

EPDM · aging · low field NMR · transverse relaxation time · inverse Laplace transform

With regard to the long-term stability of seals, “stress-relaxation” testing is known to deliver important information. The mechanism of stress relaxation is, however, difficult to interpret, as several effects take place simultaneously, with each effect itself dependent on external and internal parameters. This paper draws on a combination of stress relaxation experiments and low field NMR measurements. NMR relaxation curves as a function of aging time were analyzed using inverse Laplace transform. The resulting distributions of transversal relaxation times (T_2) shows that during thermal oxidation the network structure and the chain mobility of cured EPDM, with and without carbon black filler, changes differently.

Analyse des Alterungsprozesses von EPDM-Elastomeren durch Niedrigfeld-NMR mit Inverser Laplace Transformation und Spannungsrelaxationsmessungen

EPDM · Alterung · Niedrigfeld NMR · Transversale Relaxationszeit · Inverse Laplace Transformation

Spannungsrelaxationstests liefern wichtige Informationen bezüglich der Langzeitfunktion von Dichtungen. Allerdings ist der Mechanismus der Spannungsrelaxation komplex, da mehrere Vorgänge gleichzeitig ablaufen. Für die Untersuchungen wurde eine Kombination von Spannungsrelaxationstests und Niedrigfeld-NMR-Experimenten verwendet. Die transversalen Relaxationszeiten (T_2) wurden als Funktion der Alterungszeit mit Inverser Laplace-Transformation analysiert. Das Spektrum der transversalen (T_2) Relaxationszeit zeigt, dass sich während der thermisch-oxidativen Alterung die Netzwerkstruktur und die Mobilität der Ketten vulkanisierter EPDM-Proben mit und ohne Füllstoffen unterschiedlich ändert.

Figures and Tables:
By a kind approval of the authors.

The analysis of Aging Processes of EPDM Elastomers using low field NMR with Inverse Laplace Transform and Stress Relaxation Measurements

1. Introduction

The end of a seal's life is reached when a leakage is observed. Up to the point at which leakage actually occurs, materials gradually degrade due to several factors, such as mechanical fatigue or chemical processes. In terms of static applications, the life of a seal is largely determined by the pure thermal or thermal oxidative aging process. It is, therefore, important to continuously improve the aging resistance of elastomeric materials. For this reason, several studies have been conducted to understand and analyze the aging process of rubber. Generally, it is well known that the main reactions in the presence of oxygen are radical reactions via peroxy radicals and the abstraction of hydrogen from the polymer chain. The macro radicals generated can further react by crosslinking (recombining) or by chain scission. The two mechanisms compete with one another, depending on the polymer structure and on environmental parameters like oxygen and temperature. Macroscopically, the different reactions result in the rubber becoming brittle or soft and sticky. [1-3].

Thermal oxidative aging of rubber under static conditions as a function of polymer structure is subjected to detailed investigating, using, for example, chemiluminescence as a powerful tool, with quantification of the effect of the content of C=C-double bonds in the main chain and of the ratio between vinyl-, styrene- and 1,4-butadiene units in SBR. [4-9]. There has been scarce investigation of the influence of crosslinking and of fillers on the thermal-oxidative aging of sulfur-cured NR-SBR-systems and peroxide crosslinked EPDM focusing on i) the characterization of the chemiluminescence method for accelerated aging, ii) the temperature dependency and kinetic aspects of thermal-oxidative aging, iii) the influence of accelerators from sulfur crosslinking and their reaction products on oxidative aging, iv) the influ-

ence of peroxide crosslinking, with variation of peroxides and tempering processes, and (v) the effect of fillers [10].

Concerning the aging stability of nitrile rubbers, the positive effect of compound components with a base character and the effect of replacing the tertiary C-atoms at the nitrile substituted position in the chain with a methyl group is investigated in detail with respect to the chemical mechanism. [11] An interesting question, which several studies answer in a generally controversial way, is, in particular, the role of the nitrile group. [12]

For lifetime evaluation of seals, it is helpful to perform mechanical stress relaxation testing that correlate crosslink structural changes as reflected in stress relaxation data with theoretical elasticity theory. Low field NMR is a useful tool in determining transverse relaxation times (T_2) as a means of characterizing changes in polymer chain mobility so as to arrive at a better understanding of

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mechanical thermal-oxidative aging processes in elastomers at a molecular level.

Low field NMR has, in the meantime, established itself as a valuable method for analyzing the crosslink density of elastomers, crosslink density having a major influence on chain mobility, and for analyzing filler-polymer interaction. [13-21] The main purpose of this paper is to provide a better understanding of stress relaxation processes. The correlation between mechanically measured stress relaxation and low field NMR data will yield a more precise insight into the structural changes induced by aging processes in vulcanized EPDM with fillers.

2. Theoretical aspects of stress relaxation and material aging processes

When a constant strain is applied to a material, the counterforce typically decreases as a function of time, a behavior referred to as „stress relaxation“. There are physical as well as chemical causes for stress relaxation. In the case of mechanical deformation, the two processes can occur simultaneously. Irreversible chemical changes in the network structure occur, in particular, when rubber samples exposed to air (oxygen) experience constant elongation or compression at high temperatures. Upon removal of the stress the rubber specimen is incapable of returning to its initial state, a phenomenon referred to as “permanent set”. This is due mainly to a change in the network structure during deformation. Tobolsky’s two network theory describes the mechanism of permanent set taking into consideration structural changes. [22] The original network structure is said to degenerate due to polymer chain scission, with new crosslink structures formed via radical reactions occurring during deformation. [22-24] Fig. 1 gives an overview of the aging process of a polymer, taking into special account network changes occurring in combination with mechanical stress.

As organic and inorganic fillers are widely used to improve the physical properties of elastomeric compounds, it is worth knowing something about the effect of fillers on the aging process. Despite broad discussions on the effect of carbon black on the aging process to date a comprehensive theory has not yet been established. Several of the conclusions drawn are contradictory due to the complexity of the carbon surface morphology, as described below. On the one hand, P. J. Hart et al. suggest that carbon

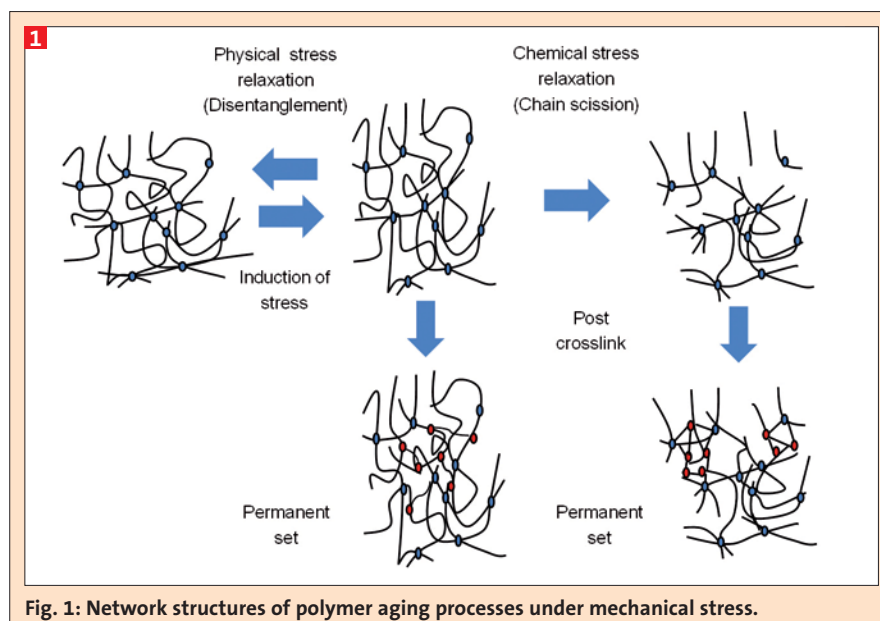


Fig. 1: Network structures of polymer aging processes under mechanical stress.

