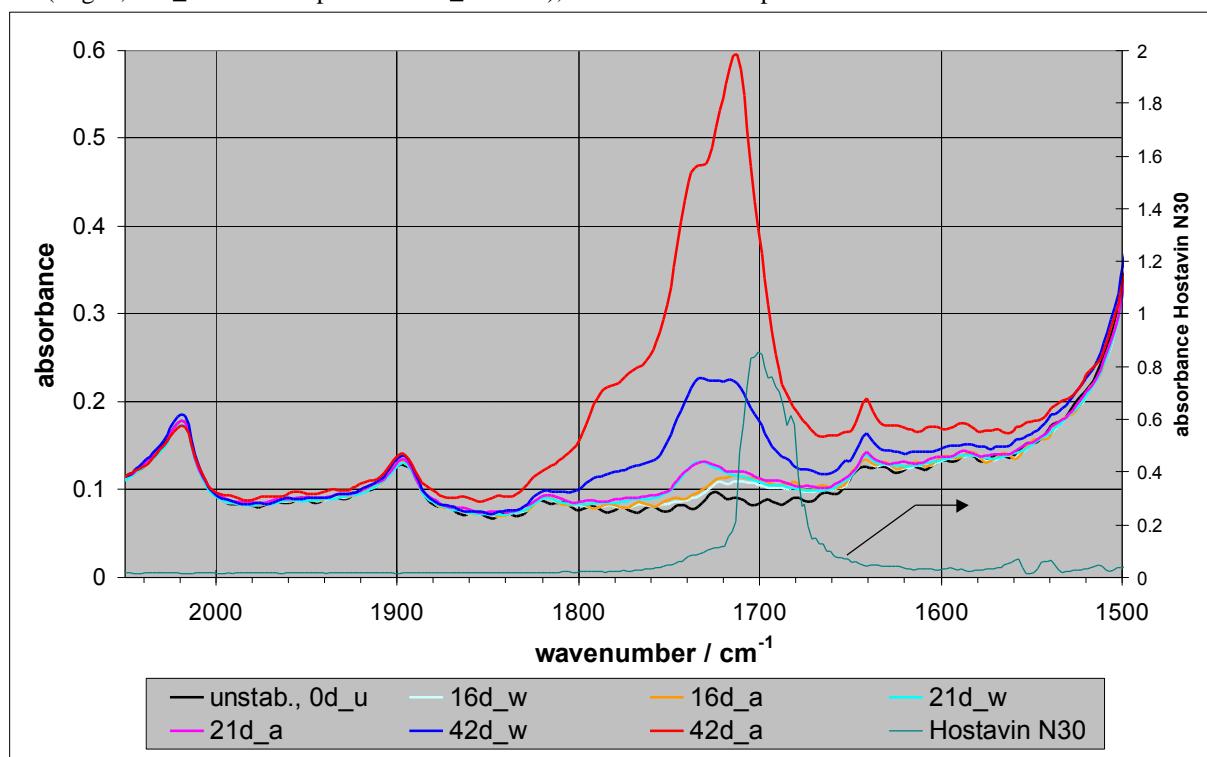


Figure 3. FTIR analysis of the effects of artificial ADF weathering for 16, 21 and 42 days on a LDPE film stabilized with 0,2 % Hostavin N30 and pure Hostavin N30 ('Hostavin N30') as well as unstabilized unexposed material ('unstab., 0d_u') as comparison. Labelling: days of weathering, followed by mode of weathering ('u' = unexposed, 'w' = ADF without acid, a = ADF with acid)

This brings up the following conclusions:

While FTIR has got undisputed virtues in identifying chemical processes and species the main difficulties for a potential use to result in a ranking of polymer stabilizer systems arises from the following facts:

- FTIR sensitivity is too low for the initial stages of the oxidation (in this case: anything during the first 21 days of weathering).
- A monitoring of the extent of oxidation by the growth of the carbonyl region with the aim to compare it to another stabilizer system becomes very subjective as to the selected area that is being evaluated and by overlapping different groups.

3.3 Chemiluminescence detection

Ahead of the actual measurements a comparison of the effects of a change in the temperature used to carry out the chemiluminescence experiment is to demonstrate a few of the basic features of chemiluminescence itself and of the dependence of the characteristics of the resulting curves on this parameter in particular.

