

APPLICATION OF ISOCONVERSIONAL KINETICS FOR PREDICTION OF THE LIFETIME OF ORGANIC MATERIALS: SIMULATION OF THE AGING OF RUBBER

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Abstract

Chemiluminescence (CL) includes all luminescence phenomena resulting from chemical reactions therefore due to the fact that the oxidative degradation process of the organics is combined with the emission of light this method can be applied for investigating the course of the oxidation processes.

Commonly applied methods of the investigation of the oxidation such as determination of oxidation induction time (OIT) or oxidation onset temperature (OOT) using Differential Scanning Calorimetry (DSC) or other conventional thermoanalytical methods are sometimes unsuitable for long-term prediction of oxidative behaviour because of the use of elevated temperatures during these experiments: the high temperatures may invoke reaction pathways which are different from those encountered under the conditions of use.

Compared to DSC and other conventional thermo-analytical methods, CL offers interesting 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 of the importance 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; moreover, the CL-signal is related exclusively to the oxidation processes and therefore is not superposed by the signals resulting from the other reactions, including phase transitions.

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 CL measurements carried out on a newly-developed instrumentation. The kinetic parameters of the oxidation process, calculated from the chemiluminescence's signals by means of the differential isoconversional method of Friedman, were subsequently applied for the simulation of the rubber aging under different temperature profiles.

1. Introduction

It is known that most of the organic materials readily react with the oxygen even at ambient temperature; therefore the oxidative degradation is a severe material-engineering problem. Monitoring, or better, predicting the stability of organic and especially polymeric

materials against oxidation is therefore of paramount importance [1-6]. Commonly applied analytical methods such as measuring oxidation induction time (OIT) or oxidation onset temperature (OOT) using Differential Scanning Calorimetry (DSC) or other conventional thermoanalytical methods are not systematically applicable for long-term prediction of oxidative behaviour because of the use of elevated temperatures during these experiments: the high temperatures may invoke reaction pathways which are different from those encountered under the conditions of use. In such situation the 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. One of these methods is the chemiluminescence (CL) [7-19]. Compared to DSC and other conventional thermo-analytical methods, CL offers interesting 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 of the importance 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 [19]; moreover the CL-signal is related exclusively to the oxidation processes and therefore is not superposed by the signals resulting from the other reactions, including phase transitions.

2. Experimental

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

The detection of the CL-emission was achieved using a photomultiplier tube (PMT) with photon counting mode [20]. PMTs are highly sensitive devices and allow short gating times, but their dynamic ranges are low and their use must be carried out with caution in order to avoid the saturation of the photocathode.

3. 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 presented results 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. The results shown in Fig.1 illustrate the influence of the stabiliser (5% IrganoxTM 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 K·min⁻¹ in the oxygen atmosphere.