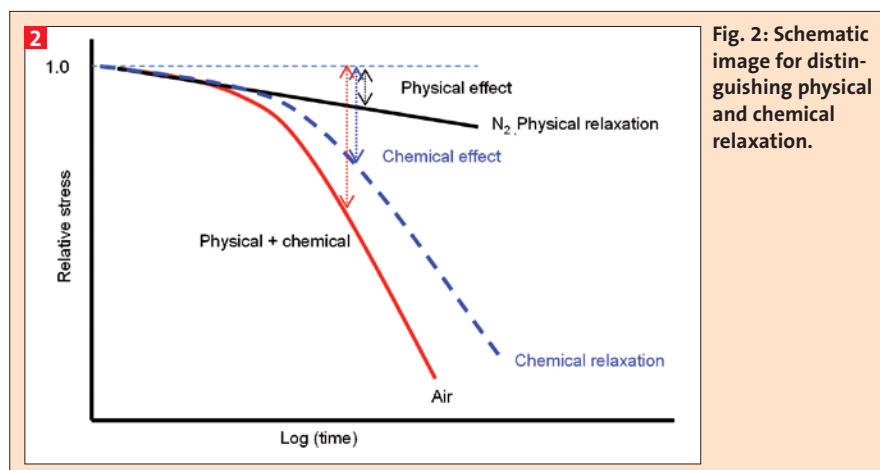


Fig. 2: Schematic image for distinguishing physical and chemical relaxation.

black has the effect of promoting thermal oxidation in that its surface is capable of adsorbing oxygen, which is then released into the rubber, subsequently accelerating the autoxidation of the polymer. What is more, a large specific carbon black surface area results in a higher rate of oxidation due to the higher oxygen absorption capacity. [25] On the other hand, M.-J. Wang et al. describe an antioxidant effect of carbon black. [26] The mechanism can be attributed to the surface chemistry of carbon black. The radicals generated by thermal oxidation and chain scission are stabilized by chemical functional groups on the carbon black surface.

Kozminski et al. note that the effect of the carbon black surface on thermal oxidation is that of both a catalyst and an antioxidant. These effects depend on the mixing process, the amount and type of filler and the polymer. [27] In other

words, the aging mechanism should be considered on a case-by-case basis. The regression of stress in air is determined, moreover, by the simultaneously occurring physical and chemical relaxations. Several approaches have been proposed for distinguishing physical and chemical relaxations. [28-31] An approach proposed by Murakami is to compare the stress relaxation curve in N_2 atmosphere and in air (oxygen). [28] The stress relaxation in N_2 can be interpreted as physical relaxation due to chain disentanglement. The additional chemical relaxation takes place due to the chain scissions of crosslink networks. Relaxation in air can thus be understood as a combination of chemical and physical relaxations. The schematic diagram in Fig. 2 shows this approach for distinguishing the different influences on stress relaxation.

Overall, aging in conjunction with stress relaxation is a complex process. To

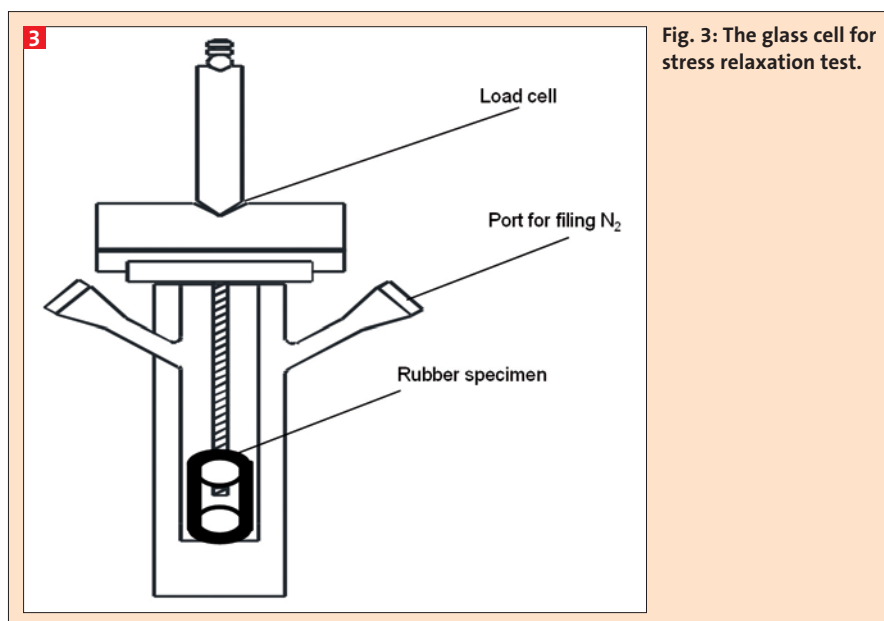


Fig. 3: The glass cell for stress relaxation test.

ginal length. Sample geometry was a ring of 1 mm thickness and 52.6 mm diameter. Fig. 3 shows the cell used for the mechanical stress relaxation tests. Immediately prior to start of testing, the cell is stored in the oven for 30 minutes at the desired temperature and under no stress condition. The specimens are then stretched to a specific elongation ratio and the force is recorded. In the case of measurements in a Nitrogen atmosphere, N₂ was filled into the cell at a flow rate of 200 ml/min during the first 5 minutes, then the flow rate was set to 100 ml/min.

4.2.2 Low field NMR with inverse Laplace transform

Cured aged and unaged as well as uncured samples were measured by NMR. The NMR experiments provide information on chain mobility [14, 19, 20, 21, 33-38], which depends on the constitution and configuration of the polymer, on molecular mass and on crosslinking density. As these are the very properties that can be altered by aging reactions, material aging can also be tracked with the help of NMR measurements.

The analysis of the molecular dynamics is based on the measurement of the relaxation of the transversal magnetization caused by the spins of the 1H nuclei that are part of the polymer chains. The relaxation properties are strongly influenced by the dipolar interaction of 1H nuclei. The strength of this dipolar interaction depends on the molecular mobility. The relaxation of the transversal magnetization is measured by the well-known Hahn-Echo-Sequence. This type of sequence cancels out effects of field inhomogeneities and chemical shifts. So the signal is mainly influenced by dipole-dipole-interactions. In the presence of a static magnetic field the Hahn-Echo-Sequence uses two high frequency pulses (90° and 180°) separated by the time interval τ . After a time period $2 \cdot \tau$ the specimen responds with an echo that is detected via an antenna, amplified and digitized. The magnetization is plotted as function of time ($2 \cdot \tau$). Typically, the signal intensity decreases mono- or multi-exponentially or in accordance with a Gaussian-shaped function or combinations thereof. The time constant determining the decay of the curve from spin-spin interaction is denoted as transverse T₂'-relaxation time, as described above. Basically, the smaller the T₂ value, the less mobile the polymer chain. The low

1 Formulas of compounds				
	Unfilled phr	low active phr	middle active phr	high active phr
EPDM (4,7 % ENB)	100	100	100	100
CB N990 ¹⁾	-	50	-	-
CB N550 ¹⁾	-	-	50	-
CB N343 ¹⁾	-	-	-	50
DCP ²⁾	3	3	3	3

1) N₂-adsorption number of carbon blacks (CB) used:
N 990: 9 m²/g (MT); N 550 (GSO): 43 m²/g; N 343: 99 m²/g (IISAF)
2)DCP: Dicumylperoxide

arrive at a better and deeper understanding of aging mechanisms, it is therefore useful to improve available methods or to combine several supplementary methods.

