



ANALYTICAL SERIES

Chemiluminescence for the Early Detection of Weathering Effects of Coatings

Part I: Fundamentals

by **Volker Wachtendorf** and **Anja Geburtig**
BAM Federal Institute for Materials Research and Testing

In this two-part series, the analytical technique of chemiluminescence for early detection of weathering effects is presented. Part I introduces the fundamentals of chemiluminescence. Part II, to be published in next month's CoatingsTech, will present the experimental set up and examine chemiluminescence modes and combinations with other techniques.

INTRODUCTION

Weathering tests are part of the group of long-term tests designed to characterize the aging of materials. Even after decades of use on thousands of different materials, these tests still are necessary to characterize new materials as their outcome is material-specific (hence, conclusions from material A to material B cannot be drawn). There still is no physical-chemical model to characterize the aging process as an alternative to the experimental evaluation. Since the aging, in terms of a certain property versus its exposure time, does not run in parallel for different materials, it is not sufficient to improve the initial value of a property. Only the experimental evaluation of the aging curve is able to ensure that the aged value of the property is still within specifications.

Advances in the UV stabilization of coatings have resulted in increased service lifetime. Subsequently, artificial tests of long-term stability need to last longer. At the same time, however, demands to

shorten the duration of testing have become more stringent. Particularly during the development phase of new coating systems, long testing times are prohibitive. Any method that can shorten the time for artificial tests, therefore, is much in demand.

The test duration shortening strategy followed here is to use chemiluminescence as a sensitive detector for weathering effects. This means that weathering (outdoor or artificial) is carried out in the conventional way, but for the evaluation of degradation effects caused by weathering exposure, use is made of chemiluminescence detection.

FUNDAMENTALS

Concepts to Reduce the Testing Duration

Three main concepts that address the goal of reducing the duration of artificial weathering tests can be differentiated:

- Exaggeration of exposure conditions far beyond the conditions occurring under field conditions. Especially the exposure to higher temperatures and to irradiation with spectral contributions below the cut-off of natural global radiation (below 290 nm) has a fair probability to result in a loss of correlation of the artificial test to field conditions.¹ This concept can be labelled as "extreme acceleration with completely erratic correlation to field results."

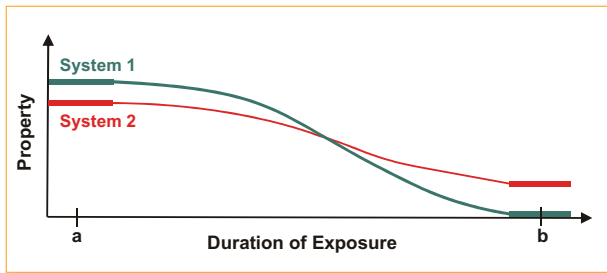


Figure 1—Different degradation rate behavior of two materials resulting in final values of a property at duration (b) that are not correlated to the initial values before weathering (a).

- Time lapse, currently, is the most applied strategy. Those exposure phases that cause the highest weathering effects are applied more frequently than under field conditions, e.g., rain phases are used more often; or instead of following the diurnal change of irradiance of the sun, the maximum irradiance occurring at noon is applied constantly for 24 hr. This strategy can be labelled as “moderate acceleration with good correlation to field results.”
- Detection that is more sensitive allows shortening the duration of the test since usually the weathering test has to be continued up until weathering effects can be detected or different systems can be differentiated in terms of weathering effects. This is the strategy followed in this work, with the use of chemiluminescence as the sensitive detection technique. This can be labelled as “moderately to highly shortening in duration with moderate to good correlation to field results.”

Even though coatings are the focus of our considerations, the term “polymer” is used here as

the more general chemical ingredient of both bulk plastics and of coatings.

Limitations of an Early Detection Method

Any early detection method, not just chemiluminescence, has to obey physicochemical principles that limit its correlation to real-time detection. This is due to possible inconsistencies in the aging behavior of early and advanced aging stages.

The sensitivity to degradation under a weathering exposure changes from one material to the next. This manifests itself in different degradation rates. Initial performance rankings may change completely during a weathering exposure (see *Figure 1*).

This means that even if the evaluation of effects only aims at rankings of property changes for different samples, for a comparison with rankings on a different moment of the exposure duration, different rankings can be obtained in the case of intersecting aging curves of different samples under investigation. Further complication can arise if the evaluation techniques used for early stages [(a) in *Figure 1*] are not related closely enough to the technique used for advanced stages [(b) in *Figure 1*].