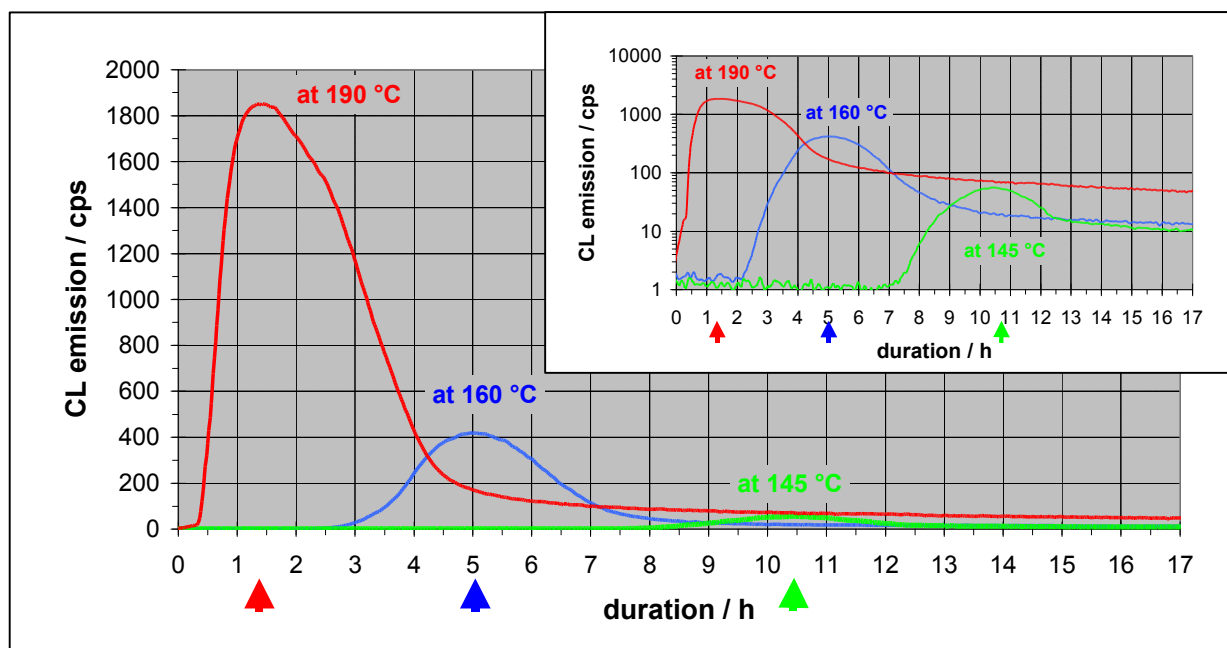


Figure 4. CL investigation of the influence of temperature. PE-LD stabilized with Hostavin N30; CL under air, isotherm conditions. Insert: semilogarithmic presentation. Times needed to reach maximum are indicated by triangles.

The following basic features of chemiluminescence (CL) can be deduced from 'Fig. 4' and can be generalised for other CL measurements:

- The CL emission over time shows a sigmoid shape.
- The oxidation starts with an induction time (curves for 160 and 145 °C) during which initiation and consumption (stabilizer) of reactive radical species are at stationary low level.
- After the end of the induction time the oxidation accelerates and spreads over the whole material.
- The maximum reached corresponds to a maximum in the rate of the oxidation reaction.
- After the maximum the CL emission asymptotically approaches a stationary end value.
- With an increase in the temperature used for the CL experiment the emission maximum shifts to a longer duration (increase in induction time) and the height of the maximum increases exponentially. (Also the stationary end value or emission increases with temperature).
- A change in the shape as occurring for the 190 °C CL curve hints to potential different reaction paths being thermally activated at higher temperatures

Additionally it can be generalised that a high stability shows as long induction time and time to reach the maximum and as low chemiluminescence intensity.

The tuning of the optimal temperature to be applied for the CL experiment therefore must find a compromise between higher temperature to achieve an acceptable duration of the CL experiment on the one hand and lowest possible temperature not to reach thermally activated states that are not relevant for the conditions to be characterised on the other.