4. Experimental part

4.1 Sample preparation

EPDM is one of the most widely used synthetic elastomers in the production of sealing parts in general industrial and automotive applications. The polymer selected was an EPDM type with an ethylidene norbonene (ENB) content of 4.7% as diene component (EPT3045, Mitsui Chemical). 3 phr of dicumylperoxide and

different types carbon black of varying specific surface were incorporated by means of a 10-inch open roll. Plates of 2 mm thickness were vulcanized in a press at 180°C for 6 minutes, corresponding to t₉₀, as determined by rheometry corresponding to DIN 53529. Table 1 shows the compound formulation. Aging was performed under air or N₂ at 150°C.

4.2 Methods Used

4.2.1 Continuous stress relaxation

Stress relaxation experiments have been performed at 150°C in air and in N₂ atmosphere for 24 hours according to ISO 6914. The elongation ratio was kept at a constant level of 20% relative to the ori-

2 Parameters for measurement	
Parameter	value
Equipment	Bruker Minispec mq 20 NMR time domain spectrometer
Resonance frequency	19.2 MHz
Pulse sequence	Hahn Echo
Temperature T in °C	100 or 150
Scans	40
Recycle delay in ms	1.0

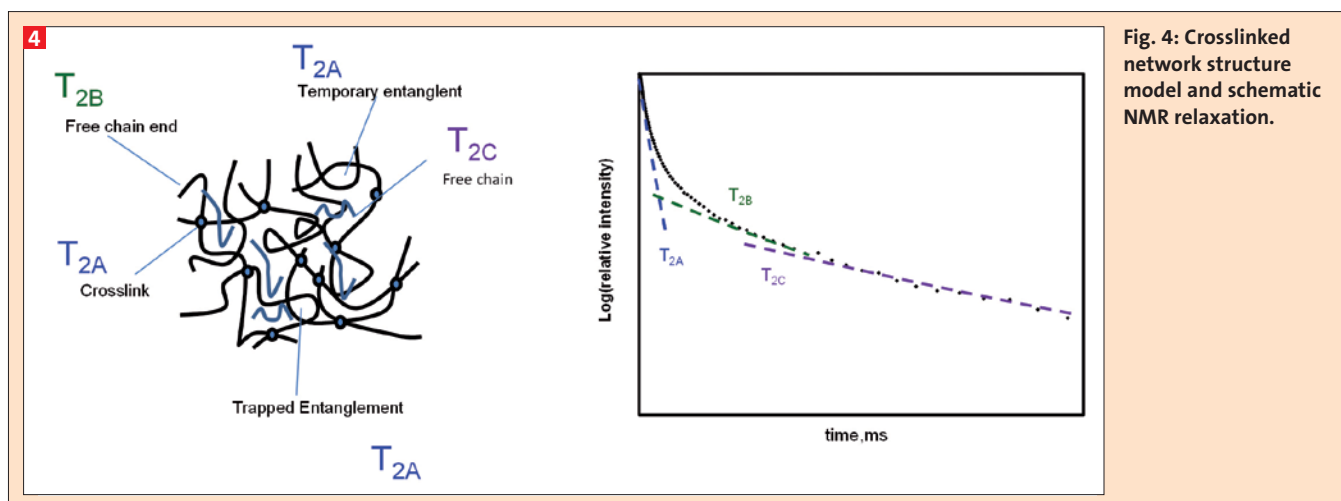


Fig. 4: Crosslinked network structure model and schematic NMR relaxation.

field ^1H NMR relaxation measurements for determination of the transverse relaxation time T_2 were performed using the parameters listed in Table 2:

Since in this study not only unfilled polymers but also carbon black filled systems are investigated, the effect of the carbon black itself on the NMR signal has to be considered. The effect of these and their influence on the reliability of relaxation measurements have been critically discussed in several studies [13-18]. An important aspect in this respect is the paramagnetic nature of carbon black acting as an additional magnetic field source and leading to inhomogeneities in the magnetic field. The following equation (1) describes the relationship between theoretical T_2 , experimentally determined T_2^* , and the inhomogeneity of the field (ΔB_0), with γ standing for the nuclear gyromagnetic ratio. In reality, experimental decay is faster than theoretical computations would predict [32].

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{\gamma \Delta B_0}{2} \quad (1)$$

This effect can, therefore, be said to get stronger with increasing relaxation time T_2 . Nevertheless, most studies investigating carbon black filled systems have used free induction decay (FID) or solid echo pulse sequences. In our context these methods have a strong disadvantage against the Hahn-Echo-sequence used in this study. They do not allow refocusing of the spins in order to cancel out the effect of magnetic field inhomogeneities. Therefore the paramagnetic effect of carbon black gives rise to the modifications of relaxation times reported in literature. By applying the Hahn-Echo-sequence we are able to ensure

that carbon blacks' paramagnetic effect is not influencing the results presented here.

The conventional way to analyse the NMR signals for polymers showing only exponential relaxation in the investigated time frame is the multi-exponential approach. For example a bi-exponential function was used by Folland et al. [33, 34] for cured poly-isoprene.

$$M(t) = A_1 \exp\left[-\frac{t}{T_{2A}}\right] + A_2 \exp\left[-\frac{t}{T_{2B}}\right] \quad (2)$$

In essence, instead of one T_2 -value several T_2 values resulting from the multi-exponential approach can be related to different rubber structures with different mobility as shown in Fig. 4 [33, 34].

In the aforementioned studies, T_{2A} was attributed to the network phase, such as chemical crosslinks and physical entanglements. T_{2B} is associated with the non-network phase – chain ends, for instance. In the case of raw polymer, the molecular weight can influence chain mobility due to the presence of chain entanglements. In addition, the inverse of T_{2A} is closely related to the crosslink density determined by the swelling method.

The multi-exponential approach mentioned above has got some significant drawbacks. First, if the approach consists of more than two exponential terms the application of standard fit algorithms is critical since the results usually depend extremely on the starting conditions. For instance, a three-exponential approach consists at least of 6 fit parameters, however the NMR relaxation curve is just a simple shaped monotonically decreasing curve, so the fit results are usually not well-defined. For rubber,

especially when analyzing the aging properties, at least three or four different structure types with different molecular mobility and different relaxation times as shown in Fig. 4 have to be taken into account, so a bi-exponential approach is not adequate.

Second, when applying a multi-exponential approach you have to know in advance how many different structure types are contributing to the relaxation curves.