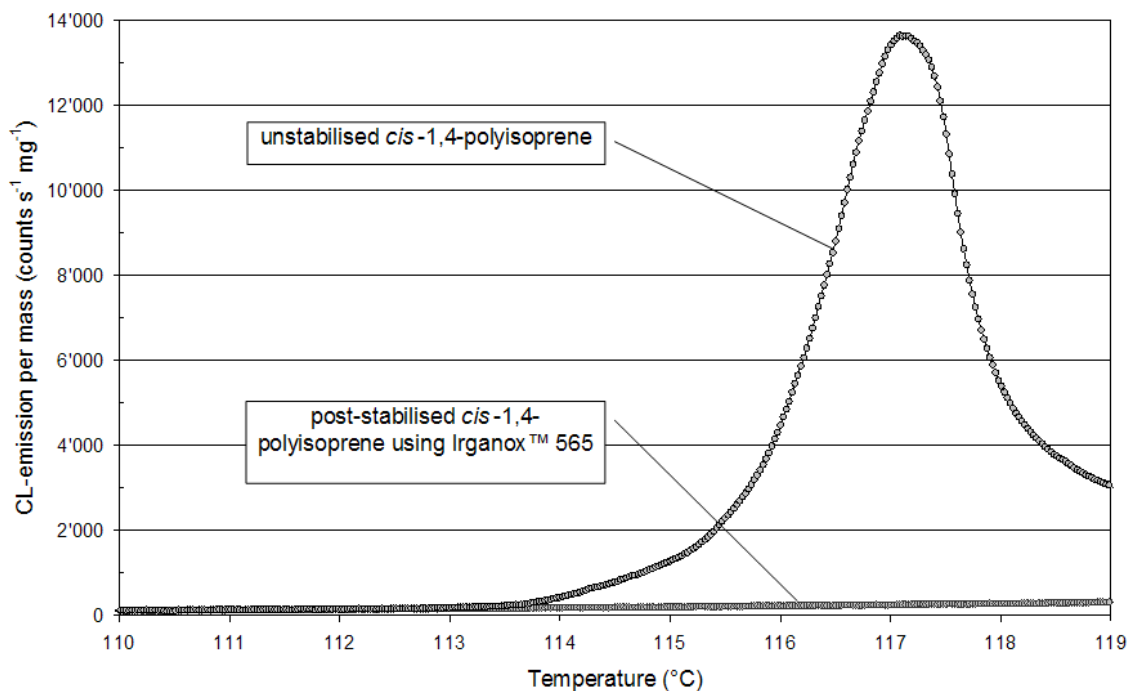


Figure 1. CL signals recorded for unstabilized) and stabilized cis-1,4-polyisoprene during non-isothermal conditioning in the oxygen atmosphere.

CL data can be evaluated using the standard procedures already used in conventional high-temperature thermal analysis methods like OIT, OOT, for defining the points of interest such as initial and extrapolated onset temperatures, temperatures of the peak and extrapolated endpoint. The CL signals can be integrated, the first and second derivation can be determined. The set of experimental data under isothermal conditions in the range 80-120°C (Fig.2) can be used for the evaluation of an Arrhenius relationship (inset).

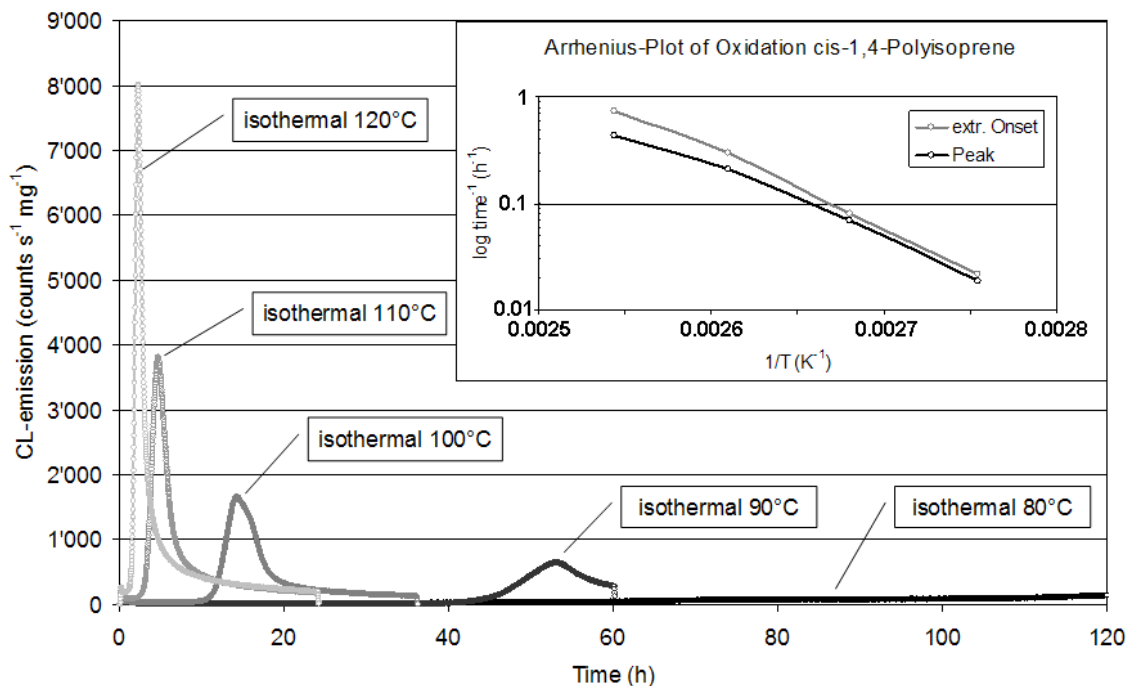


Figure 2. Normalized CL-emission signals of unstabilized natural rubber (cis-1,4-polyisoprene) recorded during isothermal oxidation at 120, 110, 100, 90, 80°C. The inset presents the Arrhenius relationship for the extrapolated onset and peak temperatures.

