

Application

Oxidation accelerated by the presence of transition metals

Example of natural rubber and copper

Introduction

The prediction of the oxidation induction of polymeric materials requires the precise characterization of the degradation kinetics. Due to the fact that organic polymers are inherently unstable against oxidative decay, they are commonly stabilized by additives like antioxidants. The oxidation's kinetics of organic substances may be completely changed by the presence of catalytically active species like transition metals (e.g. impurities, metallic components, cables): the activation parameters are reduced in this way to considerable lower levels and therefore results in the acceleration of the oxidative decay.

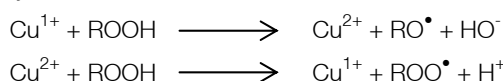
The degradation behaviour of organic substances and its kinetic parameters are commonly monitored by conventional thermal analytical methods. To prevent the disadvantage of high temperature experiments using these methods and the unreliable reaction's prediction (which are due to changes of the reaction's mechanisms due to phase transitions) to lower service temperature conditions, an alternative method with outstanding sensitivity is used: the Chemiluminescence (CL) approach provided by ACL Instruments AG and the differential isoconversional kinetic approach provided by AKTS AG is therefore of great benefit to measure, to understand and to predict the oxidations behaviour of organic solids and liquids.

Catalytic active transition metals

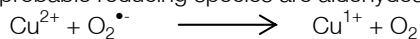
Transition metals (e.g. copper, iron, manganese, cobalt, nickel etc.) are well known to promote the oxidation of organic substances. This effect is due since transition metals support the electron transfer of redox reactions and act so as pro-oxidants.

Common examples are cable insulations, iron gall ink manuscripts, blister packaging (aluminium foil of pharmaceuticals), electronics, metallic fillers etc.

The mechanism promoting the electron transfer is the *Haber Weiss* cycle:



Other probable reducing species are aldehydes or superoxides:



Materials and testing conditions

In the present leaflet we report on the characterization of degradation in natural rubber films (NR, 0.1mm thickness) with the Chemiluminescence approach: the material is unstabilized and contaminated with low concentrations of metallic copper (0,05% wt/wt, PVD-coated). The oxidation of the substance is followed by the chemiluminescence (CL) emission directly from the solid state sample. The data acquisition was performed under non-isothermal conditions from 35°C to 150°C applying four different heating rates (0,1..0,01K/min) in synthetic air atmosphere (flow = 30ml/min) applying glass crucibles.

Kinetic parameters were visualised in the Arrhenius diagram and by applying the differential isoconversional analysis according to Friedman. From this the Arrhenius parameters are obtained as a function of the oxidation's conversion. The evaluation with the kinetic parameters quantifies the essential reduction of the activation energy levels. Tests on other substances demonstrate the high potential of the Chemiluminescence approach for specific applications like other technical goods, foodstuff, energetic materials, specialty chemistry, pharmaceuticals etc.

CL data

The resulting data are depicted in fig. 1 and 2:

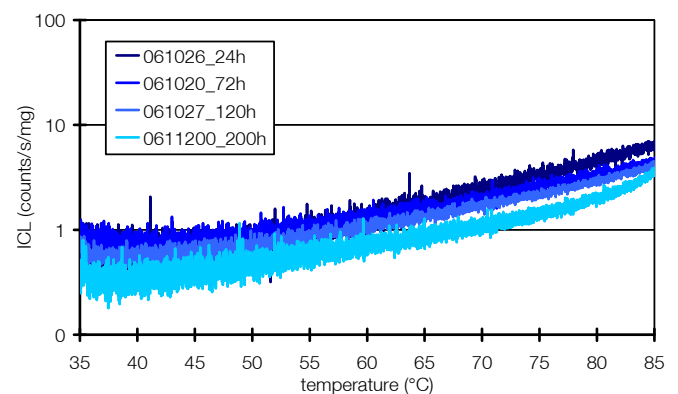


Fig 1: oxidation behaviour of natural rubber (uncontaminated) characterised applying different non-isothermal temperature profiles.