A powerful alternative to the multi-exponential approach is the Inverse Laplace Transformation (ILT).

$$M(t) = \int_0^\infty L(\tau) F(t, \tau) d\tau \quad (3)$$

Here $M(t)$ stands for the experimental NMR data, $L(\tau)$ for the distribution function, which has to be determined, and $F(t, \tau)$ for the kernel function, in our case

$$F(t, \tau) = e^{-\frac{t}{\tau}} \quad (4)$$

The integral shown above is a Fredholm integral of the first kind. Unfortunately the inversion of this integral in order to determine $L(T_2)$ is a so called ill-posed mathematical problem, so usually there is not one unique solution for $L(T_2)$. In addition measurement noise can also have a big influence on the solution.

In order to invert the Fredholm integral we apply the CONTIN algorithm [42]. This algorithm was developed especially for inverting integral equations with noisy measurement data.

To ensure that the results of the CONTIN algorithm are reliable in our case we constructed multi-exponential decay curves, added artificial noise with a comparable noise level as our measurements

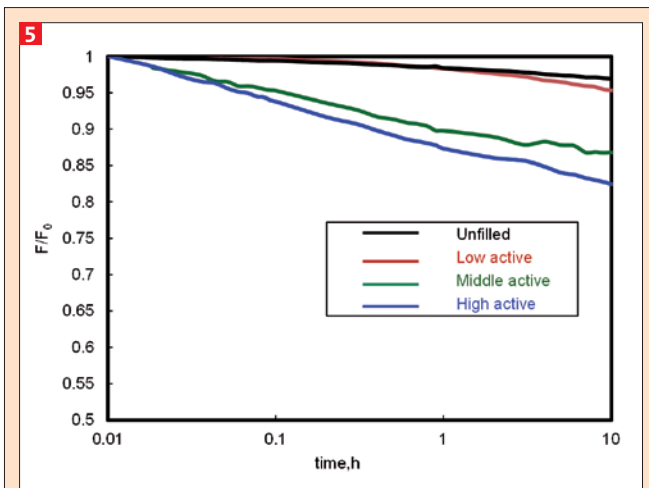


Fig. 5: Stress relaxation of cured EPDM for varying types of carbon black in N_2 atmosphere at $150^\circ C$ (F_0 = stress at $t = 0$; F = stress at time t).

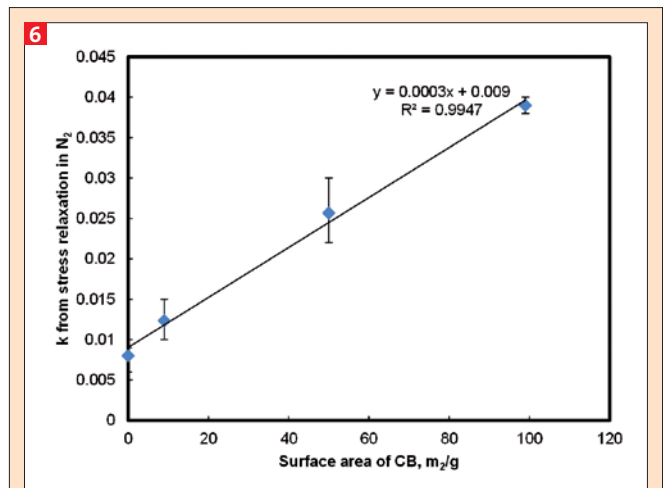


Fig. 6: Relationship between the specific surface of carbon blacks (CB) and k from equation (4).

and calculated the distribution function $L(T_2)$. Here we could show that the algorithm works in a stable and reliable way. We have to mention that noise has significant influence especially on the width of the peaks appearing in $L(T_2)$. So if the distribution functions of different samples shall be compared the noise levels of the measurements should not differ and should be as low as possible.

5. Results and discussion

5.1 Investigation of physical stress relaxation of cured and filled EPDM materials under N_2 atmosphere (anaerobe)

As mentioned above, during stress relaxation in N_2 -atmosphere physical relaxation is the dominating process due to the absence or at least reduced concentration of oxygen and therefore negligible amount of chemical relaxation pro-

cesses. It is true that for short measurement times, at low temperatures or for measurements under specific conditions (such as in N_2 atmosphere or a vacuum [without oxygen]), the relaxation observed closely approximates a logarithmic function of time [43-44]. All measured data could be approximated by logarithmic regressions. The related force curves ($F(t)/F(0)$) were fitted with equation (5) to reveal the speed of stress relaxation.

$$\frac{F(t)}{F(0)} = -k \log\left(\frac{t}{h}\right) + A \quad (5)$$

with the slope k the representative value for the physical relaxation rate, t/h is the experiment time measured in hours and A is a constant value. Fig. 5 shows the results of mechanical stress relaxation measurements on the EPDM vulcanized samples for varying carbon blacks

types as shown in Table 1 (method, see above, Fig. 3).

The slope k as a function of the surface area of the carbon black is shown in Fig. 6.

The value of k increases with increasing carbon black surface area in the rubber compound. This result could be attributed to either the chemical network or to the filler network. Due to the inhibitor effect of carbon black on the crosslinking reaction the quantity of polymer entanglements and chemical crosslinks which dominate physical relaxation might therefore decrease regardless of the same crosslinking agent amount and the conditions of vulcanization. In addition the type of filler is strongly influencing the filler-filler- or polymer-filler interactions. If the material maintains a certain force, however, the filler-filler or filler-polymer bonds would

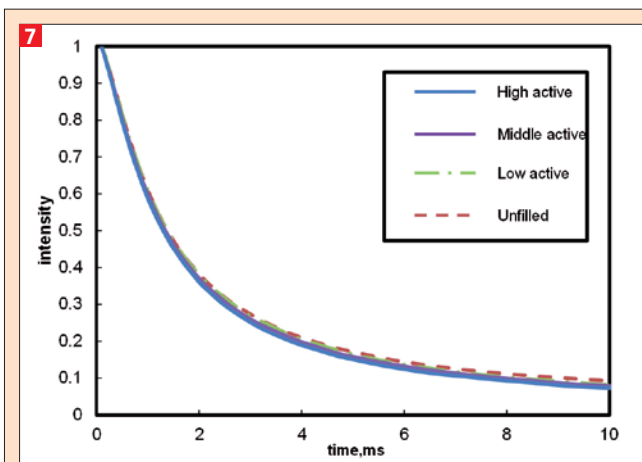


Fig. 7: NMR relaxation of uncured materials for varying carbon black types

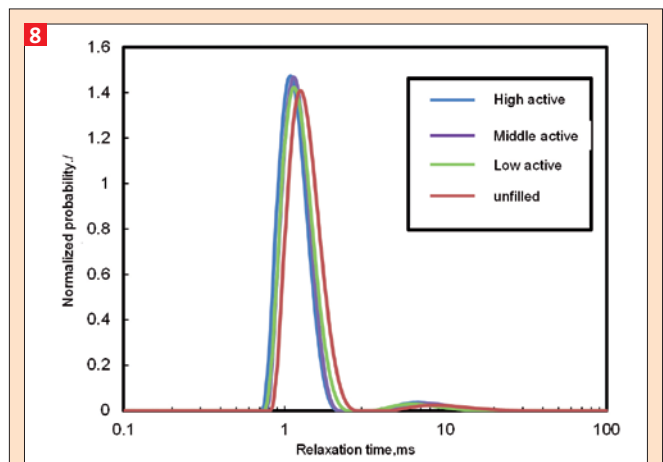


Fig. 8: NMR spectra of the uncured compounds

gradually be destroyed, and the counterforce would drop as a function of time.

