Lifetime Prediction of Rubber Using the Chemiluminescence Approach and Isoconversional Kinetics

Fabian Käser*[a] and Bertrand Roduit[b]

Abstract: A common scepticism towards the application of many materials in art or in conservation-restoration results from the fact that their long-term stability is unknown and difficult to predict. In the present study we report on a new approach of kinetic analysis of the oxidation reactions of natural rubbers with and without stabiliser in an oxygen atmosphere at moderate temperatures using chemiluminescence measurements carried out on newly developed instrumentation. The kinetic parameters of the oxidation process, calculated from the chemiluminescence signals by means of the differential isoconversional method of Friedman, were subsequently applied to the simulation of the rubber aging using different temperature profiles. The results are a first step towards the use of chemiluminescence to characterise the oxidative aging of rubber and predicting the lifetime of rubber items.

Keywords: Chemiluminescence · Isoconversional kinetics · Lifetime prediction · Natural rubber · Oxidation

Introduction

It is known that most organic materials readily react with oxygen even at ambient temperature; therefore oxidative degradation is a severe problem in conservation-restoration of art objects. Rubber artefacts are quite sensitive to oxidative degradation.[1,2] Monitoring, or better, predicting the stability of organic and especially polymeric materials with respect to oxidation processes is of general importance. Commonly applied analytical approaches such as determining oxidation induction times (OIT) or oxidation onset temperatures (OOT) using differential scanning calorimetry (DSC) or other conventional thermoanalytical methods are unsuitable for long-term prediction of oxidative behaviour because of the use of elevated temperatures during experiments: the high temperatures employed will invoke reaction pathways which are different from those encountered under normal conditions of storage at room temperature.

Oxidation processes, leading to the cleavage of the polymer chains, occur randomly and stealthily. They may not be detected for years, but then undergo rapid, autocatalytic acceleration once the reaction reaches a critical stage. Once the reduction of the molecular weight has reached a critical threshold, both adhesion and cohesion properties are critically affected which, in turn, leads to the loss of required mechanical properties.

The oxidation of materials in the solid state generally starts on the surface and the oxidation progress is often diffusion controlled. A general overview of commonly applied examination methods and mechanism of the oxidation is given by Feller[3] Zweifel,[4] and Scheirs.[5]

In the degradation of organic polymers stabilisers are consumed during the induction period, while the organic matter remains stable, maintaining its original properties. At the end of the induction period, when the concentration of stabilisers has reached a sub-critical level, oxidative decay starts and the substance's properties change. Frequently, oxidation reactions are self-accelerating (auto-oxidation) and the reaction progress may rapidly increase after the induction period.

The most common methods to test the kinetics of organic substances' thermooxidative decay are thermal analysis methods like differential thermal analysis (DTA), DSC or thermogravimetry (TG). Substances are tested using isothermal or nonisothermal temperature profiles under an oxidative atmosphere, and the OIT or OOT are determined when the heat flow (DSC, DTA) starts to become exothermal or the sample mass loss starts (TG). In some special applications, these procedures are standardised (*e.g.* for automotive oils, cable insulations or polyolefines).

Especially for industrial and commercial applications, OIT- and OOT-based examination procedures are widely applied. Their advantages include easy sample preparation, short measurement periods and well established methods of data evaluation. A significant disadvantage of these short-time experiments lies in the application of the high experimental temperatures, generally above 180 °C. The reasons for the use of such temperatures are following: i) firstly to make sure that the oxidation starts within around 2 h and ii) to provide a distinct signal larger than the baseline noise: the sensitivity of conventional TA instruments can be too low to record the beginning of the oxidation reaction. An evaluation of the bad correlation of OIT- and OOT data with the observed long-term stabilities under normal environmental conditions has been report-

Correspondence: Dr. F. Käser[a]
[a]ACL Instruments AG
Industriestr. 11
Postfach 10
CH-3210 Kerzers
E-mail: fabian.kaeser@aclinstruments.com
[b]AKTS AG
TechnoArk 3
CH-3960 Siders
E-mail: b.roduit@akts.com; f.kaeser@akts.com

ed.[6–8] Depending on the properties of the substance, one or several phase transitions can occur between the temperature ranges at which the oxidative characteristic has been measured and those for which the oxidative properties has been predicted (life-time determination). It seems to be obvious that the degradation kinetics may change for different low- and high-temperature phases and the extrapolation of high-temperature experimental results to ambient temperature may be of little value.

