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Spatially resolved and integral NMR investigation of the aging process of carbon black filled natural rubber

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Summary

A complex aging regime takes place in the course of thermal aging of natural rubber. Depending on the kind and the content of the free crosslinker, the aging temperature, the duration of the aging period and the reactivity of the atmosphere (air or nitrogen) a different aging process can be observed also by NMR. The methods used are the common spin-echo-NMR (^1H) and parameterselective NMR-imaging (^1H). The decay of the echo-magnetization was evaluated on the basis of a modified single chain model (based on the tube model of de Gennes). The thermal aging course of a filled (carbon black) sample at 100°C shows a characteristic behaviour, beginning with a strong decrease of T_2 followed by a weak increase through aging times of 10 to about 50 hours. At longer aging times the solid-like behaviour rises again.

Introduction

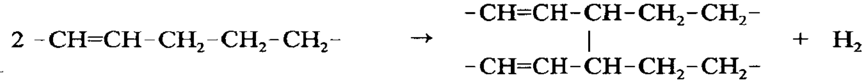
Elastomeric materials like filled natural rubber are of great technological significance. Also the drop off of the typical properties during the lifetime (shortly called: aging) is a very important cost and reliability factor. Under several aging influences we focus our attention on thermal aging in a normal atmosphere because there is a great practical relevance and, on the other hand, it is an easily controlled process.

In the last few years some fundamental work in the field of NMR-microscopy in the solid state has been done. Elastomers, having partially liquid-like properties, create a good situation for imaging compared with solids and consequently, there are a lot of investigations to show the usefulness and effectiveness of this method for rubber or rubber-like systems [1-10], but no systematical research for the several visualization effects (diffusion, swelling, stretching, chemical and thermal aging...) has been done. Nevertheless there is an undoubted interest in the rich information content of NMR-spectroscopy combined with a spatial resolution. So it is possible to detect inhomogeneities in the network density and the filler content, aging and diffusion fronts, stress pictures and others.

The aging of elastomeric material is a very complex process, which takes place mainly under the influence of heat, oxygen (ozone), other free radicals, radiation and/or mechanical stress [11]. From a molecular point of view there are mainly two competing processes - scission and linking of the polymeric chains - which dominate the aging process [11]:

- scission: $-CH{=}C(CH_3)-CH_2-CH_2-CH_2- \rightarrow -CH{=}C(CH_3)-CH_2- + -CH_2-CH_2-$

- linking:



$$2\ -CH{=}CH-CH_2-CH_2-CH_2- \rightarrow \begin{array}{c} -CH{=}CH-CH-CH_2-CH_2- \\ | \\ -CH{=}CH-CH-CH_2-CH_2- \end{array} + H_2$$

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In detail the reaction leads at first to the formation of hydroperoxides and at last - in the presence of anti-oxidants - to inert compounds. These kinds of network modifications take place without use of crosslinker, but with support of free radicals, arising easily in the presence of oxygen. Chain scissions dominate the aging process in natural rubber as well as in - e.g. - synthetic polyisopren or butyl rubber, whereas new crosslinks will arise in - e.g. - styren butadien rubber [11].

Several quantities have an influence on the velocity and the intensity of the aging process. Indeed, the presence of oxygen (ozone) beside the thermal damage and/or mechanical stress is the most important aging factor in the daily practice. It causes the creation of free radicals at the polymer backbones, leading to an additional crosslinking process. Depending on the oxygen diffusion (infiltration deepness), which is a function of the rubber sort (frequency of double bonds), even different aging velocities are produced. They can be many times faster as in inert agents (CO_2, N_2) [11]. Moreover, it will be clear, that these processes can be locally differentiated, which will become noticable first of all only in a surface layer [2,3,5,6]. When oxygen is absent, also aging processes take place:

It has been observed in some instances that the modulus and the crosslink density go through a maximum and continue to decrease with additional curing (aging) times; a result of loss of network structure by non-oxidative thermal aging [12]. On the one hand sulfur can be dissolved from the crosslinks (desulfurization) and mono- or disulfidic crosslinks will be built up. This takes place most of all in systems containing Zn-accelerator complexes such as accelerated sulfur vulcanization mixtures (investigated in this work). On the other hand crosslinks will be dissolved, and sulfuration species decompose (thermal decomposition) into modified species (cyclic sulfides, shorter sulfur crosslinks and main chain modifications). This process is known as reversion. It can be considered [5] as a first step ("soft aging") of an aging process, which leads in progress to the oxygen-consuming reactions described above and to a crosslinking arising by breaks of the olefinic double bonds by increasing thermal supply ("hard aging").