5.2 Investigation of the effect of filler on non-crosslinked materials using low field NMR

The effects out of stress relaxation experiments can be investigated deeper by low field NMR investigations. Since NMR is sensitive to polymer chain mobility which can be changed due to chemical crosslinking, but as well for filled systems by physical or chemical adsorption of chains onto the filler surface, the two effects have to be separated first. Since crosslink density has an enormous effect on NMR results, the interaction between filler and polymer was investigated using uncured material. Fig. 7 shows the NMR relaxation curve. It can be seen that relaxation accelerates very slightly with increasing carbon black surface area. This can be explained by the restricted mobility of polymer chains adsorbed on the filler surface. This result corresponds to previous research [18]

The results of the evaluation of the low field NMR curves using ILT are shown in Fig. 8. ILT was carried out using equation (3).

In sum, the differences of filler and specific filler surface in uncured EPDM are much smaller than in filled crosslinked materials (see next section). With increasing specific surface of the carbon black, chain mobility nonetheless shows a downward trend.

5.3 Investigation of the effect of fillers on chain mobility of crosslinked materials measured by NMR

As described in the previous section, the rate of physical relaxation during the stress relaxation experiment is generally determined by the quantity of polymer entanglements. It could be reduced by increasing chemical crosslink density. To arrive at an understanding of the relationship between physical relaxation (disentanglements) / chemical relaxation (chain scissions) rate and crosslink structure, the NMR with the ILT technique was applied to unfilled and filled cured EPDM. Fig. 9 shows the magnetic decay curves of EPDM compounds with different carbon black types.

NMR relaxation becomes slower as the carbon black surface increases. Fig. 10 shows the NMR relaxation spectra calculated from the curves in Fig. 9 using the ILT method – the same process as in Fig. 7 and Fig. 8.

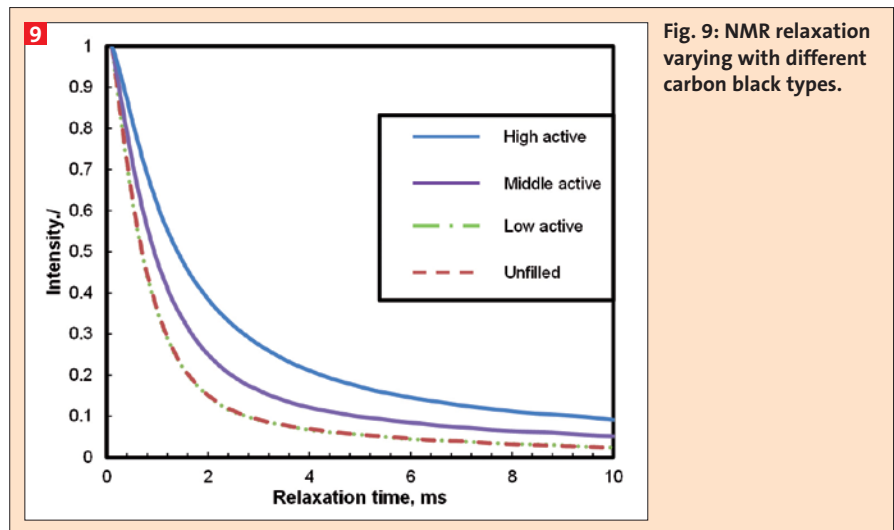


Fig. 9: NMR relaxation varying with different carbon black types.

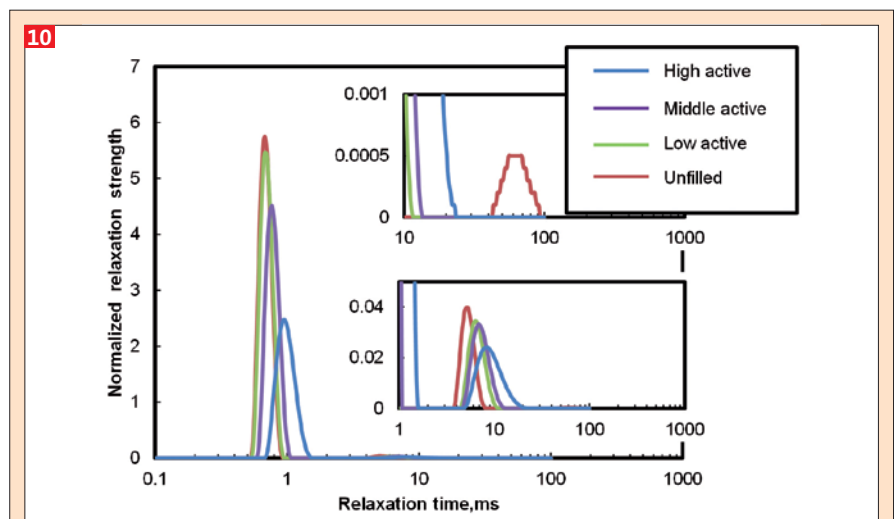


Fig. 10: Relaxation time with different carbon black types using ILT method on cured EPDM samples.

Each sample shows two or three peaks. The relaxation time is estimated from the peak maximum and leads to an T_{2A} of approx. 1ms and T_{2B} of approx. 10 ms. In the case of the unfilled material, an additional small peak T_{2C} at approx. 80 ms can be observed, as shown in Fig. 10. This results from the curing reaction using peroxide, where the side reaction induces a β -redistribution with chain scission and formation of a radical of the polymer with smaller molar mass. [45] T_{2C} was not observed, however, in the case of the filled materials. This may be connected to carbon black's inhibitor effect on chain scission, as described in the previous section.

Fig. 11 and Fig. 12 show the peak maximum time and area to be a function of the carbon black surface area. In the case of the uncrosslinked material, the peak maximum gradually decreases

(chain mobility decreases) and the T_{2A} area increases as a function of carbon black surface area due to filler and polymer interaction and absorption of free chain ends on the filler surface. The T_{2A} area represents the immobile phase.

In the case of crosslinked materials, on the other hand, an increase in the carbon black surface area correlates with an increase in T_{2A} peak maximum time (an increase in chain mobility) and a decrease in T_{2A} area. One reason for this is the inhibitor effect carbon black has on crosslinking due to adsorption of crosslinking chemicals or the filler particles acting as spacers between the polymer chains.

5.4 Investigation of chemical stress relaxation in air on cured EPDM

When performing stress relaxation experiments in air at 150°C, a logarithmic de-

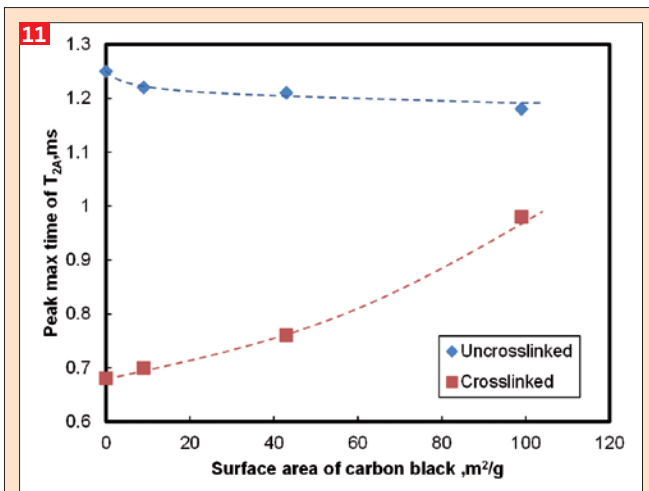


Fig. 11: Relationship of T_{2A} and surface area for unaged cured and uncured EPDM.