PRINCIPLES OF CHEMILUMINESCENCE²⁻⁷

“*Chemi-luminescence*”—as the word implies—is light generated in a chemical reaction. The detection of light emitted as chemiluminescence (CL) allows monitoring the kinetics of an ongoing oxidation reaction. As most aging processes are connected with or consist of oxidation reactions, the detection of CL allows following aging reactions, or the other way round, establishing the residual oxidative stabilization in a system.

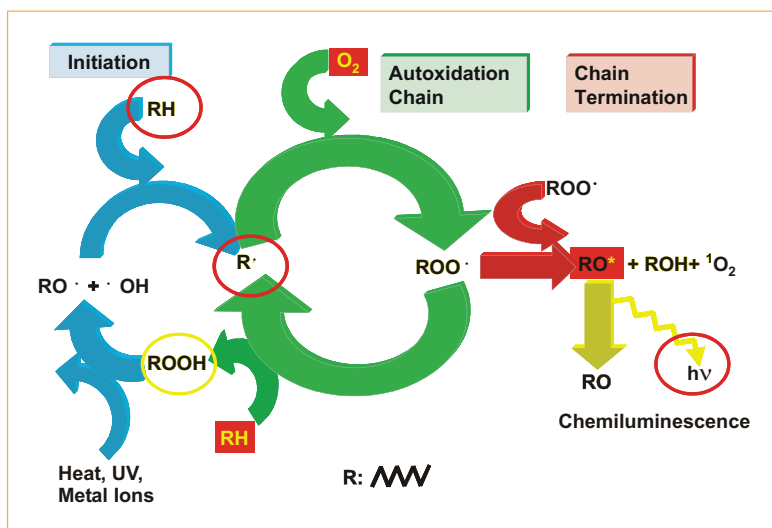


Figure 2—Autoxidation scheme for the oxidation of a saturated polymer RH with oxygen. The molecular basis for chemiluminescence detection.

In the first approach, the CL emission can be described to be proportional to the reaction rate of the oxidation reaction:

$$I_c = G \Phi r \quad (1)$$

where:

- I_c : observed CL emission
- G: the instrument's detection efficiency for each photon emitted
- F: the material specific quantum efficiency of the process ($0 \leq F \leq 1$)
- r: the rate of the CL reaction

The quantum efficiency is specific to the material used and can vary by orders of magnitudes. For the oxidation of typical polymers, its typical values can be very low, in the range $10^{-8} \leq F \leq 10^{-3}$. It is difficult to determine, but it especially is important to be considered for comparisons of chemically different samples if the absolute emission is the measure.

The CL emission is linked to the ongoing oxidation reaction via the radical chain character of the auto-oxidation process (see *Figure 2*), which at least for saturated carbon bonds is regarded as the dominating mechanism.

The auto-oxidation scheme⁸ consists of three different phases:

- Initiation
- Auto-oxidation chain
- Chain termination

The initiation usually is the rate-determining step in the whole process. In response to exposure with UV, heat, and catalyzed by metal ions, hydroperoxides (ROOH) can be decomposed into two radicals allowing one hydrogen to be abstracted from a polymer R-H under formation of polymer radicals R•.

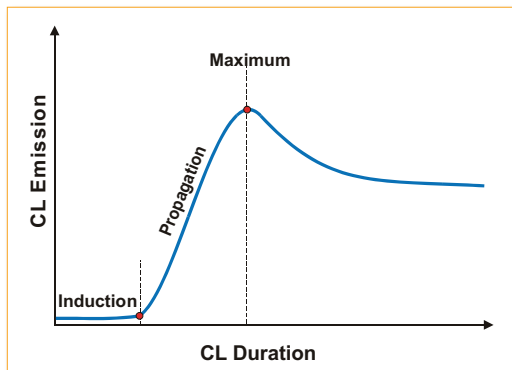


Figure 3—Principal course of a CL curve showing an induction period followed by a propagation phase, which is ended by reaching a maximum, after which the emission levels off. The investigation temperature is assumed constant for the duration of the measurement.

These polymer radicals R• are the starting point of the auto-oxidation chain as they readily react with oxygen to form peroxy radicals ROO•. The whole cycle repeats itself several times until the concentration of ROO• is sufficiently high for termination reactions to become more likely.

Among several possible termination steps in which free radicals can react with each other with a certain probability after a certain number of cycles in the propagation step, the depicted termination steps render an electronically excited carbonyl group RO*. The latter can relax to a ground state by emission of a CL photon. This way, CL becomes a lap counter of the ongoing oxidation reaction. The ratio of terminations to propagation cycles is specific to a polymer and to the reaction conditions (especially the temperature).

These events on a molecular scale are reflected in the macroscopical world of a CL measurement. The typical shape of a CL curve is depicted in *Figure 3*.