In this work a series of differently aged carbon black filled natural rubber will be investigated by parameterselective MRI [9], and some statements are given about the aging regime in the body and in the surface layer. An air and a nitrogen aged sample series will be compared by means of spatially resolved and integral ^{1}H-NMR to find out the role of the oxygen.

Theory

1. Model of polymer network

The wellknown elastomeric network is shown in Fig. 1. Besides the essential network signed by chemical crosslinks also physical loops exist, acting like crosslinks. These steric hindrances lead to an anisotropic molecular motion, well observable by NMR-relaxation. The motion of the free polymer chains (sol-part) and the dangling ends of the network molecules shows also a weak anisotropy, but - of course - the hindrances are much smaller.

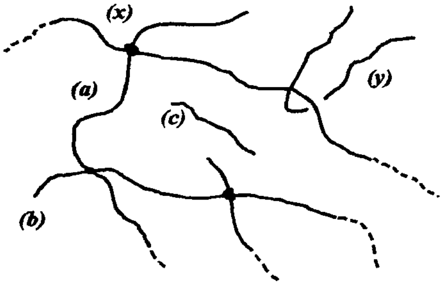


Fig. 1
Network model
(a) intercrosslink chain
(b) dangling chain end
(c) free chain (sol part)
(x) chemical crosslink
(y) physical loop

The three-component model [4], based on the de Gennes reptation model [13,14], differentiates between three typical motions:

- Fast local motions (i) with correlation times $\tau_f \approx 10^{-9}$ s which show a slight anisotropy caused by sterical hindrance. Consequently, a remaining second moment will occur with a magnitude of about 1‰ in relation to the total amount at the starting point..
- Slower and more isotropic motions ($\tau_s \approx 10^{-3}$ s) which reduce the remaining moment near to zero. First of all this is a random walk process of the chain fluctuations inside a tube formed by the hindrance potential of the neighbouring polymer chains called reptation (ii).
- An isotropic fluctuation of the tube (iii) is less important in crosslinked polymer chains and there is no experimental separation to (ii). Also there can be small molecules (short chains, residue of solvents), which influence the correlation times liquid-like.

2. Correlation and relaxation

In accordance with [9,15,16] the modified single chain model used here leads with temperatures well above the glass transition and only dipolar interaction to the following statement for the course of the transversal magnetization decay (relaxation function) [17]:

$$M(t) = A * \exp\left(-\frac{t}{T_2} - q * M_2 * \tau_s^2 * \left[\exp\left(-\frac{t}{\tau_s}\right) + \frac{t}{\tau_s} - 1\right]\right) + B * \exp\left(-\frac{t}{T_2} - q' * M_2 * \tau_s^2 * \left[\exp\left(-\frac{t}{\tau_s}\right) + \frac{t}{\tau_s} - 1\right]\right) + C * \exp\left(-\frac{t}{T_{2,sol}}\right) \tag{1}$$

To get this relation the Andersson-Weiss formula for the decay of magnetization in solids and the assumptions $\tau_f << \tau_s$ and $q << 1$ (always fulfilled) are used. The fractions A, B and C represent the parts of magnetization of protons in inter-crosslink chains, dangling ends and sol fraction respectively. τ_s has the meaning described above, q is the factor of anisotropy of the motion of the intercrosslink chains and q′ relates to the anisotropy of the dangling chain ends [18]. The relaxation rate $1/T_2$ corresponds to τ_f, linked by the well known BBP-theory. In the case of a bad signal to noise ratio, equation (1) must be simplified to get a stable fit:

- $q' = 0$,
- $\exp(-t/\tau_s) \approx 1 - t/\tau_s + t^2/(2\tau_s^2)$

leading to:

$$M(t) = A * \exp\left(-\frac{t}{T_2} - \frac{q\, M_2 * t^2}{2}\right) + B * \exp\left(-\frac{t}{T_2}\right) + C * \exp\left(-\frac{t}{T_{2,\,sol}}\right) \tag{2}$$

The long parts of the FID were optionally removed by the program, so that we ignored the parameter C (sol fraction). So we have all in all four characteristic parameters: T_2, A, B and $(q * M_2)$. The determination of the averaged molecular mass of inter-crosslink chains M_c is possible using the factor of anisotropy q (q_0 takes into consideration the influence of physical entanglements.) by:

$$M_c = \frac{3}{5 * \sqrt{q - q_0}} * c_\infty * \frac{M_{ru}}{N} \tag{3}$$

M_{ru}/N is the molecular mass of one monomeric unit per number of backbone bonds in it. The quantity c_∞ is the number of backbone bonds in one Kuhn-segment.

Samples and experiments

The sample came from Continental AG Hannover. It was a 50phr N550 carbon black filled natural rubber made by rheometer controlled vulcanization ($T_{95\%}$).

Content (parts in phr):

nr (pale crepe): 100; carbon black N 550: 50; LSW standard: 1; koresin: 1; stearin acid: 2; zinc white: 3; aging protectors IPPD: 1; aging protectors DTPD: 1; sulfur: 2; accelerator CBS: 2; acc DPG: 0.5

The sample was cut in 5·5 mm² pieces of a thickness of 0.5 mm. The aging process took place in a dry box at 100 °C. The rubber pieces were placed in a glassy tube filled with nitrogen for aging in an inert atmosphere. The nitrogen atmosphere was replaced several times before the aging took place and refreshed shortly before to remove oxygen residues.

The MRI was made at room temperature on a 400 MHz Varian Unity equipped with a broadband probe with a home-made 5 mm solenoidal coil insert (IBMT, St. Ingbert). The 90° pulse length was 1.5 µs. The echo time 2τ was varied between 300 µs and 6 ms in 24 steps. A gradient of 35 G/cm was stepped by 128 angle increments. The pixel resolution (256·256) was 70 µm. No slice selection was applied. The measurement of the transverse decay of the magnetization has been performed using a Hahn spin-echo sequence with variation of the spin-echo time to eliminate the influence of magnetic field inhomogeneities and of chemical shift on the transverse decay (see Fig. 2).

For the integral investigations, performed also on a 400 MHz spectrometer from Varian, the 90° pulse length was 3.5 µs and the echo time varied between 50 µs and 100 ms in 58 steps. The MRI probe has no temperature control, therefore the measurement had to be at room temperature (20°C). The temperatures for the integral measurements were 20°C to have a comparision to the spatially resolved one and 60°C to get a better fit of the relaxation data in a region far away the glass point.

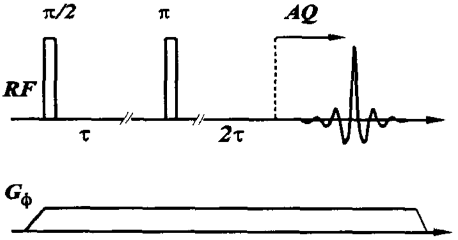


Fig. 2
Pulse sequence used for the measurement of the spin-spin-relaxation time T_2 using a Hahn spin-echo magnetization filter

Results

1. Spatially resolved measurements

To determine the local dependence of the aging course parameterselectively, NMR-pictures are calculated for the air and the nitrogen aged samples. For example in Fig. 3 the NMR-images of the parameter T_2 - fitted by using eq. 2 - are shown as a function of aging time (aged by 100°C in air, no slice selection by a sample thickness of about 500 µm). It shows no remarkable surface layer (unfortunately, the sharpness of the images is not good enough for such details), but an ascent of inhomogeneities for intermediate (5 - 10 h) aging times. Note the darker colours as a hint of shorter relaxation times and keep in mind that the spin density has no influence on the picture. Relaxation times T_2 become shorter at increasing aging times, such showing a tendency to solid-like behaviour. This is also shown in a decrease