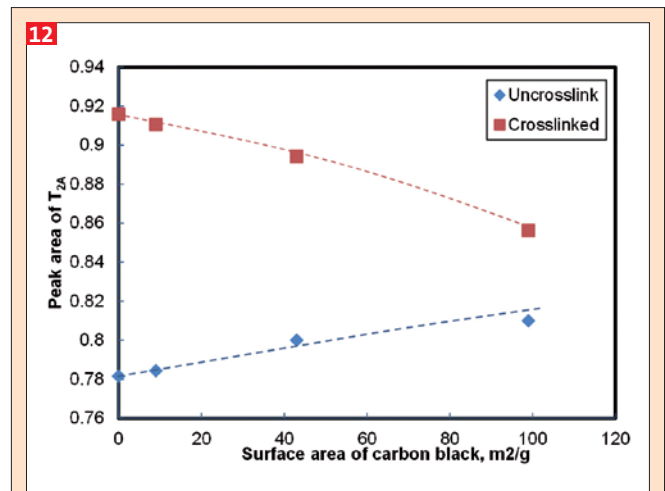


Fig. 12: Relationship of T_{2A} and surface area for unaged cured and uncured EPDM.

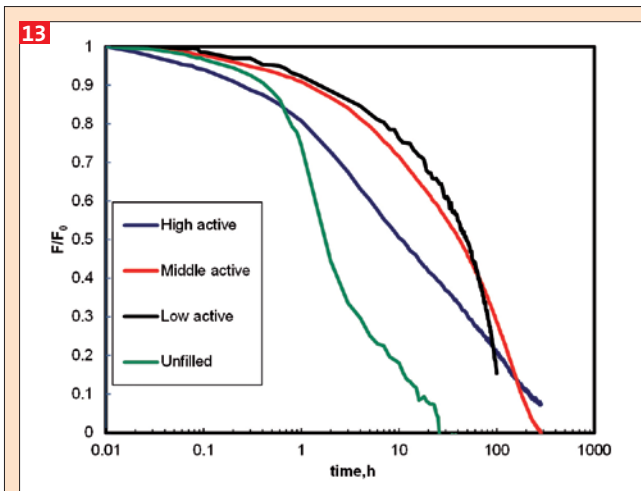


Fig. 13: Stress relaxation of cured EPDM as a function of the type of carbon black in air at 150°C.

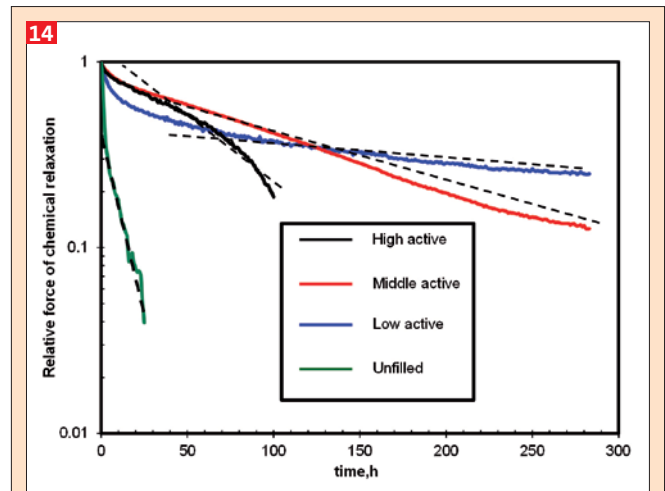


Fig. 14: Chemical relaxation curves simulated by relaxation in air and N_2 atmosphere.

decay of the stress is observed only at the very beginning of the test (< approx. 1h). Later on, the shape of the decay curve changes, undergoing a sharp decrease as shown in Fig. 13.

To determine only the amount of chemical relaxation, the contribution of physical relaxation as determined by stress relaxation experiments in N_2 , has been subtracted from the original ex-

perimental data in air resulting in the chemical relaxation curves depicted in Fig. 14. In order to compare the chemical relaxation speed, the characteristic aging time constant can be defined as an exponentially decreasing variable dropping from an initial force. The characteristic aging time constant $\tau_{aging\ CSR}$ can be estimated by fitting with the following function.

$$\frac{F(t)}{F(0)} = \exp\left(-\frac{t}{\tau_{aging\ CSR}}\right) + A \quad (6)$$

with $F(t)$ the force at aging time, $F(0)$ the initial force, t the experiment time and A a constant value. According to Tobolsky, the rate of chain scission can additionally be determined via the slopes of the chemical stress relaxation curves (linear part at short times), as in Fig. 14. [46-48]

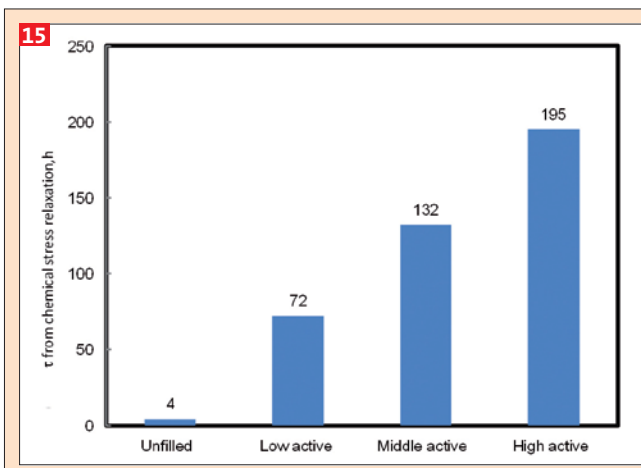


Fig. 15: Relationship between carbon black surface area and chemical stress relaxation time applying equation (5).

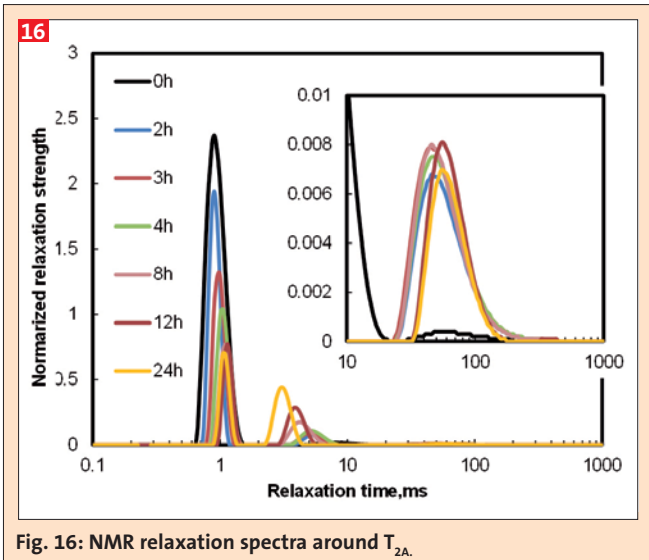


Fig. 16: NMR relaxation spectra around T_{2A} .