At the start of the CL measurement, the CL emission is at a very low level. This is the so-called induction period, and on the molecular scale of the auto-oxidation cycle this is equivalent to the initiation period. As the energy as well as the kinetic barrier to break a C-H bond or a C-C bond in a polymer is rather high, only very few polymer radicals are formed that could react with oxygen (in the auto-oxidation chain) and ultimately form an excited carbonyl (termination step) that could relax by emitting a CL photon. The polymer itself has an inherent stabilization that might be increased by adding a stabilizer. The few polymer radicals ultimately generating a CL photon are responsible for the low CL emission detected in this phase.

At the end of the induction period, the CL emission starts to increase: with ceasing concentration of stabilizer and an increasing amount of oxidizable polymer molecules formed, the stabilization of the polymer against oxidation is not efficient enough any longer and more radicals are formed than are scavenged by the stabilizer. As in the radical chain reaction of the auto-oxidation, more radicals are formed than there are going into it, the reaction auto-accelerates, and the propagation phase is observed as a rapidly rising CL emission.

The maximum of the CL emission indicates the point where the oxidation reaction does not accelerate further, and after which it usually slows down. In terms of the auto-oxidation process, this means that from this point on the number of termination reactions that reduce the number of radicals outnumbers new radicals formed in the chain reaction with oxygen.

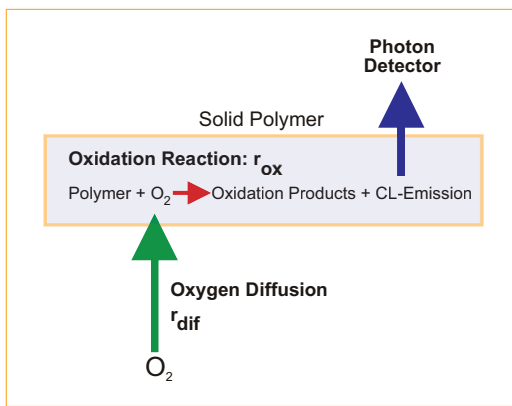


Figure 4—Superposition of chemical reactions (oxidation of the polymer) and transport processes (oxygen diffusion into solid polymer) during the CL investigation.

As the oxidation reaction in our case refers to a solid polymer that reacts with oxygen from the gaseous atmosphere, physical transport processes also influence the chemical reaction and hence the CL emission.

The influence of temperature during the CL experiment is twofold:

It increases the reaction rate, r , of the oxidation reaction via the temperature dependence of the reaction rate constant k ($r = k c_{\text{polymer}} c_{\text{oxygen}}$)

It increases the diffusion rate of oxygen into the polymer via the temperature dependence of the diffusion constant D

Superposition of the Oxidation Reaction by Transport Processes

The CL emission reflects the rate of the ongoing oxidation reaction(s) in the sample material, which are not absorbed from sample layers above the area that the respective emission is originating from and that finally reaches the detector.

External influences on the rate of the reaction are the temperature (which influences the reaction rate constant) and the oxygen partial pressure. Oxygen, being the reactant to the sample, already may be in the sample (dissolved oxygen or oxygen from the decomposition of peroxides) or may diffuse into the solid sample from the surrounding atmosphere (Figure 4).

Apart from the sample material, the diffusion rate is both influenced by the temperature in the sample and partial pressure gradient of oxygen in the sample and the surrounding atmosphere. The temperature dependence of the diffusion rate is especially critical near the glass transition temperature, T_g , of amorphous and semi-crystalline polymers and the vitrification temperature (gel point) of duromers (thermosetting resins), where many related properties can change by orders of magnitudes (see Figure 5).

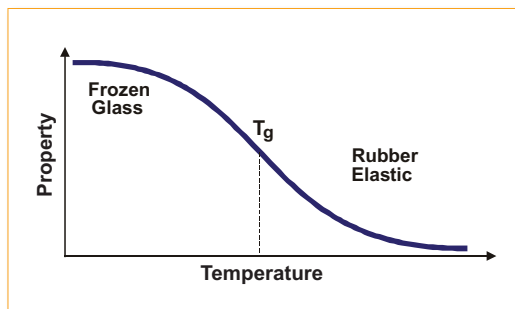


Figure 5—Property change at T_g for amorphous or semi-crystalline polymers, which can change related properties like the diffusion rate by orders of magnitudes.

This also means a feedback of chemical reaction to diffusion rate: as the chemical reaction consumes oxygen in the sample, especially at high oxidation rates, the diffusion of new oxygen from outside into the sample can become rate determining.

CL Detection of Weathering Effects⁹⁻¹²

In a weathering test,¹³ the stability of a relevant property under the action of a weathering exposure is examined.¹⁴ The aging process manifests itself in the change of certain properties of the material under investigation, which usually means a degradation of functional properties. Both chemical reactions (most important: oxidation reactions) and physical processes (such as transport reactions) contribute to the aging process, but usually the chemical reactions are the dominant ones in terms of the magnitude and persistence of resulting effects.

