

Stress Relaxation · Chemiluminescence · Thermal-oxidation · Ageing · Life-time Prediction · Natural rubber

The durability of NR-based elastomer material has been examined by stress relaxation and chemical analytical methods in order to investigate the impact of chemical ageing on relaxation processes. The secondary relaxation process, which is derived by separation from the stress relaxation curve, is found to be closely related to the oxidation induction time detected by chemiluminescence. It is suggested that thermal exposition during the initial phase of stress relaxation is mainly due to rearrangement of the filler network and polymer-filler interactions.

Der Einfluss der Oxidation von Polymerketten auf die Spannungsrelaxation von NR-Elastomeren und Lebensdauervorhersage

Spannungsrelaxation · Chemilumineszenz · Thermo-oxidation · Alterung · Lebens-dauervoraussage · Naturkautschuk

Die Lebensdauer von NR-basierenden Elastomermaterialien wurde mit Hilfe von Spannungsrelaxation Untersuchungen und unterschiedlichen chemisch-analytischen Methoden verfolgt. Die durch Kurvenanalyse identifizierte sekundäre Relaxationszeit, die aus der Relaxationsdiagramm berechnet wurde, entspricht der Oxidationsinduktionszeit (OIT), die über die Chemilumineszenz-Methode bestimmt wurde. Weiterhin wird gezeigt, dass die mechanisch thermische Belastung während der Anfangsphase der Relaxation, vor allem die Füllstoff-Füllstoff und Polymer-Füllstoff Wechselwirkung beeinflusst.

The Impact of Chain Oxidation on Stress Relaxation of NR-Elastomers and Life-Time Prediction¹

The prediction of component life-time is always at the forefront of product development the elastomer industry. Its importance has grown in the past decade not only due to the increased demand for high quality components but also the stringent requirements of product safety in service through law enforcement. A standardised physical stress relaxation test is commonly employed for this purpose. Stress relaxation occurs when a constant strain is applied to a sample and the counterforce exerted by the test piece decreases with time. The cause of stress relaxation may be physical or chemical and under normal conditions both processes can occur simultaneously [1]. They contribute to the complex ageing processes that influence the life-time of elastomers.

Life-time prediction is commonly carried out by applying the time-temperature superposition/WLF principle and Arrhenius concept, as described in the ISO standard 11346:2004. Both approaches utilize the temperature dependency of the stress relaxation processes. Therefore, extrapolation can be made to lower temperatures. The temperature dependency of the physical relaxation process has been found to comply well with the WLF equation, whereas the Arrhenius concept fits well to the chemical processes [2]. After investigating the credibility of both methods the WLF concept revealed a pessimistic estimation while the calculation of the Arrhenius concept provided grossly optimistic values [3]. This finding motivated further studies for the development of a separation method using spectral analysis and/or numerical fitting where critical relaxation times are calculated. Having found the relaxation times at elevated tempera-

tures extrapolations and subsequent life-time predictions at lower temperatures can be made using a modified Arrhenius concept. This analysis method is capable of recognising and separating both physical and chemical processes. From the activation energy calculation, the chemical process is found to be more temperature sensitive compared to the physical one [4].

As there is still insufficient information to characterise the chemical processes occurring in stress relaxation it is the aim of this paper to make a comparison between the stress relaxation and chemical analytical methods, i.e. chemi-luminescence (CL) and infrared spectroscopy, also in term of activation energy and life-time analysis. CL has been used to monitor the thermal oxidation behaviour of rubber and elastomers, particularly the initial stage and the kinetics of the reaction. The beginning of oxidation can be used as a parameter to determine the life-time of the product at a certain temperature [5]. Moreover, infrared spectroscopy is also utilized as a versatile method for investigating the oxidation stages. This may lead to a brief understanding of the processes during stress relaxation.