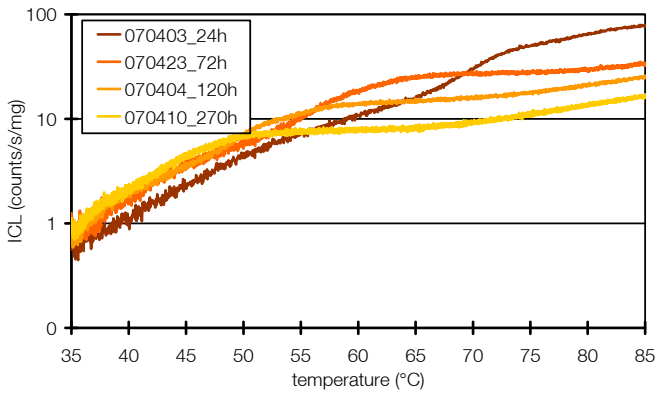


Fig. 2: oxidation behaviour of PVD-coated natural rubber (copper, 0,05% wt/wt) tested at identical conditions like data depicted in Fig. 1.

It is obvious that the oxidation reaction curve shape is completely different between the two test series depicted in fig. 1 and 2: there is a significant change in the reaction mechanism and rate due to the presence of small amounts of metallic copper.

Simple Arrhenius kinetics

Translating the experimental data to the Arrhenius diagram and construct tangential lines to the curve shape at the moderate temperature profile (e.g. the beginning of the experimental data; right side since the inverse temperature is applied in the Arrhenius diagram) elucidates the different reaction kinetics appearing:

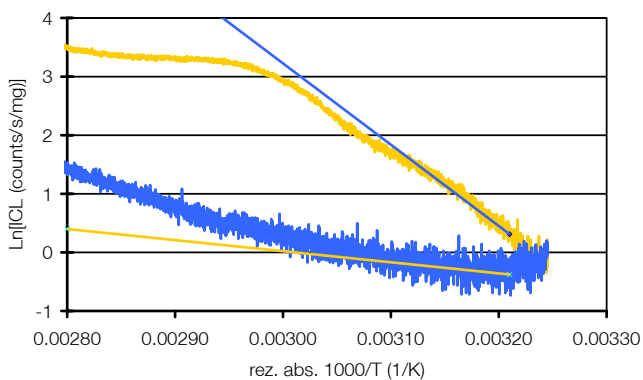


Fig. 3: Arrhenius diagram depicting one experiment of each test series (heating rate of the two experiments was 0.03K/min). The following activation energies were obtained from the calculation of

the slope of the tangential lines: 110..115kJ/mol (uncontaminated NR) and 20..25kJ/mol (copper-contaminated NR).

Advanced isoconversional kinetics

Applying differential isoconversional kinetics to analyse the activation energy parameters depending on the oxidation reaction's progress, the shelf life may be predicted in a very accurate way.

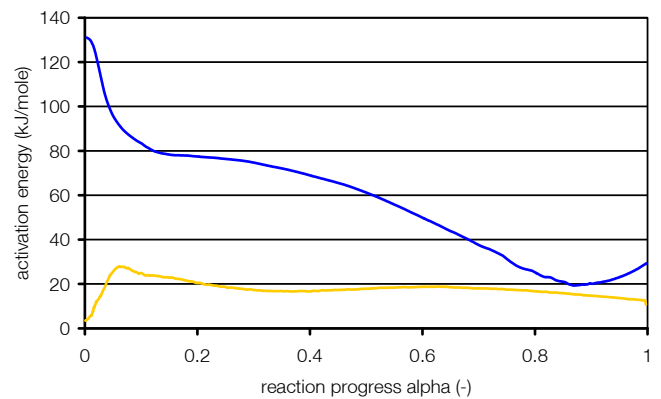


Fig. 4: Activation energy parameters (the blue curve represents the uncontaminated natural rubber, the orange curve represents the copper contaminated natural rubber) as a function of the oxidation reaction's progress calculated applying differential isoconversional kinetics.

Conclusion

The presence of small amounts of transition metals (e.g. impurities or only the contact to such elements) results to the catalysed decay of hydroperoxides (the lifetime or ROOH in the presence of transition metals drifts to zero). Due to this fact, the oxidation's kinetics is completely different. The service life time of organic substances in contact or contaminated with transition metals is reduced dramatically if such substances aren't stabilised adequately (e.g. by the addition of chelate building agents).

Applying the CL method in combination with advanced kinetics, the shelf life of complex systems and stabilisation measures may be analysed in a very sophisticated way representing realistic service and storage conditions.