



QUALITY ASSURANCE OF ELASTOMERS BY INVESTIGATION OF MOLECULAR DYNAMICS OF THE HYDROCARBON BACKBONE USING NUCLEAR MAGNETIC RESONANCE

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Magnetic Resonance Techniques have been used to measure the crosslink density of differently compounded and cured rubber materials. The crosslink density or related parameters were measured as a function of composition of the compound, curing time, sample tempering and mixing time of the uncured compound. Physical, chemical and total crosslink density was determined on uncured compounds and cured rubbers. The results show clearly the ability of the Magnetic Resonance Crosslink Density Measurements to determine not only crosslink density, but also several more parameters characterizing the molecular dynamics of the network in dependency of rubber compounding, preparation and composition.

Introduction

The knowledge of crosslink density and crosslink density inhomogeneities is inevitable for the assessment of rubber quality, as well as for the optimization of curing conditions and tailored design of new products with improved mechanical and aging properties.

The determination of crosslink density in industrial manufacturing processes, but also in research laboratories, requires a fast and efficient, simply to use and, if possible, automated measurement procedure. Hence, the use of Nuclear Magnetic Resonance Techniques in a production environment would eliminate the need of time consuming and chemical or mechanical laboratory tests for crosslink density measurements.

Many publications over the past years (1-4) have demonstrated the ability of NMR Techniques, to determine crosslink density of almost all possible kind of rubber materials by the measurement of molecular dynamics of the hydrocarbon chain.

The determination of crosslink density using Magnetic Resonance Techniques is based on the measurement of the NMR spin spin relaxation time T₂. The spectral density function of the spin spin relaxation time T₂ is sensitive to molecular motions as they typically appear in rubber networks, covering the dynamics of the crosslinked network as well as dangling free chain ends and small molecules such as oil or solvents.

Experimental

All measurements were performed using IIC's MR-CDS 3500 Quality Control/Quality Assurance (QC/QA) Spectrometer. The standard XLD technique

based on IIC's modified Hahn-Echo technique has been applied.

64 data points between tau=30 μs and up to 50 ms were acquired at a repetition time of up to 800 ms. The total measurement time per experiment was approx. 8 min. Averaging has been done to improve signal to noise ratio SNR.

Data analysis has been performed using a non-linear curve fitting algorithm optimized for the XLD relaxation function. The results reveal all the parameters such as crosslink density, T₂, and the relative fraction of uncrosslinked and crosslinked material, as well as a statistical data analysis.

Equ. 1 is the basic XLD relaxation function used for data analysis of the proton magnetization.

$$M(t) = A_0 + A_1 e^{-\frac{t}{T_2} - \frac{1}{2}qM_2 t^2} + A_2 e^{-\frac{t}{T_2}} \quad (1)$$

M(t) corresponds to the magnetization decay function,, A₀ reflects an additive constant without any physical meaning, used to compensate for a possible DC offset and hence improvement of the fitting procedure,

A₁ represents the amplitude of the rigid fraction of the rubber network,,

T₂ corresponds to the highly mobile part of the rubber network, including solvent molecules and freely rotating molecular end groups,

A₂ represents the relative amount of the mobile fraction of the rubber.

qM₂ corresponds to the remaining dipolar magnetic coupling of the hydrocarbon chain protons as a consequence of the anisotropic motion of the chain segments.

The translation of NMR relaxation parameters is commonly done using the Gotlib relation (3).