Stress relaxation processes

If a rubber sample is deformed under constant strain the reaction force exerted by the test piece decreases over time. This behav-

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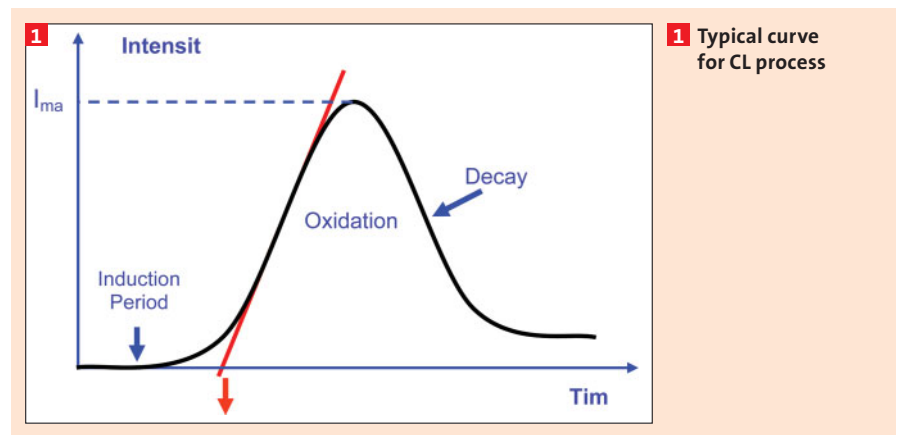
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our is called “stress relaxation”. Stress relaxation measurements may be made in compression, tension or shear, compression testing being the most important for materials used in seals and gaskets. The causes of stress relaxation may be physical or chemical and under normal conditions both processes can occur simultaneously. Physical relaxation is linked with the reorientation of molecular crosslinks under strain with disengagement and rearrangement of crosslink chain entanglements, including movements of free chain ends. Additionally, in filled elastomers, it is associated with the breaking of physical bonds due to secondary valence forces between filler particles (filler crosslink) or chains and filler particles (polymer-filler interaction). Consequently, the strain history of the material may also be influential. Initially these processes are comparatively fast (varying between a few milliseconds and a few seconds) and decelerate with time to produce a transitional plateau. Physical relaxation depends on the mobility of the polymer chains and the temperature of use. The proximity of the service temperature to the glass transition temperature T_g is generally the dominant factor in determining physical relaxation rates. Thus physical relaxation rates are high at high temperatures when molecules become more mobile. The temperature dependence complies well with the William-Landel-Ferry (WLF) equation [6]. The crosslink density of the elastomer can have some effect on the relaxation rate where increased crosslink density leads to a lowered relaxation rate. Since fillers cause additional relaxation mechanisms filled elastomers can give rise to higher physical relaxation rates. At high temperatures and long times chemical processes can overlap the physical relaxation. The main mechanisms which cause chemical

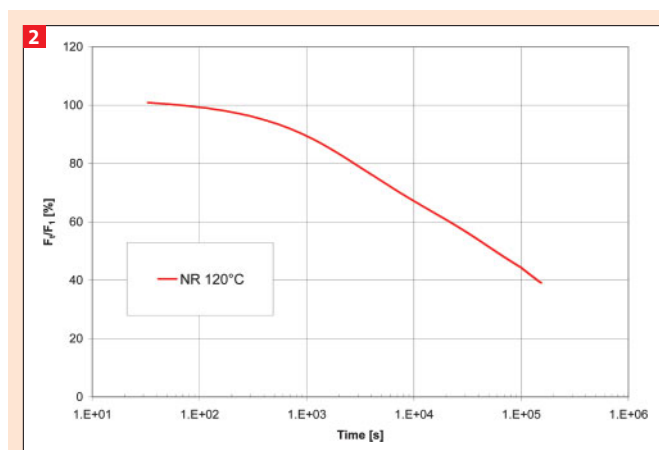


changes are oxidative reactions of the polymer chains or modification of crosslink structure. Chain scission decreases the crosslink density producing free ends with released stress. The release of stress may be caused by the breaking of crosslinks producing longer strands and lessening entanglements (reducing of physical crosslink density) [2].

