

Characterization of aged nitrile rubber elastomers by NMR spectroscopy and microimaging

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Abstract

¹H spin–lattice and spin–spin NMR relaxation times change markedly during the aging of nitrile rubber elastomers. NMR microimaging reveals heterogeneous changes in the aged samples. Aging proceeds mainly via additional chain cross-linking, and scission of the polymer chains does not appear to contribute. *T*₁ imaging shows that there is no spatial distribution of spin–lattice relaxation times. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Nitrile rubbers are copolymers of butadiene and acrylonitrile (Fig. 1) [1,2]. The monomer ratio is varied within a wide range, reflecting the specific application of the product. A high acrylonitrile-to-butadiene monomer ratio increases polarity and thus resistance to swelling, but renders the polymer mechanically inflexible at low temperatures [3]. While the macroscopic properties of nitrile rubbers are relatively well known, the relationships between molecular structure, molecular dynamics and physical properties, all crucial for the practical applications of nitrile rubbers, need much better understanding. The amount and type of chemical cross-links is closely related to macroscopic properties. The steric constraints caused by chain entanglements and chemical cross-links also strongly influence the dynamics of the polymer chains.

The aging of elastomeric materials is a complex chemical process, which occurs under the influence of heat, oxygen or mechanical stress, and results in a time-dependent change in their chemical and physical properties. Aging is a very important factor from the point of view of cost and reliability. Thermal aging is most often studied, in view of its

practical importance and also because it can be easily controlled under laboratory conditions. On the molecular level, aging is dominated by two competing processes: molecular scission, which results in shorter chains and more dangling ends, and cross-linking which gives a more tightly networked structure [4]. Heterogeneous oxidation caused by the aging of nitrile rubbers was studied using infrared microscopy and modulus profiling [5]. Heterogeneous changes due to diffusion-limited oxidation have also been reported [6].

Elastomers have been the object of intensive studies by NMR, a technique which has the advantage of being non-destructive [7–12]. The aim was to determine the different relaxation mechanisms and rates, which are related to molecular motions. In addition, the liquid-like properties of elastomers enable microimaging techniques [9] to be used. The small residual dipolar coupling, a consequence of the fast motion of the polymer chains [13], also facilitates NMR examination of rubbers. Dipolar coupling can be probed via *T*₂ measurement [8–10] and by the dipolar correlation effect [14–16]. As the aging process results in heterogeneous changes in relaxation times [4,10], measurement of bulk relaxation times and parameter-selective imaging can be very informative.

2. Experimental

Samples. Rubber sheets consisting of 100 parts of Hycar

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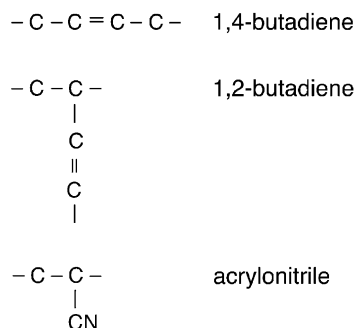


Fig. 1. Monomers used in the synthesis of nitrile rubbers.

1052 (acrylonitrile) resin, 65 pph N774 carbon black, 15 pph Hycar 1312 (butadiene), 5 pph zinc oxide, 1.5 pph sulfur, 1.5 pph MBTS (2,2'-benzothiazyl disulphide) and 1 pph of stearic acid were obtained from Burke Rubber Co. Strips 6 mm wide and 150 mm long were cut from the sheets and aged in ovens with circulating air at the Sandia National Laboratories. Treatment of the samples is summarized in Table 1.

NMR measurements. NMR experiments were performed on a Bruker Avance spectrometer at 400 MHz ^1H resonance frequency. The spectrometer was equipped with a microimaging probehead with three orthogonal gradients of maximum field strength 100 G/cm. Experiments were performed with a 15 mm resonance coil at 60 °C. Spin-lattice relaxation was measured by the saturation recovery method. The resulting intensities were fitted to the formula

$$M(t) = M_0(1 - e^{-t/T_1}) + y_0 \quad (1)$$

where M_0 and $M(t)$ represent the magnetization at equilibrium and at time t , respectively, and y_0 is the offset in the microimaging experiments.