Results and Discussion

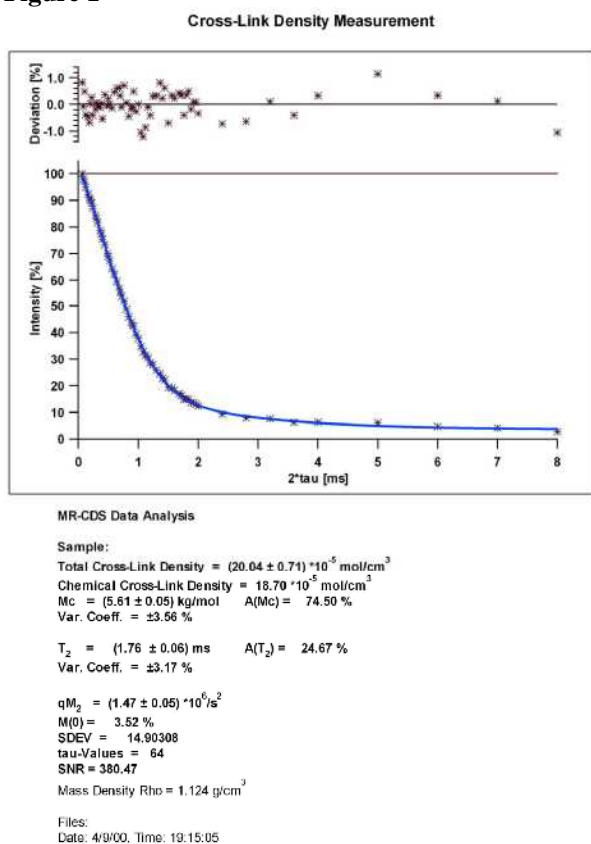
The results of MR crosslink density measurements agree very well with those obtained by swelling and Mooney Rivlin tests.

Table 1

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample 10
Act ISIRI	00	00	100	100	120	120	100	100	100	00
N330					50	50	50	50	50	80
Oil	10	10	10	0	15	10	10	10	10	10
ZNO	0	0	0	0	0	0	0	0	0	0
Wax	1	1	1				1	1	1	1
MD	1	1	1				1	1	1	1
8 FPD	1	1	1				1	1	1	1
Sulfur	0.5	1.5	3.0	3.0	3.5	1.5	3.0	6.0	1.0	0
C/S	0.53	1	2	4	0.33		2	2	1	1
Mass (g/cm ³)	0.647	0.653	0.661	0.676	1.104	1.109	1.12	1.022	1.176	

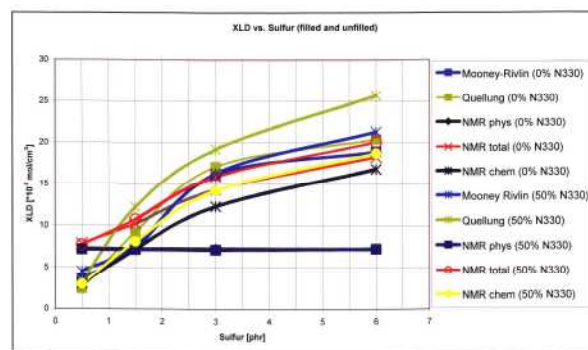
Samples composition used for crosslink density measurements on NR

Figure 1



Typical print out of a crosslink density measurement

Figure 2



Comparison of swelling, Mooney Rivlin and MR-CDS

Conclusions

This paper demonstrates the use of a low cost and very compact NMR system with dedicated features for quality control and quality assurance in rubber testing. Using the **IIC Magnetic Resonance Crosslink Density Spectrometer MR-CDS 3500**, measurements of the physical and chemical crosslink density can be performed within 16 sec to 15 minutes typically, with a standard deviation of about 3%. No special sample preparation is required. Additionally, NMR relaxation parameters such as T_1 , T_2 or $T_{1\rho}$ can be determined and used for a more detailed characterization of the mobility of the elastomer network, e. g. filler-matrix interactions, aging processes, oils and other organic compounds typically found in rubbers.

Online observation of vulcanization process on the molecular level with a time resolution of about 16 sec may provide a new insight into rubber curing and will contribute to the optimization of rubber processing parameters.

Results of a study on differently filled rubbers with various crosslink densities performed in collaboration with Bayer AG, Germany, and the DIKare shown in comparison to the well known methods of swelling, Mooney-Rivlin plots and compression set measurements. Examples of investigations on car tire surfaces are also given.

References

1. W. Gronski, U. Hoffmann, G. Simon, A. Wutzler, E. Straube, Rubber Chem. Technol. 65, 63 (1992)
2. G. Simon, K. Baumann, W. Gronski, Macromolecules 25, 3624 (1992)
3. (21) W. Kuhn, P. Barth, S. Hafner and G. Simon, H. Schneider, Macromol. 27, 5773-5779 (1994)
4. W. Kuhn, I. Theis, E. Koeller, Adv. Tomogr. Imag. Meth. Anal. Mater., Materials Research Society Symp. Proc. 217, 33 (1991)