The actual CL measurement for PE-LD stabilized with Hostavin N30 in respect to the effects of preceding weathering including acid precipitation is presented in 'Fig. 5'. For comparison, the respective CL measurement for an unexposed sample is shown.

- The time to reach the maximum decreases and the maximum increases with the duration of weathering. After 21 days of weathering the height of the maximum decreases again (competing yellowing of the sample).
- In the time to reach the maximum there is a noticeable reduction between 16 and 21 days of weathering which can be explained in a change in the degradation mechanism.
- While a maximum in intensity is reached for a exposure period of 21 days it decreases again for an exposure of 42 days.
- The exposure period causes a systematic increase in the slope of the respective CL curves for the first period.
- A comparison for the performance of the two stabilizers Hostavin N30 and Chimasorb 119 in PE-LD is given in 'Fig. 6' for 16 days of weathering:
- Already for this exposure period, CL allows to make a differentiation in the performance of the two stabilizers.
- PE-LD stabilized with Chimasorb 119 in all cases (unexposed, weathered without acid precipitation for 16 days, weathered with acid precipitation for 16 d) shows higher stability than PE-LD stabilized with Hostavin N30.
- While the stability of unexposed PE-LD stabilized with Chimasorb 119 is outstanding the same system shows strong effect to all kinds of weathering, with the weathering including acid precipitation showing the strongest destabilizing effect.
- For PE-LD stabilized with Hostavin N30 the effect of weathering with added acid precipitation only just shows in comparison to weathering without precipitation.

4 CONCLUSIONS

- Chemiluminescence allows to directly evaluate the relative residual stabilization of a polymeric system that determines the lifetime of a polymer.
- It is more sensible than the other techniques compared.
- A particular sensitivity for the first stages of an oxidation reaction allows an early differentiation of different systems in terms of their stabilisation against oxidation.
- The higher sensibility, apart from the detection principle, could be due to another procedure (e.g. another effective dimension) the technique counts degraded species.

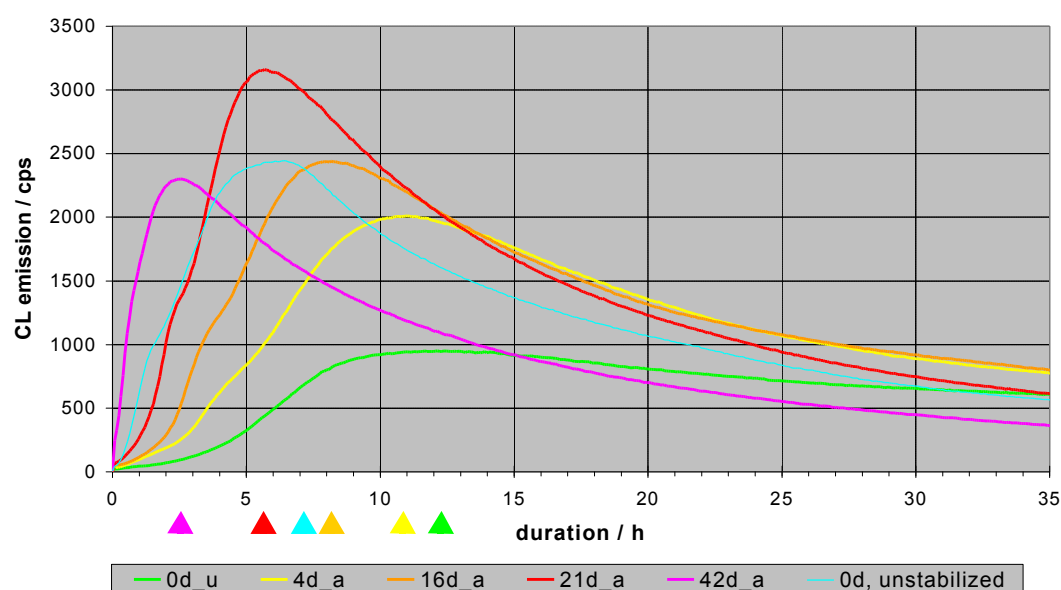


Figure 5. CL investigations at 172 °C for unstabilized unexposed PE-LD ('0d, unstabilized') compared to PE-LD stabilized with 0,2 % Hostavin N30 that remained unexposed ('0d_u') or was weathered including acid precipitation for 4d, 16d, 21d and 42d. Times to reach maximum indicated by triangles.