At higher temperatures ($> 100^{\circ}\text{C}$) the CL data corresponds well with the DSC data. When testing oxidative stabilities below 100°C , the limitations of DSC become obvious: Useful evaluation of such data about oxidation onset becomes tricky and is not reliable (Fig. 3).

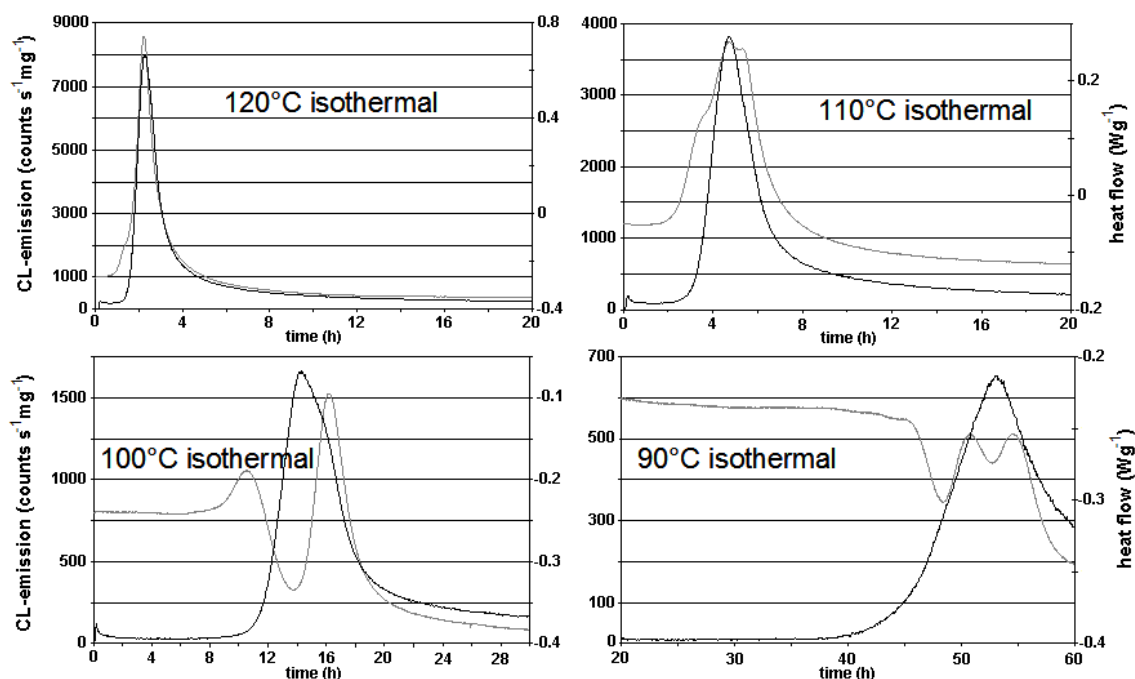


Figure 3. Comparison between CL emission (black) and DSC heat flow (grey) signals at different isothermal conditions ($120, 110, 100, 90^{\circ}\text{C}$) recorded during oxidation of unstabilized cis-1,4-polyisoprene.

3.1 Application of an advanced kinetic analysis of CL signals for the lifetime prediction

Generally kinetic analysis of decomposition processes or any gas-solid reaction can be applied to any type of thermoanalytical 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 predicting 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. Applying Thermokinetics software [21-25], the rate and the progress of the reactions can be predicted on the basis of various well-defined temperature profiles.

The CL signals collected during the oxidation of unstabilized and stabilized 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 normalized reaction rates determined by AKTS-Thermokinetics software after correction and optimization of the base line are depicted in Figure 4.