In this situation alternative methods, based on the experiments carried out at low temperatures, should be applied for the characterisation of the long-term stability of organic substances. Chemiluminescence (CL) is very appropriate for this purpose.

Chemiluminescence

Luminescence is a term used for various phenomena originating from electronically excited states. Luminescence is a 'cold light', not an incandescent light. The emission of photons results from the relaxation of excited electrons (triplet-state) into their ground-state. This may be a quite rapid process: the delay between the excitation and light emission is at least 10^{-10} seconds. Chemiluminescence (CL) includes all luminescence phenomena resulting from chemical reactions.[9] The fact that organic substances undergoing oxidation emit light was recognised already during the second half of the 19th century.[10] In the past few years, chemiluminescence has gained wide acceptance as a sensitive method to study the oxidative degradation of organic solid substances.[11–13]

Principles of Chemiluminescence in Organics

The emission of light during the oxidative degradation process of organic materials is part of the reaction pathway. Usually, the first step is the formation of unstable alkyl radicals, which immediately scavenge the oxygen from the atmosphere to form peroxy radicals. These react further and transform into different species in an accelerating degradation cycle (auto-oxidation, left part of Fig. 1). Chemiluminescence is normally attributed to a relaxation of excited triplet-carbonyl-functions (^{3}R=O*) into their ground state. The spectral range of the light emitted varies according to the type of substances involved. In most cases chemiluminescence is observed in the short wave region of the visible spectrum from 380 to 450 nm. However, there are well-known exceptions: the relaxation of $^1O_2$ can be detected in the infrared region at *ca.* 1200 nm.
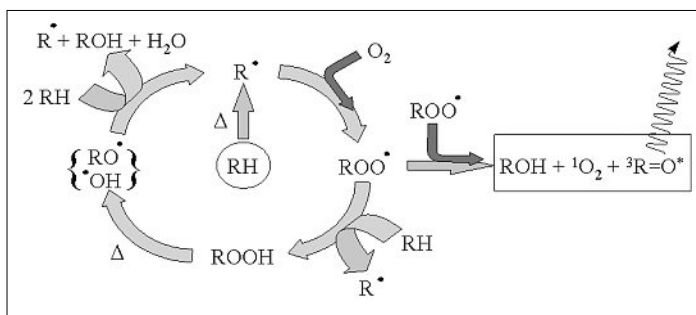

Fig. 1. Simplified scheme of auto-oxidation of organics including a Russel mechanism (adapted from ref. [14])

The required energy (290–340 kJ mol^{-1}) to produce the excited state may be supplied by basically three different chemical mechanisms:
i)   The combination of two peroxy radicals with concomitant fragmentation following a Russell mechanism[15] is strongly exothermal (460 kJ mol^{-1}).[16] The CL-emitter is an excited 'triplet' carbonyl function (right-hand part of Fig. 1).
ii) Direct homolysis of hydroperoxides followed by a cage reaction leads to an excited carbonyl function and is combined with the evolution of 315 kJ mol^{-1}.[17]
iii) The metathesis of alkoxy or peroxy radicals provides 374 kJ/mol and 323 kJ/mol, respectively.[18] It has been shown that the CL signal intensity reveals the existence of two kinetic stages during oxidative degradation of organic materials: The first one is correlated with the concentration of peroxide groups,[19] the second stage corresponds to the oxidation propagation by the hydrogen abstraction responsible for the carbonyl formation.[20]