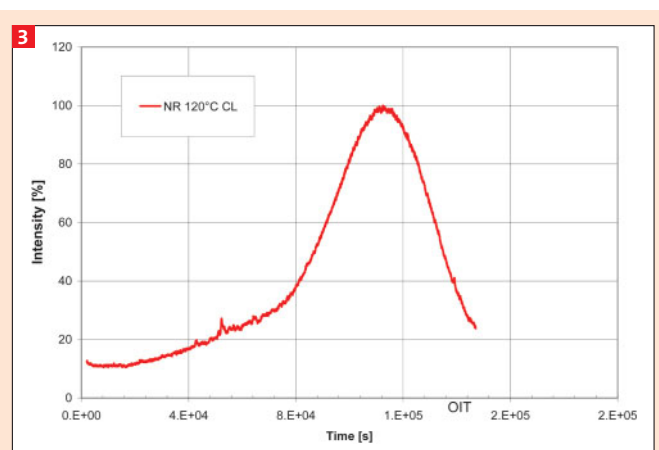
Characterisation of thermal oxidation reaction using chemical analysis

The fundamental mechanism of thermal oxidation reactions of polymers is recognised as radical formation due to heat, UV-light or shear. The termination of alkyl peroxy radicals form a highly energetic triplet carbonyl species before singlet molecular oxygen and the typical oxidation reaction products (epoxide, carbonyl or carboxyl groups) are generated in the excited state. Photon will be emitted if these products return to the ground state. This phenomenon is called chemi-luminescence (CL) and can be employed to characterise the thermal oxidative reaction of polymer materials, particularly concerning the initial stage of the reaction and the kinetics of the reaction [7]. This

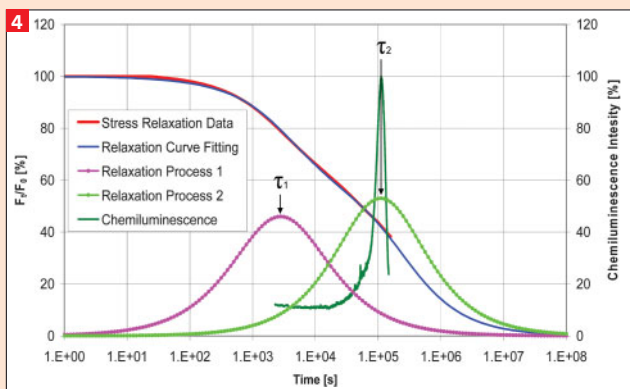
method has recently been validated and employed for analysing the thermal oxidative behaviour of rubber and elastomers [8,9]. The beginning of the oxidation reaction is indicated by the sharp increase in intensity and, thus, the detected CL signal. This signal normally shows a sigmoid form as seen in Figure 1. The intersection between the base line and the linear elevation line is referred to as the “oxidation induction time” (OIT) indicating the initialisation of the oxidation reaction. After the maximum intensity is reached the reaction abates until it finally ends. The OIT is indicating the initial stage of irreversible failure of the polymer material due to the thermal oxidation reaction. As the OIT describes the failure parameter of materials the temperature dependency of OIT can be used to determine the durability of materials by employing an Arrhenius plot. Using the attenuated total reflectance (ATR) method by infrared spectroscopy it is possible to investigate the extent of oxidised solid materials particularly for rubber and elastomers. In previous studies, it has been shown that the coupling of CL with IR gives further information about the generation of typical