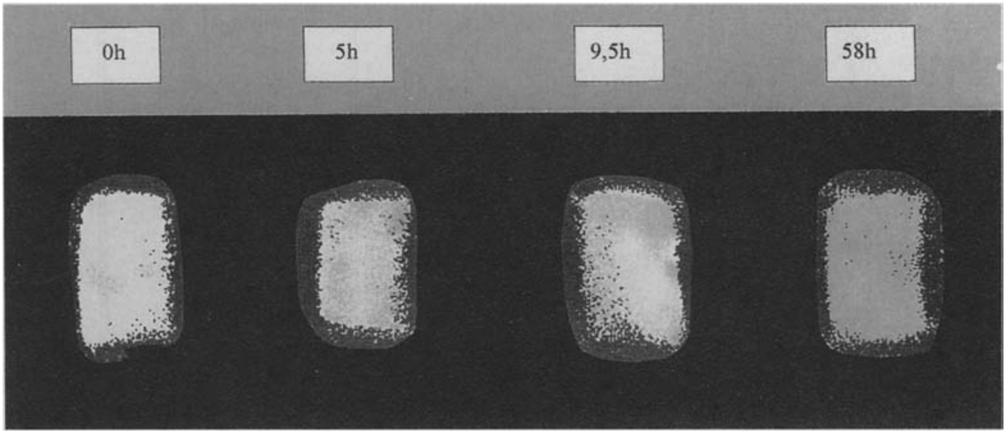


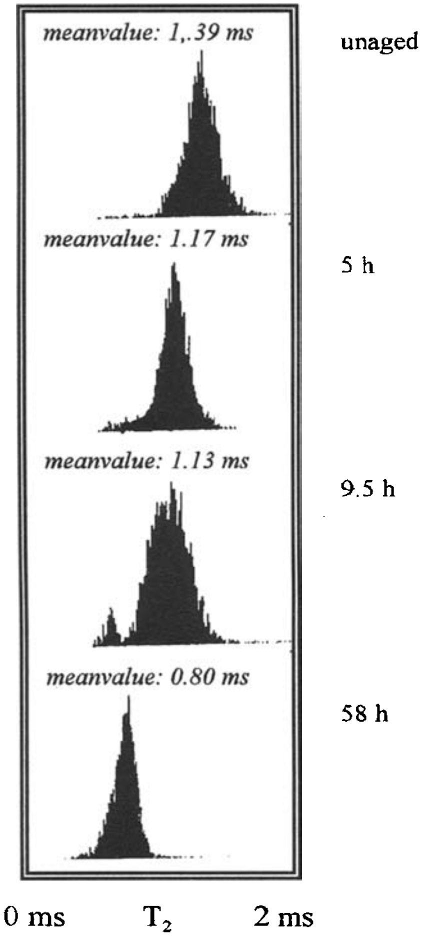
Fig. 3
NMR-images of the parameter T_2 (fitted by using eq. 2) of rubber pieces as a function of aging time (aged at 100°C in air). The grey areas around the rubber pieces are the real background (air). Note the inhomogeneity for short aging times (5h, 9.5h), but opposite to the histograms (Fig. 4) there is no remarkable evidence of a surface layer.

of M_c corresponding to a greater network density. However, the values for a longer (72 h) aging again show an opposite tendency (see also the integral measurements), characterized by an increase of T_2, caused by a greater degree of freedom of the network chains (destruction of crosslinks). In opposite to the images, inhomogeneities caused by the surface layer can be observed undoubtedly by a statistical analysis of the image pixels. Indeed, the histograms (see Fig. 4.: 5h and 9.5h aging time) show little shoulders at about 7 µs as a indication of a surface influence. The reliability of this has been proofen by the observation of the inner regions of the sample only. A homogeneous picture (histogram without shoulders) was observed here. Furhtermore no surface effect was measured at longer aging times ($\geq$58 h). As expected, the N_2-aged samples (see Fig. 5) show no inhomogeneities caused by a surface layer.
For long aging times (72 h; only Fig. 5) the relaxation time rises again - a consequence of the reversion.