Advantages of Chemiluminescence in Monitoring Oxidation of Organics

Compared to DSC and other conventional thermo-analytical methods, CL offers many advantages: due to its much higher sensitivity, experiments can be performed at much lower temperatures, *i.e.* closer to the application-related conditions. This fact is important for the characterisation of substances with low-temperature melting points, glass transitions, *etc.* The outstanding baseline stability of CL is of great benefit when performing long-term experiments;[21] moreover the CL signal is related exclusively to the oxidation processes and therefore is not superposed by the signals resulting from the other processes, including phase transitions. The instrumentation setup is quite simple and may be designed individually for special fields of applications and research goals. The experiments can be performed with the sample masses as low as approx. 0.1 mg. Instrumentation

will not be more expensive than a commercial DSC apparatus.

Determination of the Kinetic Parameters – Isoconversional Analysis

The noticeable weakness of the 'single curve' methods (determination of the kinetic parameters from single run recorded with one heating rate or isothermal condition only) has led to the introduction of 'multi curve' methods over the past few years, as discussed in the International ICTAC kinetics project.[22–25]

Degradation reactions are often too complex to be described in terms of a single pair of Arrhenius parameters and the commonly applied set of reaction models. As a general rule, these reactions demonstrate profoundly multi-step characteristics. They can involve several processes with different activation energies and mechanisms. In such situation the reaction rate can be described only by complex equations, where the activation energy term is no longer constant but is dependent on the reaction progress α *(E ≠ const but E = E(α))*.

Isoconversional methods were introduced by Friedman[26] and Ozawa-Flynn-Wall.[27,28] A detailed analysis of the various isoconversional methods (*i.e.* the isoconversional differential and integral methods) for the determination of the activation energy was presented by Budrugeac.[29] The convergence of the activation energy values obtained by means of a differential method (Friedman) with those resulted from using integral methods (Ozawa-Flynn-Wall) comes from the fundamentals of the differential and integral calculus.

The differential isoconversional method of Friedman is based on the Arrhenius Eqn. (1):

$$\frac{d\alpha}{dt} = A exp\left(-\frac{E}{RT(t)}\right)f(\alpha) \qquad (1)$$

with f (α): the model function; A: the preexponential factor; E: the activation energy; T: the temperature; t: the time.

Friedman has applied the logarithm of the conversion rate $d\alpha/dt$ as a function of the reciprocal temperature at any conversion α (Eqn. (2)):

$$\frac{d\alpha}{dt} = A(\alpha)exp\left(-\frac{E(\alpha)}{RT(t)}\right)f(\alpha)$$

$$\ln(\frac{d\alpha}{dt}) = \ln(A(\alpha)) - \frac{E(\alpha)}{RT(t)} + \ln(f(\alpha)) \quad (2)$$

As $f(\alpha)$ is a constant in the last term at any fixed α, the logarithm of the conversion rate $d\alpha/dt$ over $1/T$ shows a straight-line dependence with the slope of $m = -E/R$.

By the extension of the expression in Eqn. (3) with Eqn. (4) one can predict the reaction rate or reaction progress having determined $A'(\alpha)$ and $E(\alpha)$ using the following expression (Eqn. (5)) at any temperature profile such as isothermal, non-isothermal, stepwise, modulated temperature or periodic temperature variations, *etc.*

$$\ln(\frac{d\alpha}{dt}) = \ln(A'(\alpha)) - \frac{E(\alpha)}{RT(t)} \quad (3)$$

$$A'(\alpha) = A(\alpha)f(\alpha) \quad (4)$$

$$\frac{d\alpha}{dt} = A'(\alpha)exp\left(-\frac{E(\alpha)}{RT(t)}\right) \quad (5)$$

Experimental

The CL emission intensities during oxidation of organic substances at ambient temperatures are too low to be detected. However, only moderate temperatures are required to provide stronger detectable signals. The requirements for the oven are similar to those used in conventional TA measurements such as DSC or TGA: exact control of the required temperature profile is necessary even in long-term experiments and a gas-exchange facility must be installed. Additionally the sample compartment must be absolutely light-tight.