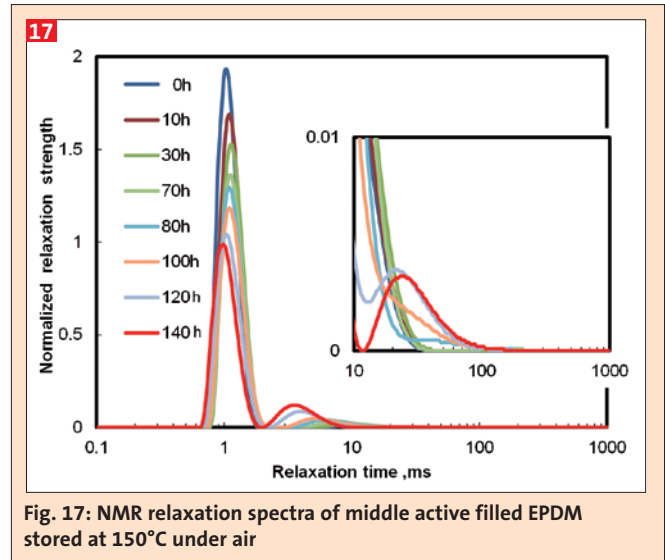


Fig. 17: NMR relaxation spectra of middle active filled EPDM stored at 150°C under air

Fig. 15 shows the influence that the surface area of carbon black has on $\tau_{aging CSR}$ resulting from equation (6). $\tau_{aging CSR}$ increases with increasing carbon black surface area. In other words, high active carbon black inhibits the degradation of the polymer.

5.5 Investigation of the correlation between chain mobility evaluated by ILT from low field NMR measurements and aging

The evaluation of the NMR relaxation data by ILT technique was applied to EPDM compounds during aging in air. All the results were obtained using the same samples as described in the previous chapter without any stress or deformation and aged only in air at 150°C. Fig. 16, 17 and 18 show NMR relaxation using ILT for unfilled, middle active and high active filled materials during aging in air.

All materials show a decreasing maximum of the T_{2A} - peak during aging. The T_{2B} -peak behaves vice versa. Besides that, in the case of the unfilled material, the T_{2C} -peak around 80ms is observed and increases as a function of aging time as shown the magnification of the spectra in Fig. 16, 17 and 18. This means that the initial crosslink part (T_{2A}) is changed irreversibly into several types of structure, such as short chains (T_{2B}) or free chains (T_{2C}) due to the chain scission caused by thermal oxidation.

Fig. 19 shows the peak area corresponding to T_{2A} as a function of aging time for unfilled and filled EPDM. In all cases the peak area is decreasing with aging time. The more active the carbon black the smaller is the effect. Besides that, the area changes approximately in an exponential way. So we can attribute a characteristic aging time constant $\tau_{aging NMR}$ as shown in formula (7) using

the same approach as in the analysis of the chemical stress relaxation results in the previous section.

$$\frac{\text{Peak area of } T_{2A}(t)}{\text{Peak area of } T_{2A}(0)} = \exp\left(-\frac{t}{\tau_{aging NMR}}\right) + A \quad (7)$$

with peak area of $T_{2A}(t)$ is the peak area of T_{2A} at experimental time t , peak area of $T_{2A}(0)$ is the initial peak area, and A is a constant value. The characteristic aging time constant $\tau_{aging NMR}$ is shown in Fig. 20.

Fig. 21 shows the correlation of the characteristic aging time constant delivered by NMR and chemical stress relaxation. Obviously there is a good correlation between both methods. However, the absolute values of characteristic aging time constant from the two methods differ. This could be caused by the geometry of sample or aging condition (expo-

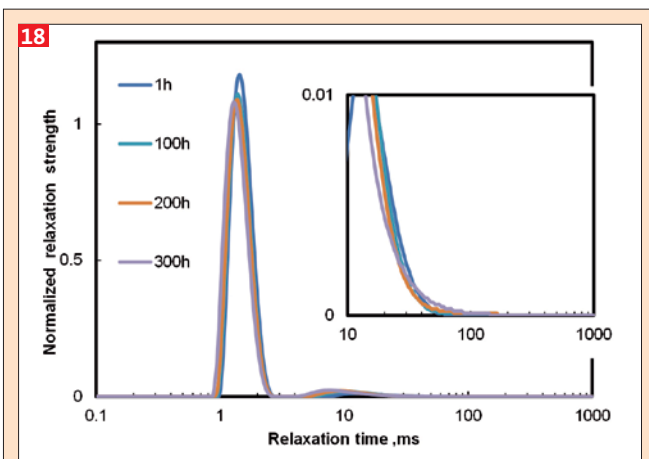


Fig. 18: NMR relaxation time spectra of high active filled EPDM stored at 150°C under air

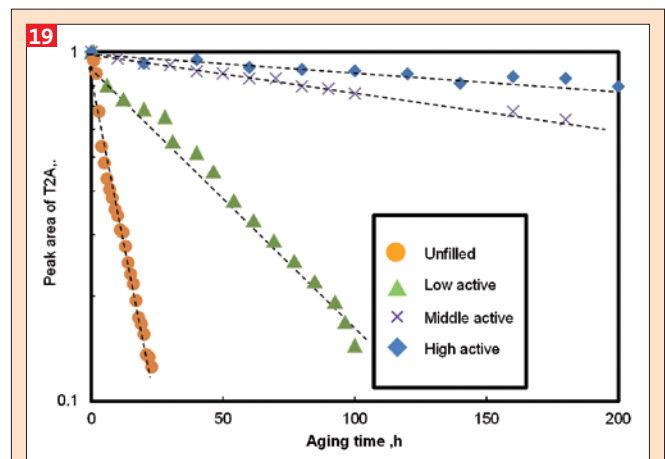
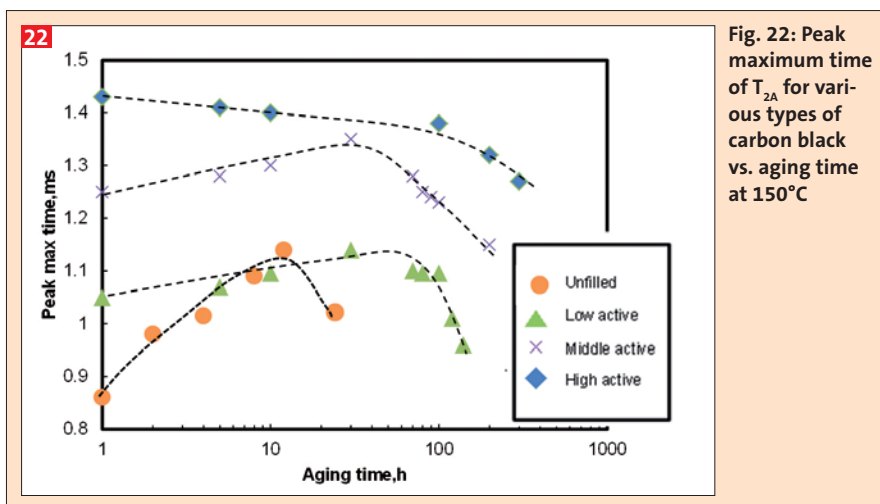
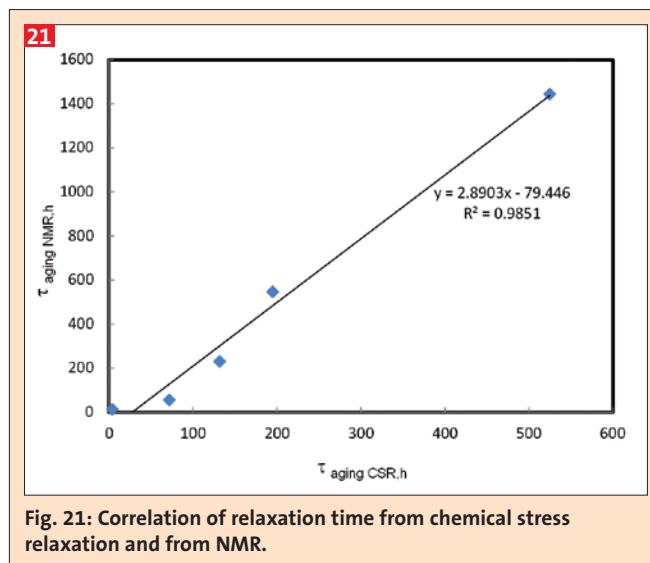
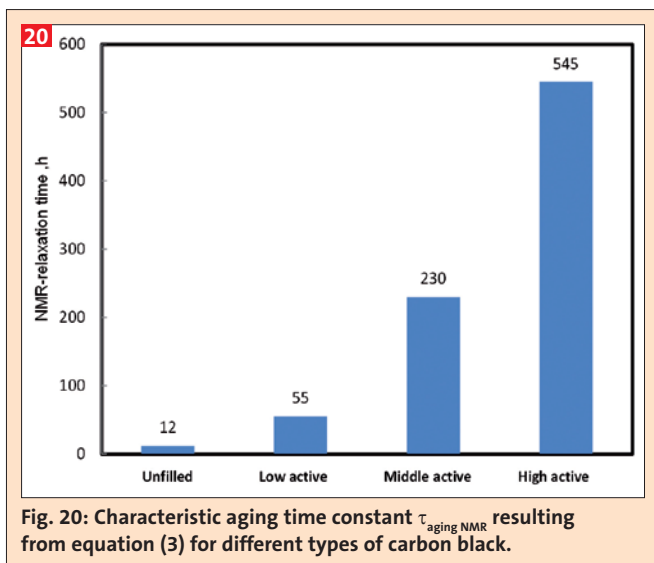