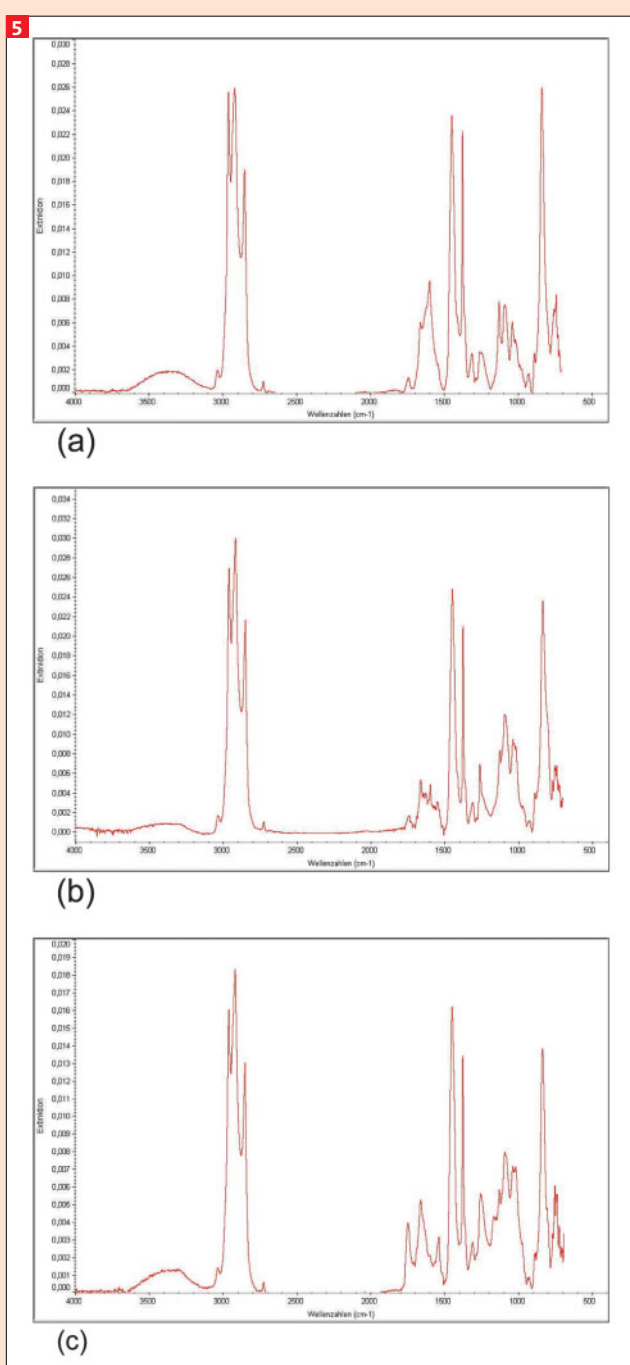
2 The stress relaxation curve of cured NR at 120 °C



3 Chemiluminescence curve of cured NR at 120 °C



4 Stress relaxation fitting and the correlation with CL signal of cured NR at 120 °C



5 Stress relaxation diagram of cured NR at 120 °C in correlation with infrared spectra of NR after (a) 0 hour, (b) 18 hours and (c) 36 hours

oxidation products after OIT and quantitatively measure the decrease of double bond concentration in the polydiene chain [9].

Experimental part

Materials and sample preparation

The compound investigated was a conventionally vulcanised natural rubber (Table 1). The components were mixed in an internal mixer followed by two roll mill and then pressed in 6mm and 2 mm thick plates according to t_{90} . The plates are then cooled for the specified duration (ISO 3384).

Continuous stress relaxation (CSR)

The 6mm thick plate is cut into cylindrical samples, $d = 13$ mm, using a rotating hole-cutter. The sample is subjected to CSR under 25 % constant strain. CSR experiments were performed in an Elastocon™ relaxation tester (EB02) in accordance with ISO 3384:1999. Before each test samples are mechanically and thermally conditioned in order to improve repeatability. Each material was tested at 150 °C, 120 °C, 100 °C and 70 °C.

Chemiluminescence (CL)

A 2 mm thick sample on an aluminum pan is placed into a tightly sealed cell oven. A lens covering the sample focuses the light emission. The analysis is carried out under low oxygen flow atmosphere (gas pressure: 6.9 ± 2.0 kPa) at 150 °C, 120 °C, and 100 °C. The light emission is detected by the highly-sensitive photomultiplier tube (PMT) which has to be calibrated with a constant radioactive standard intensity (approximately 10 μ C).

Infrared spectroscopy (IR)

After a certain period of stress relaxation the sample is conditioned again at standard pressure and room temperature. The sample is then cut into approximately 1 mm thick slices. Both the centre and edge surface were analysed by IR. Attenuated total reflectance (ATR/FTIR) is the method used for this analysis.

Results and discussion

Comparison between stress relaxation and chemical analytical methods

Stress relaxation experiments were carried out on cured NR samples. As shown in Figure 2 the results are represented by a graph of stress relaxation ratio F_t/F_0 , where F_t is the force at a given time t and F_0 is the force after 60 seconds, against the logarithm of time in seconds (s). Typically, the semi-logarithmic curve does not show a monotonic decrease

but can be separated into individual processes. The primary relaxation process follows a logarithmic (straight line) regression at low temperatures and lower times. The secondary process is seen as an accelerated decrease at high test temperatures.