The instruments produced by *AKTS - Chemiluminescence* are fully automated, including a cooled PMT with photon counting mode and an oven chamber in combination with an optical path with shutter system (to protect the highly sensitive detection unit against extensive light during sample handling and to provide background measurements). The single-cell instrument is designed especially for sensitive measurements at moderate temperature conditions (isothermal and non-isothermal mode) additionally allowing the experiments to be carried out under controlled
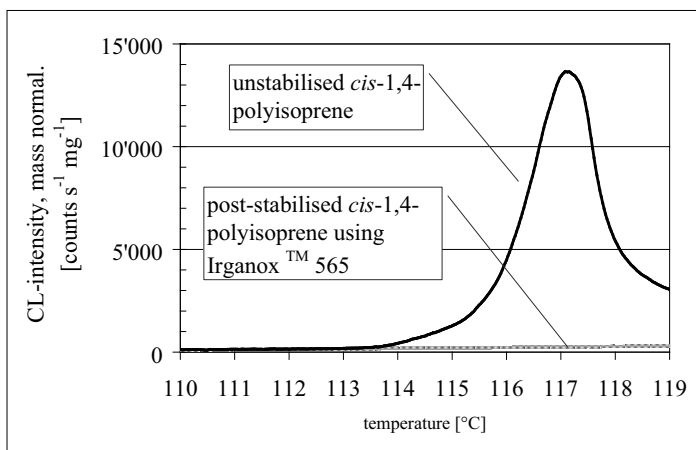

Fig. 2. CL signals recorded for unstabilised and stabilised *cis*-1,4-polyisoprene during identical non-isothermal temperature profile in an oxygen atmosphere
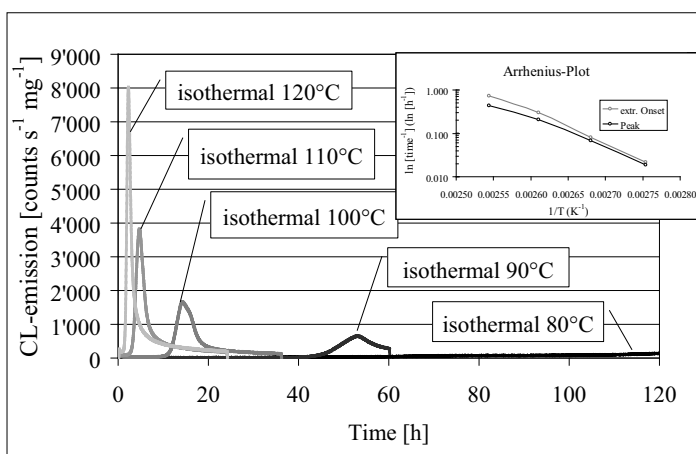

Fig. 3. Normalised CL-emission signals of unstabilised natural rubber (*cis*-1,4-polyisoprene) recorded during isothermal oxidation at 120, 110, 100, 90, 80 °C. The inset presents the Arrhenius relationship for the extrapolated onset and peak temperatures.

relative humidity in the temperature range up to 95 °C. In addition, the CL instrument may be extended by optical filters or by a spectrometer to obtain spectral information on the CL emissions produced.

Results

In the present study we report on a new approach of kinetic analysis of the oxidation of organic solids at moderate temperatures using CL measurements carried out on newly developed instrumentation. The kinetic characteristics of the oxidation process calculated from the chemiluminescence signals are subsequently applied for the prediction of the reaction progress under different temperature profiles.

The results presented depict the comparison of the oxidation reactions of natural rubbers with and without stabiliser in an oxygen atmosphere.

This system is representative for many hot-melt formulations, especially HMPSA.