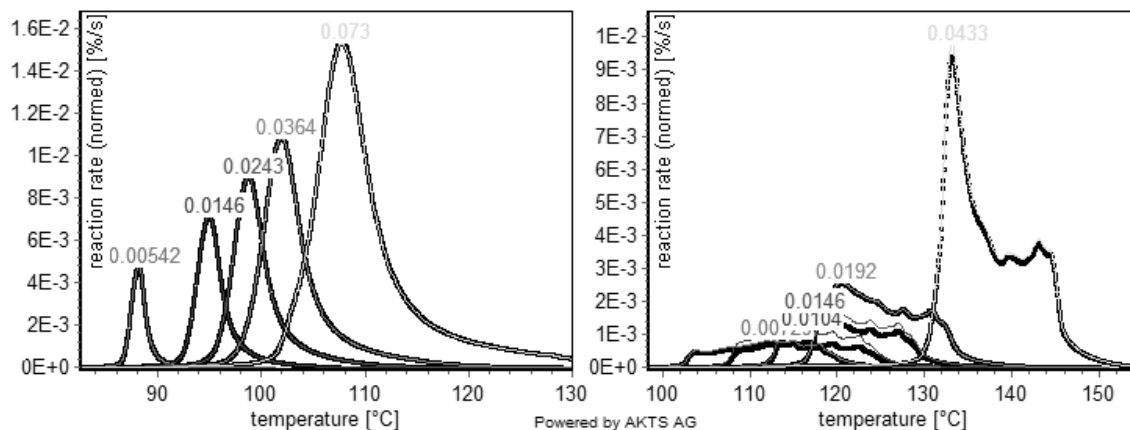


Figure 4. Normalised CL signals recorded during oxidation of unstabilized (left) and stabilized (right) natural rubber with different heating rates β (0.0054 - 0.073 K min⁻¹).

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

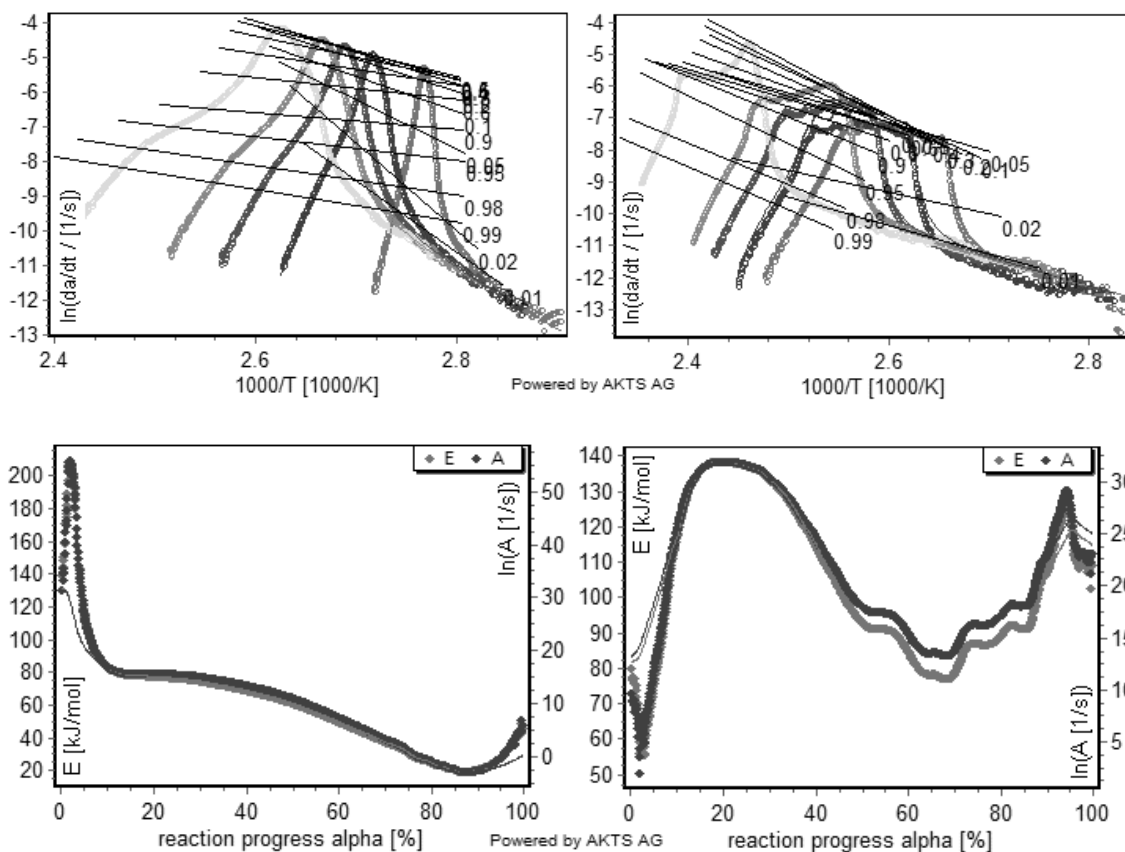


Figure 5. Top: Friedman differential isoconversional analysis of the long term oxidation process of unstabilized (left) and stabilized (right) natural rubber; Bottom: Dependence of the activation energy and the pre-exponential factor of natural rubber oxidation on the reaction progress α calculated by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

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 (4-40°C) is shown in Fig. 6.