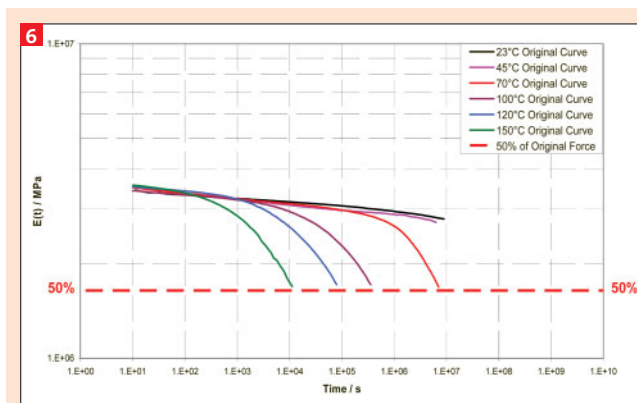
In parallel, chemiluminescence (CL) analyses are carried out for similar samples at identical test temperatures. The resulting CL curve can be seen in Figure 3. The OIT is determined by the intersection of the baseline and the linear increase of the curve.

The stress relaxation behaviour of cured NR is compared with CL analysis and infrared spectroscopy in order to corroborate the relaxation processes as physical relaxation or chemical ageing. The fitting of a stress relaxation curve produces in two relaxation times (τ_1 and τ_2) as depicted in Figure 4.

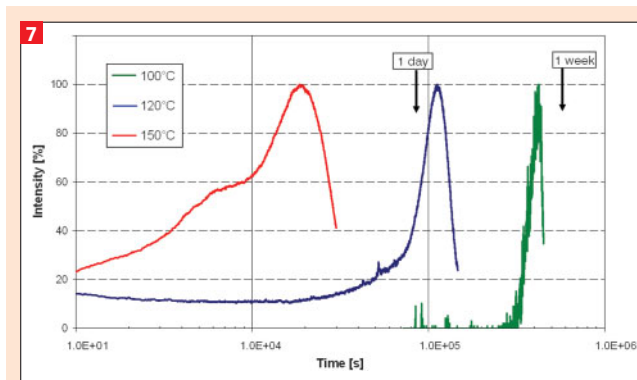
The primary relaxation process may be caused by thermal exposition which leads to physical relaxation. Furthermore, chemical ageing processes dominates the secondary relaxation process. As seen in Figure 4 the OIT value determined by the CL signal of cured NR overlaps the second relaxation process (τ_2) of the stress relaxation diagram at approximately 19.5 hours. The similarity of OIT and τ_2 shows that the second relaxation is influenced mainly by thermal oxidation reactions. At this time the oxidation reaction begins, leading to the irreversible chain deterioration and extreme drop in the stress relaxation curve.

However, a closer look at the diagram shows that, under mechanical stress, the oxidation process is triggered at a slightly shorter time. To cross check this result the cured NR sample was removed from the stress relaxation test after 18 hours (before the OIT) and after 36 hours (following the OIT). The samples were then subjected to infrared spectroscopy investigations to analyse the oxidation state of the system. The oxidation state is determined by observing the evolution of typical bands for oxidation products such as carbonyl band (1720 cm^{-1}), hydroxyl band (3500 cm^{-1}) or ether band (1500 cm^{-1}). Figure 5 provides the IR spectrum of the cured NR system, at the reference time (a), after 18 hours (b) and after 36 hours (c).

It can be well observed that after 18 hours of stress relaxation there is no hint of oxidation reaction. The spectra remain the same as the reference indicating that at this stage, oxidation has not yet begun. After 36 hours of stress relaxation, i.e. after the OIT point, the typical bands for oxidation can be clearly observed. There is a growth of carbonyl band at 1720 cm^{-1} and also ether functional group at



6 Temperature dependency of stress relaxation curve of cured NR



7 Temperature dependency of CL signals of cured NR

1500 cm^{-1} . This indicates that at this point the oxidation reaction has already begun.