Initiated mostly by UV radiation, the degradation process usually starts with single molecules on the surface, then spreads over the whole surface, and finally can reach ever-deeper layers of the bulk of the material¹⁵ (see Figure 6).

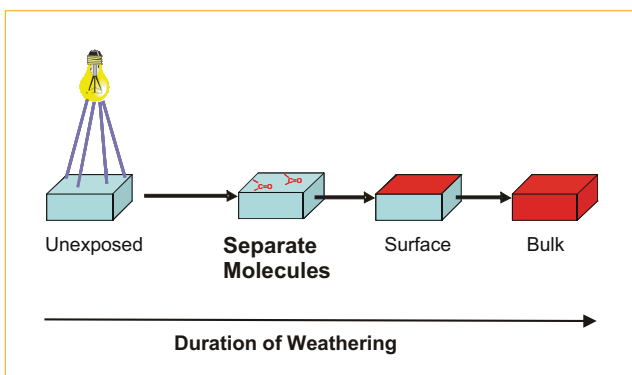
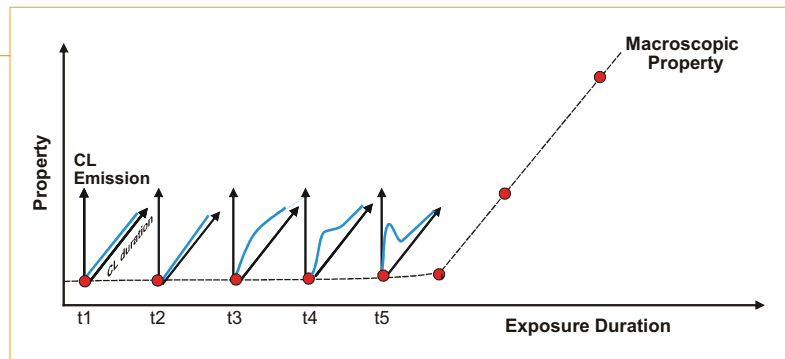


Figure 6—Schematic illustration of the weathering process starting at separate molecules, spreading over the surface, and finally reaching ever-deeper layers of the bulk of the material.

Figure 7—Titration of the respective weathering stage in terms of residual stabilization using CL.



If the concentration of degradation products on the surface has accumulated beyond certain threshold values, even macroscopical physical properties can change. Depending on their nature, macroscopic properties can be related more closely to molecular changes (for instance, yellowing to the formation of double bonds) or they can be only very indirectly related (like gloss retention to carbonyl-group formation).

A weathering test usually has to be continued until changes in certain properties of the material can be detected. Many established detection techniques are not able to detect the degradation products but detect a physical or technological property (such as gloss or mechanical strength), which needs degradation products to be accumulated until this physical property is affected. That means that a transfer function mediates the change in concentration as a change of a physical property. This extra transfer function implies a loss in sensitivity and selectivity as well as a differentiation of different properties in terms of the shape and exposure response of their curve over exposure duration.

Replacing conventional detection with more sensible means of detection techniques that are capable of detecting separate molecules, it is possible to shorten the necessary weathering duration by at least a factor of two.

The most useful approach to use CL for the characterization of weathering-induced material degradation consists in making CL investigations not only of the unexposed material and of the finally weathered state but to define several shorter weathering intervals, after which a sample is removed from the weathering and investigated in CL. However, as CL means a destructive testing technique, each weathering stage to be evaluated with CL needs a separate sample, which needs to be weathered in parallel with the samples of different weathering stages. CL this way can be used to “titrate” the resulting stabilization at a certain weathering stage as indicated in *Figure 7*.

SUMMARY

There is an ever-increasing demand for accelerated tests that will aid in predicting the service life of coatings. Chemiluminescence is a sensitive detection technique that is offered as a method for shortening the time for artificial weathering tests. In this first article, the fundamentals of the technique are presented. Part II, to be published in the May 2010 issue of *CoatingsTech*, examines the experimental set-up and applications of chemiluminescence. Special CL modes and the advantages that can be attained through combination with other techniques will be presented. **CT**

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AUTHORS

Volker Wachtendorf, BAM Federal Institute for Materials Research and Testing, Unter Den Eichen 87, Berlin, Germany, 12205. Ph: +49-30-81041613; fax: +49-30-81041617; email: volker.wachtendorf@bam.de.

Anja Geburtig, BAM Federal Institute for Materials Research and Testing, Unter Den Eichen 87, Berlin, Germany, 12205.



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