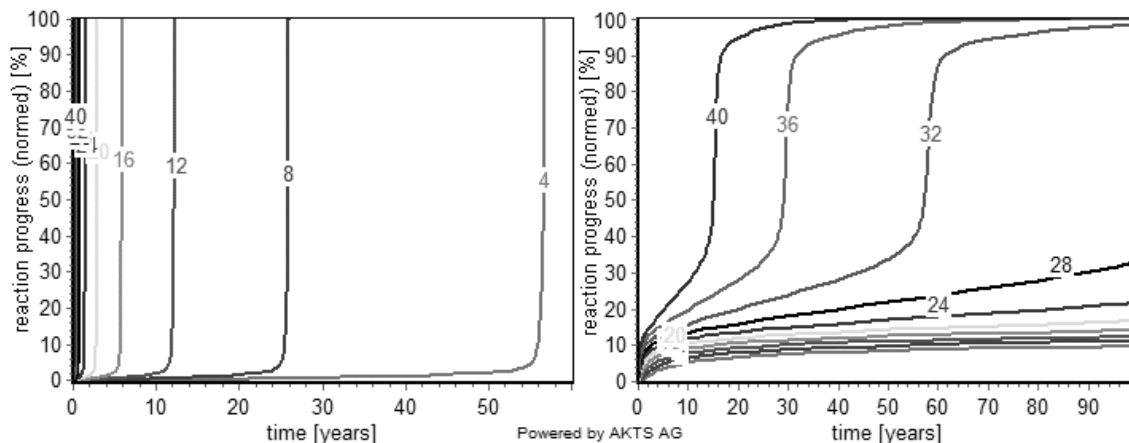


Figure 6. Prediction of the oxidation progress of unstabilized (left) and stabilized (right) natural rubber at isothermal temperatures between 4 and 40°C.

The important goal of the investigation of the kinetics of the thermal decompositions is the need to determine the thermal stability of substances, i.e. the temperature range over which a substance does not decompose with an appreciable rate. 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
- the exact experimental temperature profile

The example showing the prediction of the properties of the rubber under more complicated temperature profile is depicted in Figure 7 presenting the oxidation progress of natural rubber at 20°C when the temperature changes with the modulations of 0, 5, 10 and 20 K each 24 h. The dependences shown in Fig. 7 indicate that even small temperature fluctuations can significantly change the stability of the substance: e.g. the amplitude of 10K at 20°C lowers the oxidation stability of natural rubber by half of lifetime.

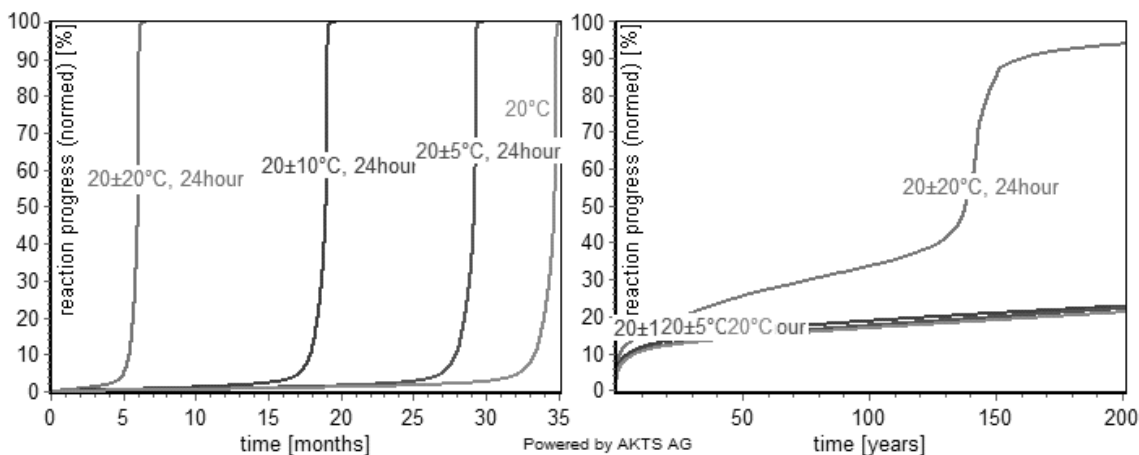


Figure 7. Prediction of the oxidation progress of unstabilized (left) and stabilized (right) natural rubber at modulated isothermal temperature of 20°C, amplitudes 0, 5, 10 and 20 K each 24 h. Note that the average temperature is the same for all temperature profiles. Depending on the type of reactions and stabilization the effect of the temperature fluctuations can have significant influence on the reaction rate.