Fig. 19: Peak area T_{2A} for different carbon black types vs. aging time at 150°C.



sure of air) For this point to clarify, further investigation is necessary.

Additionally to the peak area also the position of the peak maximum can be analyzed in more detail. In Fig. 22 the peak maximum time for T_{2A} is plotted vs. the aging time for the different filled and unfilled samples. As can be seen, the dependencies depend to high extend on the type of filler. For the unfilled and filled materials with low active or middle active carbon black there is an increase in the peak maximum time of T_{2A} at low times, which we attribute, first of all, to chain scission. At longer times a decrease of the peak maximum time of T_{2A} sets in which might be due to post-crosslinking. Apparently we observe two competitive effects: chain degradation and aging induced cross linking. The type of carbon black has an influence on the kinetics of both processes.

The time where the change in the behavior is taking place seems to be

filler type dependent but is not increasing with the filler surface area. In addition, in the case of the high active carbon black, the peak maximum shifts directly to shorter times. The reason is not clear up to now and gives rise to future research.

6. Conclusion

Low field ^1H NMR with inverse Laplace transform and stress relaxation both provide suitable methods for examining the aging process of EPDM. This NMR technique contributes to a better understanding of the results of stress relaxation. The characteristic aging time constant estimated on the basis of the results of stress relaxation and NMR correlate closely, both showing an increase in relaxation times with increasing carbon black filler surface area.

What is more, the surface area of carbon black has a strong influence on the stress relaxation mechanism. By means

of low field NMR measurements, it could be observed that carbon black works to inhibit thermal oxidation. NMR can thus be helpful in understanding the degradation mechanism and in predicting the lifetime of seals.

7. References

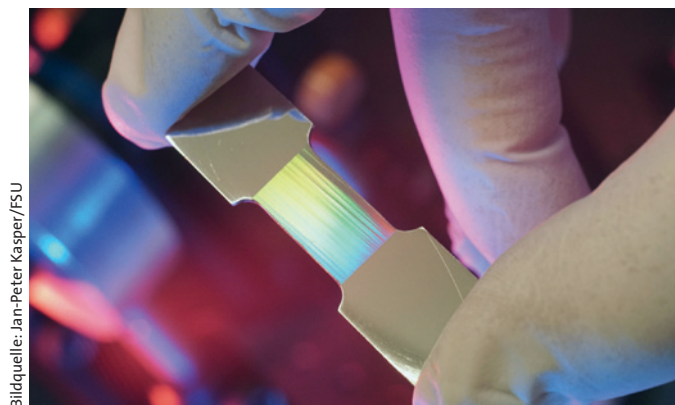
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Materialwissenschaftler gestalten Oberfläche winziger, gekrümmter Kohlenstofffasern

LASERSTRUKTURIERUNG VON OBERFLÄCHEN

Die Oberfläche von Materialien hat einen enormen Einfluss auf deren Funktion. Verändert man die äußere Beschaffenheit, so erweitert man auch die Bandbreite der Verwendungsmöglichkeiten. Deshalb erforschen Materialwissenschaftler der Friedrich-Schiller-Universität, Jena, wie sie die Oberfläche verschiedener Werkstoffe mit Lasertechnik gestalten können. Sie konzentrieren sich dabei vor allem auf laserinduzierte periodische Oberflächenstrukturen. Damit lassen sich besonders feine Strukturen hervorrufen. Bestrahlt man eine Oberfläche mit einem Femtosekundenlaser - also einem Laser mit sehr kurzen Lichtpulsen -, so bilden sich an dem Punkt, an dem der Laserstrahl auf die Oberfläche trifft, charakteristische Strukturen aus. Interferenzeffekte in die-



Forscher ist es erstmals gelungen, selbst gekrümmte Oberflächen mit laserinduzierten periodischen Strukturen zu versehen, mit denen sich Oberflächen auch farblich gestalten lassen.

sem Fokuspunkt rufen die LIPSS (Laser-Induced Periodic Surface Structures) hervor. Diese Strukturen sind kleiner als die, die man durch normale Laserstrukturierung erreicht. Die Größe der Strukturen hängt unter anderem von der Laserintensität und der verwendeten Laserwellenlänge ab. Verändert man also die Parameter der Laserstrahlung, lassen sich die Strukturen nahezu maßgeschneidert aufbringen. Durch das Abrastern der Oberfläche mit dem Laserstrahl wird sie vollständig mit dem periodischen Muster versehen. Generell funktioniert die

Methoden auf verschiedenen Materialklassen. Bisher allerdings konnte sie nur auf ebenen Flächen angewendet werden. Den Forschern ist es nun gelungen, auch gekrümmte Oberflächen mit den laserinduzierten periodischen Strukturen zu versehen. Dadurch bieten sich neue Möglichkeiten für die Praxis. So werden etwa die Kohlenstofffasern bei der Herstellung von Verbundwerkstoffen in andere Materialien eingebettet. Um die Festigkeit der Verbundwerkstoffe zu verbessern, werden sie bisher mit Chemikalien behandelt. Durch die LIPSS lässt sich nun ihre Oberflächentopographie gezielt verändern, so dass es zu einem Verankern zwischen Polymer und eingebetteten Fasern kommt. ■

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