2. Integral measurements

Spatially resolved measurements take a lot of time. To investigate a greater range of aging times and to measure not only at room temperature, we returned to the integral NMR-modus. The NMR-images have shown, that neglecting of the very small inhomogeneities and/or surface layers has no remarkable influence on integral measurements. Fig. 6 shows a comparison of air- and nitrogen-aged T_2-measurements at room temperature. The following statements are evident:

a) In all cases the samples aged by air have undoubtedly shorter values T_2 than the ones aged in nitrogen.The reason is not evident, because aging caused by oxygen should lead to a softening of the material and consequently to longer relaxation times. However, the mea-



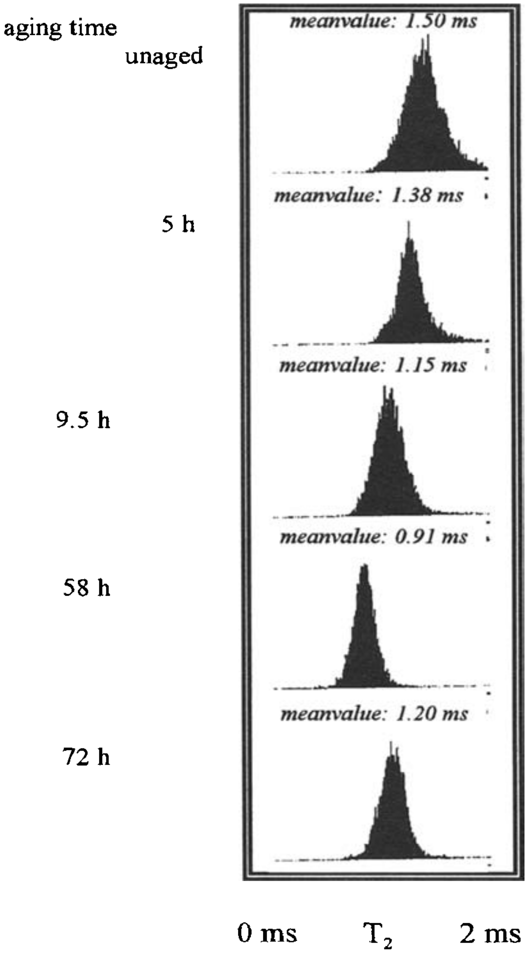


Fig. 4
T_2-histograms of air aged rubber.
From top to down: 0h, 5h, 9.5h, 58h
aging time; T_{aging}= 100°C
ordinate: abundance in arbitrary units

Fig.5
T_2-histograms of N_2-aged rubber
From top to down: 0h, 5h, 9.5h, 58h, 72h aging time; T_{aging}= 100°C
ordinate: abundance in arbitrary units

surements of the nitrogen aged samples were made after those of the air aged (several months). Therefore it is possible, that some aging effects - due to an additional crosslinking - influence the material, although the samples were stored in a freezer (but at temperatures far **above** the glass point). Further investigations to study this detail are in progress.

b) Due to the more extensive pulse program of nmr-imaging, the minimal echo times were longer than in the simple Hahn echo (~10x). The calculated relaxation times tend to be slightly shorter in this case /18/. Nevertheless, the tendency of the T_2-plot (Compare Fig. 4, 5 and 6) is the same.

c) The aging course has a minimum in T_2 at about 40 - 50 h and a maximum at about 70 - 80 h. This is also confirmed by measurements at 60° C (Fig. 7), thereby the elastomeric behaviour will be better because of the greater distance to the glass temperature (T_g ~-60°C)