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

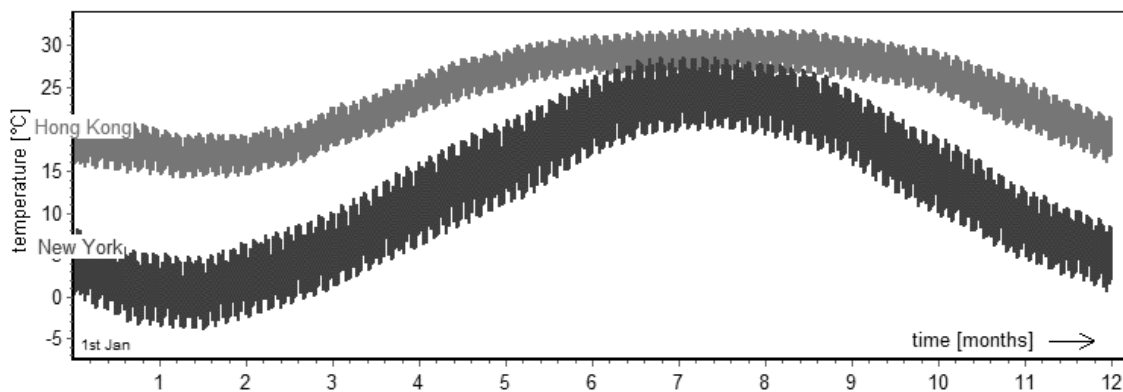


Figure 8. Average daily minimal and maximal temperatures recorded for each day of the year between 1961 and 1990 (New York and Hong Kong).

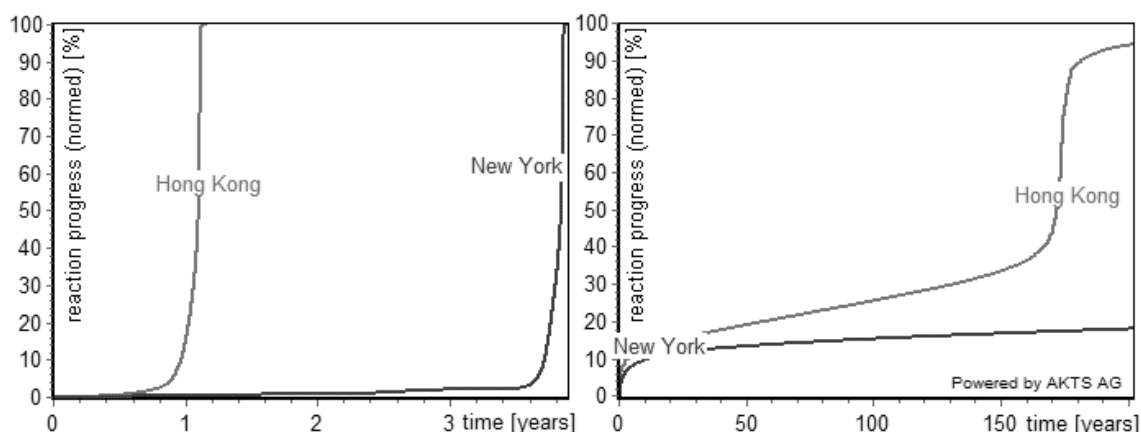


Figure 9. Prediction of the oxidation progress of unstabilized (left) and stabilized (right) natural rubber at different climatic locations (New York and Hong Kong).

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.

4. Conclusion

Oxidative degradation of polymers can be monitored by the chemiluminescence signals resulting from the oxidation reaction. This method is orders of magnitude more sensitive as compared to the conventional methods of thermal analysis such as Differential Scanning Calorimetry, Differential Thermal Analysis or Thermogravimetry. The data collected 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 life time of organic materials in temperature domains which are representative for the life-cycle of the investigated materials. The method is illustrated by the results of the investigation and prediction of the efficiency of the stabilizers on the significant increase of the life-time of the natural rubber. The results of the investigation of the prediction of the properties of adhesives on the basis of the elaboration of the chemiluminescence signals by advanced kinetic method (in preparation) will additionally illustrate the potential of the application of chemiluminescence for the prediction of the life-time of organic solids.

5. References

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