On the other hand, rubber stabilization is a major topic in preservation research of rubber objects.

The results shown in Fig. 2 illustrate the influence of the stabiliser (5% Irganox™ 565) on the oxidation behaviour of the rubber (*cis*-1,4-polyisoprene) during non-isothermal heating in the range 30–120 °C with a rate of 0.0132 Kmin⁻¹ in oxygen atmosphere. Pfenninger has applied Irganox 565 in rubber art object conservation experiments.[1]

The set of experimental data under isothermal conditions in the range 80–120 °C (Fig. 3) can be used for the evaluation of an Arrhenius relationship (Fig. 3, inset).

Application of an Advanced Kinetic Analysis of CL Signals for the Prediction of Lifetime

Generally kinetic analysis of decomposition processes or any gas–solid reaction can be applied to any type of thermoanalyti-
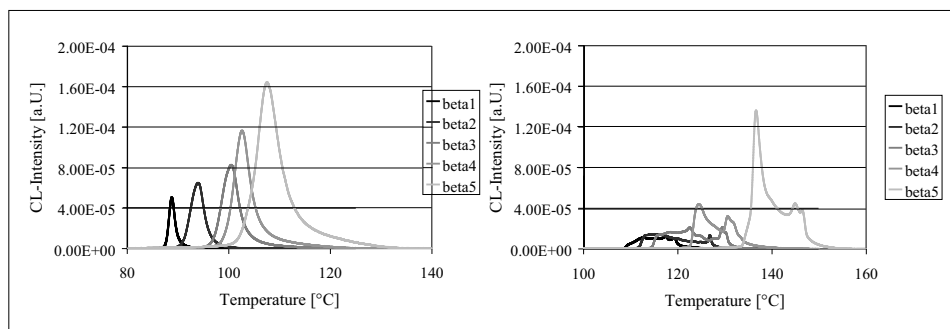
Fig. 4. Normalised CL signals recorded during oxidation of unstabilised (left) and stabilised (right) natural rubber with different heating rates β (0.0054–0.073 K min^{-1}).
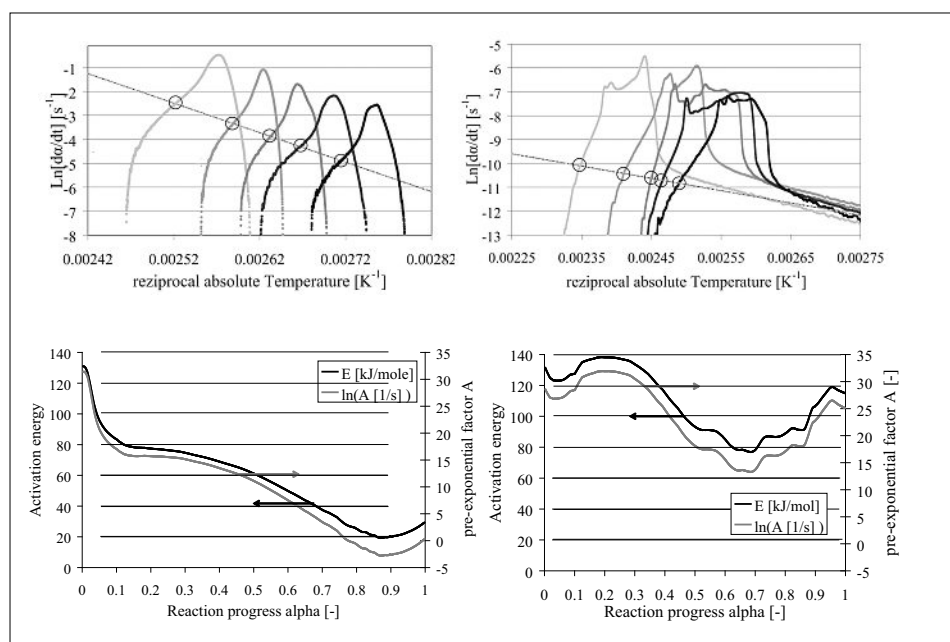