Lifetime prediction

The lifetime prediction is approached by the calculation of the temperature dependency of OIT and relaxation time according to the Arrhenius equation. As illustrated in Figure 6 the stress relaxation behaviour of elastomers is highly dependent on the temperature. The relaxation time, whether τ_1 or τ_2 , is thus also temperature dependent. As mentioned previously the relaxation times are calculated through a fitting procedure. The calculated relaxation times at elevated temperatures are shown in Table 2. At 150°C τ_1 and τ_2 are approximately 0.5 hours and 4 hours respectively. On the other hand, at 70°C τ_1 and τ_2 increased by a factor of 43 and 250 respectively. The incremental increase of τ_2 due to higher temperature is significantly greater than for τ_1 .

The dependency of temperature is also observed by chemiluminescence. As displayed in Figure 7 the OIT values from the CL signal are shifted to the left as the temperature increases. The OIT values of cured NR at 100°C , 120°C and 150°C are approximately 75, 20 and 3 hours respectively.

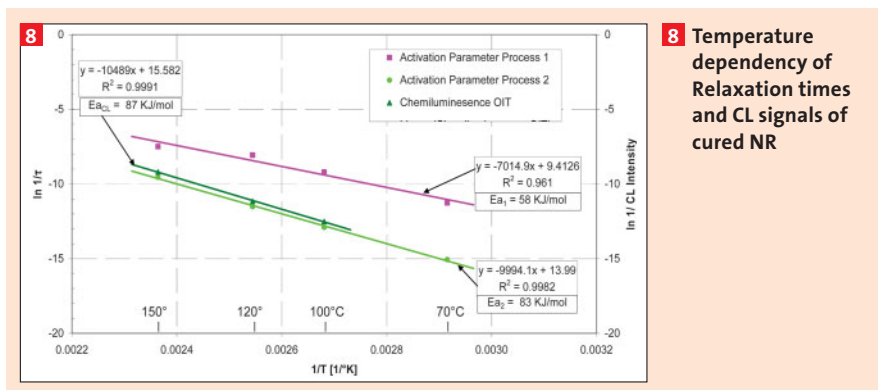
A plot of temperature against relaxation time and OIT is depicted in Figure 8. It clearly shows that the OIT at certain temperatures is closely related to the secondary relaxation time τ_2 . This verifies that, according to the Arrhenius equation, the activation energy of the secondary relaxation processes and the initialisation of thermal oxidation reaction is also analogous (approx. 85 kJ/mol). This result justifies again the dominance of thermal oxidation reactions in the secondary relaxation processes. On the other hand, the primary relaxation process has a lower activation energy of approx. 60 kJ/mol , indicating that this process is less temperature

1 Composition of elastomer sample mixtures

Ingredients	Amount (phr)
NR/RSS1	100
ZnO	5
Stearic acid	1
CBS	1
Sulphur	2.4

2 τ_1 and τ_2 data from stress relaxation curve of cured NR at elevated temperatures

Temp [$^\circ\text{C}$]	τ_1 [s]	τ_2 [s]
70	78 000	3 500 000
100	10 000	400 000
120	3 200	100 000
150	1 800	14 000



sensitive than the secondary process. By applying the equation derived from each process the value of OIT, τ_1 and τ_2 at lower temperatures and more importantly longer times can be predicted, as shown in Table 3. It must be bourn in mind that these values are not actual lifetime prediction values. This shows that the deterioration of materials during the second relaxation process is attributed to the thermal oxidation processes.

3 τ_1 , τ_2 and OIT prediction

Temp [°C]	τ_1 [hr]	τ_2 [hr]	OIT [hr]
23	* 445	* 107491	* 116439
45	* 86	* 10397	* 10032
70	22	972	* 906
100	3	111	75
120	1	28	20
150	1	4	3

*: extrapolated values

Conclusion

Stress relaxation as a widely utilised method for life time prediction is influenced by both physical processes and chemical ageing. The chemical ageing, mainly due to thermal oxidation processes, is verified by chemiluminescence (CL). The OIT values of CL analysis which indicate the start of oxidation correspond very well to the critical relaxation times of the secondary fitting of stress relaxation. The primary relaxation process, on the other hand, is mainly influenced by physical changes as justified by infrared analysis. It is suggested that thermal exposition during the initial phase of stress relaxation is due mainly to rearrangement of the filler crosslink, polymer-filler interaction in addition to the scission and rearrangement of sulphur crosslinks.

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