Pulsed NMR in Elastomer Analysis

Brief description of basic experiments realized by the **Spin Track** NMR analyzer

1. Introduction

The rheology is widely known as one of the basic methods for rubber investigations for many years. At the same time, a variety of other methods of physical and chemical analysis suitable is available for rubber industry. One of them, the Time-Domain Nuclear Magnetic Resonance (TD--NMR) Spectroscopy is very sensitive to structural properties of elastomer materials. Moreover, by using NMR it is possible to obtain information complementary for rheology. Several experiments devoted to elastomer structure investigations by LR NMR are described below.

2. Equipment

Fig. 1. NMR analyzer **Spin Track**

The wide band universal mobile NMR-analyzer **Spin Track** (Fig. 1) was used in all experiments with rubber made by various investigators.

The main advantages of **Spin Track** are mobility, low cost and excellent technical characteristics.
For the experiments the analyzer was supplied with 2 types of sensors: convenient with 10 mm tubes and surface NMR sensor (Fig. 2). Using the surface variant it is possible to investigate large objects just placing them onto the sensor surface, thus cutting and any complicated preparations of samples are not required.

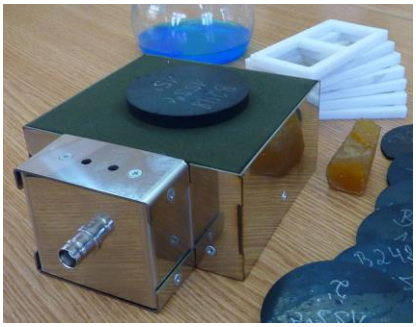

Fig. 2. Surface NMR sensor **Spin Surf**

3. Temperature dependencies in carbon-black filled rubber

Stiffness of polymer chains is directly coupled with mobility of hydrogen nuclei - protons. And the information about proton mobility can be derived from NMR relaxation decay (Fig. 3).

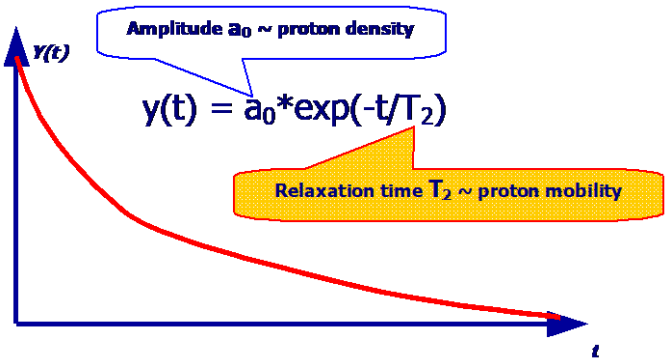

Fig. 3. Spin-spin relaxation T_2 characterizes proton mobility.

Carbon black filler bonds polymer chains which form structures with restricted proton movability. A set of carbon-black filled rubber samples of different degree of cross-link density was investigated using original equipment from Resonance Systems Ltd.

Clear dependence of T_2 (spin-spin relaxation time) on vulcanization degree (Fig. 4) is observed more effectively at high temperatures (more than 90^0C).

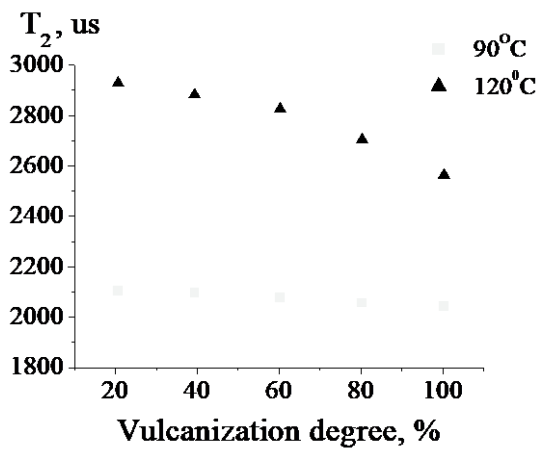

Fig. 4. Dependence of T_2 on vulcanization degree at different temperarures

Using these data it is possible to predict polymer elasticity behavior at high temperatures.