Fig. 5. Top: Friedman differential isoconversional analysis of the long term oxidation process of unstabilised (left) and stabilised (right) natural rubber; Bottom: Dependence of the activation energy and the pre-exponential factor of natural rubber oxidation on the reaction progress α calculated by Friedman's differential isoconversional method: unstabilised (left) and stabilised (right) natural rubber.
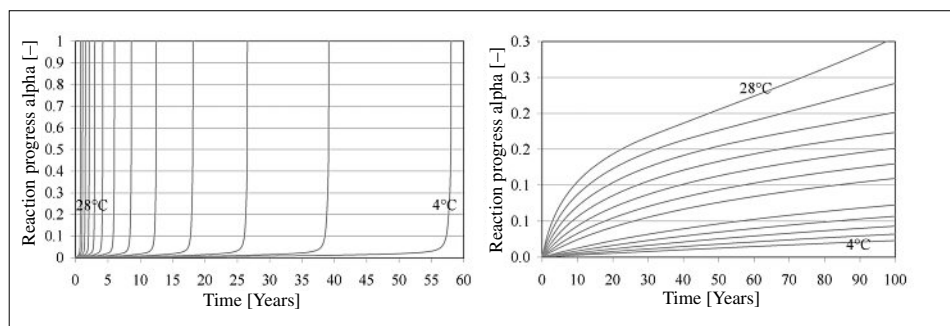

Fig. 6. Prediction of the oxidation progress of unstabilised (left) and stabilised (right) natural rubber at isothermal temperatures between 4 and 28 °C (steps = 2K)

cal data (DSC, DTA, TG, *etc.*) for the study of raw materials and products within the scope of research, development and quality assurance. The experimental procedure starts with the collection of the data directly related to the degradation kinetics such as mass loss or heat flow signals. These data are then used to determine the kinetic parameters such as activation energy (*E*) or pre-exponential factor (*A*) which allow the prediction of the reaction progress under various temperature modes. Generally, direct investigation of the reaction is very difficult at low temperatures (requiring very long measurement times), as well as under complex temperature profiles. Application of Thermokinetics software (*www.akts. com*), the rate and the progress of the reac-

tions can be predicted on the basis of various well-defined temperature profiles.[30]

The CL signals collected during the oxidation of unstabilised and stabilised natural rubber under non-isothermal conditions at different heating rates were used for the determination of the kinetic parameters used later for the prediction of the reaction progress. The normalised reaction rates determined by the Thermokinetics software after correction and optimisation of the base line are depicted in Fig. 4.

The results of the evaluation of the kinetic parameters by the isoconversional method of Friedman are presented in Fig. 5.

Once the kinetic parameters are determined, they can be applied to predict the course of the oxidation under different temperature profiles. The presented results clearly indicate the oxidative induction period after which the rate of the oxidation accelerates rapidly. The prediction of the oxidation of the natural rubber under isothermal conditions at low temperatures (4–28 °C: steps = 2 K) is shown in Fig. 6.

The important goal of the investigation of the kinetics of the thermal decompositions is to determine the thermal stability of objects, *i.e.* the temperature range over which a substance does not decompose with an appreciable rate or the influence of temperature variations during storage and /or display. The correct prediction of the reaction progress of materials which are unstable under ambient conditions requires accurate application in the calculations of both:
– the kinetic parameters and
– the exact experimental temperature profile

The example showing the prediction of the properties of rubber under a more realistic temperature profile is depicted in Fig. 7. The oxidation progress of natural rubber at 20 °C can be seen, with temperature modulations of 0 and 1 to 7 K every 24 h period. Fig. 7 indicates that even small temperature fluctuations can significantly change the stability of the substance: *e.g.* the amplitude of 10 K at 20 °C lowers the oxidation stability of natural rubber by one half of its lifetime. This result is quite important to be able to specify museum storage conditions for art objects.