In order to determine the transverse relaxation rate, we measured the intensity of the signal as a function of the delay between pulses. The intensities of the signal follow the model proposed by Kuhn et al. [8], according to which

$$M(t) = A \exp\left(-\frac{t}{T_2} - \frac{qM_2 t^2}{2}\right) + B e^{-t/T_2} \quad (2)$$

where the parameters A and B describe the contribution from the parts of the chains between cross-links and from the dangling ends, respectively, and the factor qM_2 is the reduced value of the second moment of the resonance line.

Microimaging experiments were performed using the

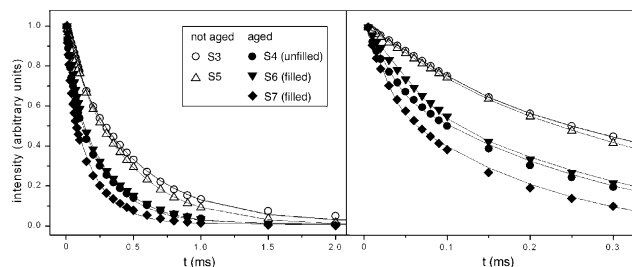


Fig. 2. Left: Decay of transverse magnetization for a series of samples. Right: enlarged initial part of the decay curves, showing non-exponential decay of transverse magnetization in the aged samples.

spin-echo method without slice selection and a relaxation filter [17] at the beginning of the spatial encoding part. A series of images with varying delay during the preparation period was acquired. The parameter-selective image was calculated by analyzing and fitting the data for each individual pixel of the image.

3. Results and discussion

Aging shortens T_2 (Fig. 2), as demonstrated by the most aged samples S7 (filled) and S4 (not filled). In contrast, the bulk values of T_1 increase with aging (Fig. 3). The values of parameters fitted using Eqs. (1) and (2) are given in Table 2. We interpret the relaxation times as follows. Stohrer et al. [18] found that the swelling of (not filled) polyisoprene results in a greater mobility of chain defects (kinks) and thus a shift of the high-temperature minimum of $1/T_1$ towards lower temperatures (to the right-hand side on the reciprocal temperature scale). By analogy, we believe that the extra cross-linking in an aged polymer reduces the mobility of chain defects, and thus the shift of the minimum towards higher temperatures (to the left). If, during the measurement, we are to the right of the minimum, we observe an increase in the value of T_1 .

The spin-echo image reveals that sample S6 (Fig. 4(a)) is very inhomogeneous. The intensity of the NMR signal at the edges of the sample is much lower than in the middle region, suggesting the existence of a surface layer of aged elastomer. By contrast, the T_1 image (Fig. 4(b)) shows that the spin-lattice relaxation time is homogenous across the entire cross-section. The average value of T_1 calculated from the image is 805 ms, compared with 708 ms obtained for this sample from bulk measurements.

Table 1
Treatment of the samples

Sample	Filler	Aging	Aging temperature (°C)	Aging time (days)
S3	None	None	–	–
S4	None	×	140	16
S5	Carbon black	None	–	–
S6	Carbon black	×	125	7
S7	Carbon black	×	125	18

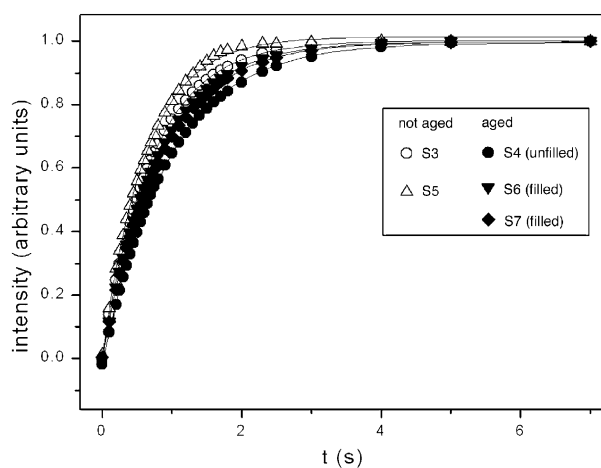


Fig. 3. Recovery of longitudinal magnetization after the saturation recovery pulse sequence for a series of samples.

The transverse relaxation time depends very strongly on aging. T_2 varies by a factor of ca. 2 between samples S3–S4 and S5–S7 (Table 2). The fitted value of the second moment, qM_2 , increases by a factor of ca. 10. The aged samples therefore have a stronger residual dipolar coupling, through additional topological constraints introduced during aging.