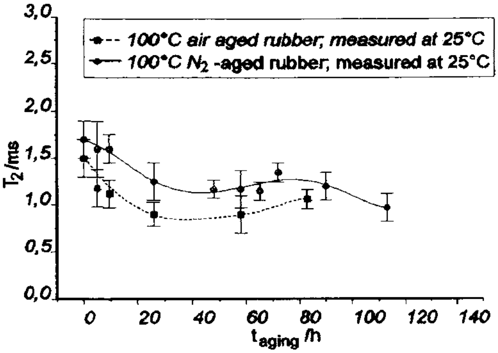


Fig. 6
T_2-measurements of aged rubber in dependence on the aging time (measured near room temperature)

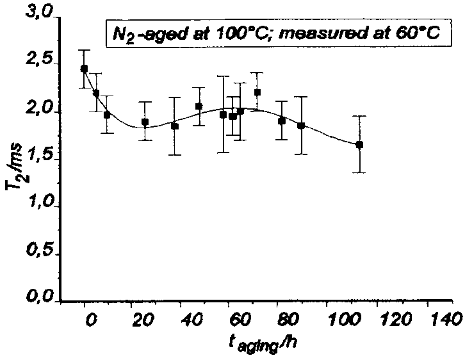


Fig. 7
T_2-measurements of aged rubber in dependence on the aging time (measured at 60°C)

and consequently the fit of the network parameters (see above) will become more stable and well defined. The minimum is well discernible and occurs at about 20 h aging time. The maximumin T_2 will be confirmed between 70 and 80 h. Obviously there is unused crosslinker in action for shorter aging times, and we can consider the aging more as a crosslinking. After 20 h the degradation of the network by thermal aging becomes more evident. At longer aging times (about 70 h; "hard aging") T_2 becomes shorter again, showing a new kind of crosslinking: The olefinic double bonds will break off and a crosslinking is possible without the help of crosslinker or oxygen. An analog trend shows the model parameter $q \cdot M_2$, slightly increased at 70 h aging time ($0.7\ ms^{-2} \rightarrow 0.9\ ms^{-2}$) related to a decrease for M_c (s. equ.4). Surprisingly the parameter B, showing the relative part of chain ends, doesn't decrease, but increases from about 10% to 20% in this region. The only explanation we have is, that besides the crosslink reactions making the network chains shorter, an increasing break of polymer backbones takes place providing more chain ends and consequently a higher B.

The measurements were made in nitrogen and there is no possibility for any oxygen induced reactions or for the formation of an observable surface layer. This is also confirmed by histograms of the surface areas showing a very homogeneous distribution of correlation times and giving no hints of any surface layers.

In the case of very long aging times (several weeks) any rubber-like behavior will be destroyed and only a very short exponential decay will be observed.

Conclusions

We have shown the following course of the aging process for carbon black filled soft cured natural rubber systems.

Under the given aging conditions (100°C in air or nitrogen) we can observe mainly a "soft" aging regime. At short (0 - 20h) aging times we can see a decay of spin-spin relaxation time T_2. The reason should be the occurence of free crosslinker (sulfur) in the sample, eventually arising from desulfuration processes. Also the local homogeneity of the samples increases. We will interprete these events as a continuation of the curing process of the samples. By this, inhomogeneously cured spheres will get a greater equality and the variation of network parameters becomes smaller. There is no or only a small (in the case of air influence)

tendency for formation of a surface layer.
After aging periods of approx. 20 - 70 h, T_2 becomes longer, indicating a higher molecular mobility, which may be caused by a lower crosslink density (→ reversion).
At longer aging times the olefinic double bonds may be destroyed and give opportunities for new crosslinks. The relaxation time T_2 becomes shorter and the behaviour is more solid-like again. This decrease of T_2 after reaching a maximum at longer aging times was observed in NMR for the first time by Kuhn et al. [5], and the explanation given there is, that at shorter aging times chemical bonds with low activation energies such as sulfidic will be broken by thermal treatment and lead at least to crosslink decompositons. While at longer aging times (hard aging) the olefinic double bonds in the backbone will be broken and make the formation of new crosslinks possible. Additionally we want to say, that a simultaneous destruction of the polymeric backbone (chain scissions) takes place thus leading to a smaller M_c and a decrease of the modul. Further investigations will be made to get a better verification of the aging process roughly described here, especially in the aspect of a harder aging and a formation of surface layers.

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