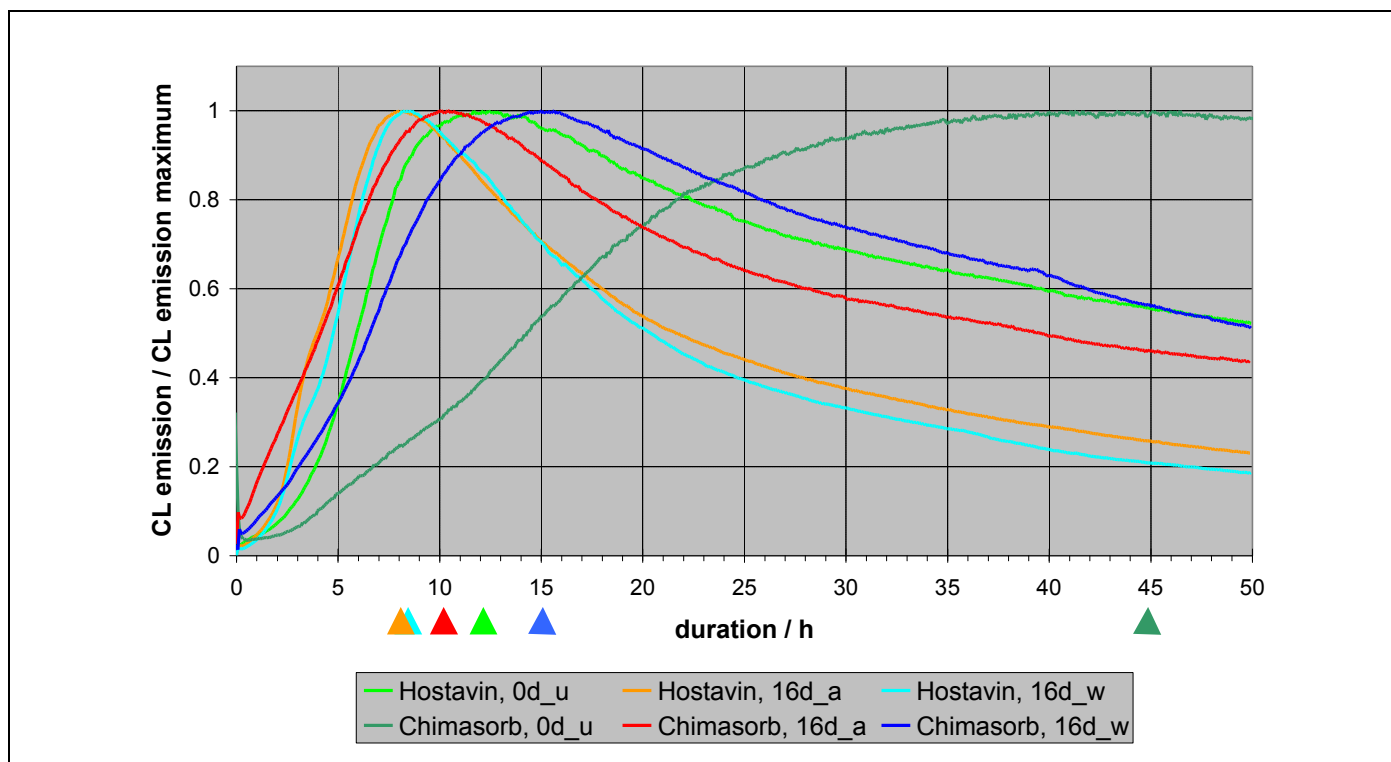


Figure 6. CL evaluation at 172 °C of the performance of PE-LD with Hostavin N30 compared to PE-LD with Chimasorb 119 as maximum normalised emission as a function of CL duration. Days given (0d=unexposed, 16d) relate to respective exposure period. Weathering either with acid precipitation ('a') or without ('w').

5 OUTLOOK

Initial experiments with polycarbonate roof materials that were weathered in BAM and characterised in CSIRO indicate a systematic CL response to preceding exposure and promise to complement FTIR and other results (Schulz, U. & Tjandraatmadja (2002)) of the effects of weathering on this material. In addition, these CL experiments may offer further insight into the degradation mechanism.

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