The fitted values of the parameters A and B (Table 2), related to the relative contributions from the inter-crosslink segments of the chains and the dangling chain ends, also change greatly with aging. Parameter A is 50% larger for the aged sample, S4, than for sample S3, and ca. 3 times larger for sample S7 than for sample S5. In contrast, parameter B decreases with aging from S3 > S4 and from S5 > S7. This suggests that aging increases the relative quantity of inter-crosslink chains in comparison to dangling ends. Considering the contributions of the inter-crosslink segments, the dangling ends and the measured value of qM_2 , we conclude that aging proceeds via additional cross-linking.

The longitudinal relaxation time, T_1 , increases in the course of aging, from 715 ms for the unaged sample, S3, to 940 ms for the aged sample, S4, and from 668 ms for sample S6 to 833 ms for the more aged sample, S7. This results from the difference in molecular mobility introduced in the course of aging [10].

The image in Fig. 4(a) shows a 50% variation in signal intensity between the edges and the middle region. Imaging with slice selection was not possible because signal intensity

Table 2
Parameters of Eqs. (1) and (2) fitted to the experimental data

Sample	T_1 (ms)	A (a.u.)	B (a.u.)	T_2 (μ s)	qM_2 (s^{-2})
S3	715	0.13	0.87	490	1.5×10^8
S4	940	0.19	0.79	260	1.5×10^9
S5	668	0.08	0.93	420	1.7×10^8
S6	782	0.22	0.77	290	3.9×10^8
S7	833	0.26	0.74	190	1.9×10^9

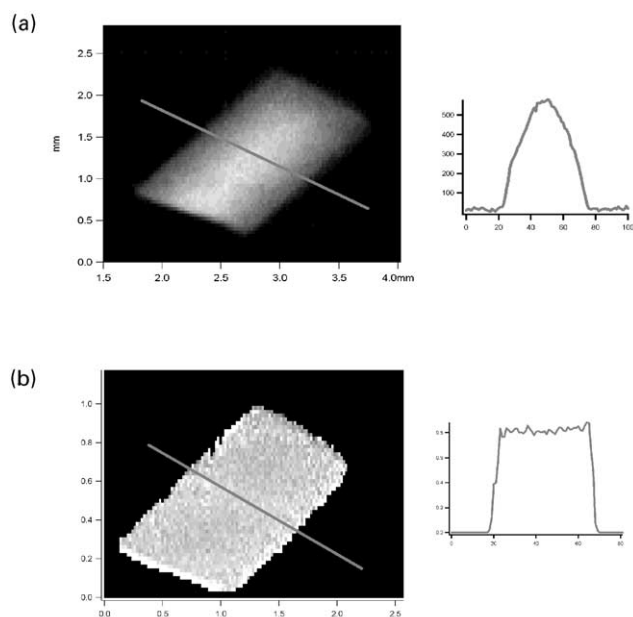


Fig. 4. (a) Left: ^1H spin-echo image of sample S6 with 128×256 pixels, read gradient 45 G/cm, phase gradient 18.2 G/cm, no slice selection, pixel resolution $80 \times 40 \mu\text{m}$, repetition time 4 s, echo time 1.2 ms. Right: spin-echo profile. (b) Left: T_1 image of sample S6, 128×256 pixels. Right: T_1 profile.

was very low. The parameter selective image was calculated instead from a series of imaging experiments. The resulting T_1 map (Fig. 4(b)) provides reliable information on spatial changes in NMR parameters across the sample. T_1 is uniform across the sample. On the other hand, T_1 imaging does not confirm the reported existence of a surface layer in the aged samples [10]. The variation of the intensities in the standard spin-echo image is probably caused by T_2 weighting, which suggests that T_2 imaging provides better contrast for observing the spatial distribution of aging changes than does T_1 imaging. Unfortunately, imaging of systems with such a short T_2 using the spin-echo method does not give reliable results, so that another fast imaging method, such as single point imaging, must be used.

4. Conclusions

NMR relaxation times and parameter-selective imaging are very sensitive to changes caused by aging in nitrile rubbers. Both bulk and spatially resolved NMR methods can be used. Measurements of the relaxation time show that aging proceeds mainly via additional cross-linking. Scission of the polymer chains does not appear to contribute to aging. T_1 imaging shows that there is no spatial distribution of spin–lattice relaxation times.

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