More generally, calculations can be achieved for any fluctuation of the temperature which makes possible the predictions of thermal stability properties for varying climates (Fig. 8).

Exact consideration in the calculations of daily minimal and maximal temperature variations of worldwide climates provides therefore very valuable insight when interpreting and quantifying the reaction progress of materials subjected to atmospheric conditions.
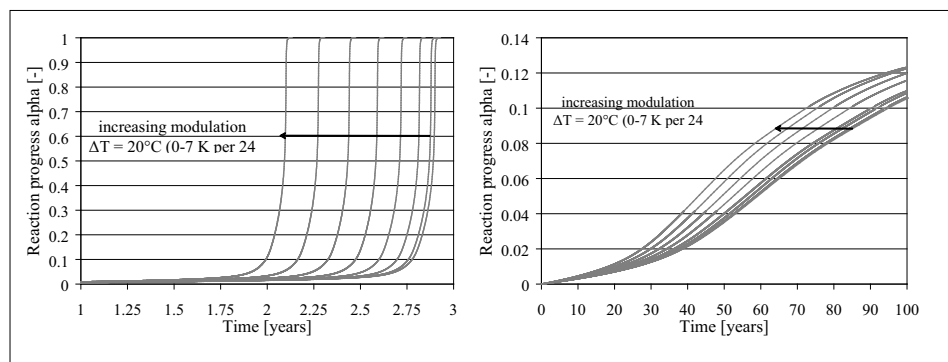
Fig. 7. Prediction of the oxidation progress of unstabilised (left) and stabilised (right) natural rubber at modulated isothermal temperature of 20 °C, amplitudes 0 and 1 to 7 K for each 24 h period. Note that the average temperature is the same for all temperature profiles. Depending on the type of reactions and stabilisation the effect of the temperature fluctuations can have significant influence on the reaction rate.
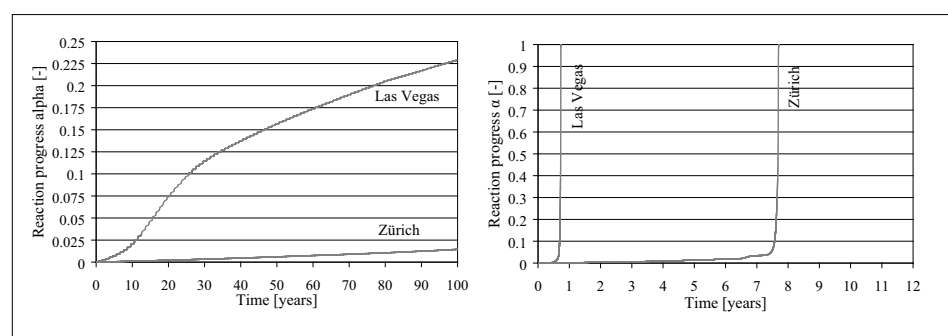

Fig. 8. Prediction of the oxidation progress of unstabilised (left) and stabilised (right) natural rubber at different climatic locations (Las Vegas and Zürich)

Conclusions

Oxidative degradation of polymers can be efficiently monitored by the chemiluminescence method. Compared to the conventional methods of thermal analysis such as differential scanning calorimetry, differential thermal analysis or thermogravimetry, this method is orders of magnitude more sensitive. The data acquired during the chemiluminescence experiments carried out iso- or nonisothermally can be evaluated by differential isoconversional kinetic analysis to obtain meaningful and accurate predictions of the lifetime of organic materials in temperature domains which are representative for the life-cycle of artworks and other objects. Within the same context the efficiency of stabilisers or influence of environmental factors such as relative humidity, UV-radiation, pollutants can be forecast.

The results presented are the first stage of research by using the chemiluminescence method to measure the oxidative aging of rubber and predicting the lifetime of rubber items.

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