4. Temperature dependencies in EPDM rubber with different fillers

6 samples of EPDM with different fillers (table 1) were investigated using the method mentioned above.

Table 1

Filler	Nº sample
No filler	211
N121	215
Ecorax1720	219
N990	224
Ultrasil7000	234
Ultrasil7000+Si69	238

The results are shown at Fig. 5. As it is easy to see the dependence is observed better at high temperatures.

Using WLF equation, VFT equation and theory of free volume original approach of glass transition temperature determination was utilized.

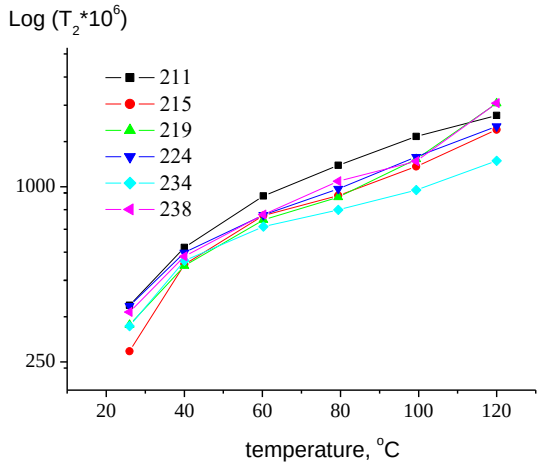

Fig. 5. Dependencies T_2 on temperature in EPDM samples

Any sensor can be calibrated by compound with known glass transition (Tg) temperature using original equation:

$$T_2 = e^{2.303\left[a+b\left(\frac{C_1(T-Tg)}{C_2+T-Tg}\right)-1\right]}$$

Table 2

Sensor type	a	b	c
Surface	-7	4.5	0.2
10mm tube	-5.9	5.58	0.27

The results of calibration for used sensors are shown at table 2. With such calibration it is possible to determine glass transition temperature at any ambient temperature.

Results of glass transition temperature calculation using presented approach are shown at table 3.

Table 3

Filler	T_g*1, °C	T_g*2, °C	T_g, °C
No filler	-76	-75	-75
N121	-79	-79	-80
Ecorax1720	-80	-84	-85
N990	-85	-80	-82
Ultrasil7000	-74	-71	-79
Ultrasil7000+Si69	-74	-72	-77

Measures were done with *1 - 10 mm tube sensor and *2 - surface NMR sensor. The very right column contains values of glass transition temperature estimated by the rheological method[1].

6. Curing of PDMS compounds

PDMS self-curing compound was using both analyzer configuration mentioned above. Whole curing process observed by NMR shown at Fig. 6.

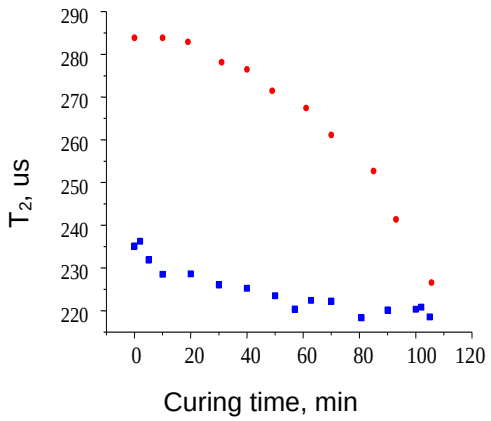

Fig. 6. Dependence of T_2 relaxation time on curing time of PDMS samples in closed sensor of convenient NMR-analyzer at 40°C (●) and open-air surface NMR sensor at 26°C (■)

To observe curing process using surface NMR sensor is the best way because sample is held at normal conditions.
As for NMR sensitivity to curing process it should be mentioned that it more reliable than standard rheology. Full curing process of PDMS shown at Fig. 7.

Producer warrants that 24 hours are enough for full curing of whole volume of sample. But it can be clearly seen that process did not finished during this time. T_2 significantly decreases after that point. It means that viscosity decreases and curing process goes on.

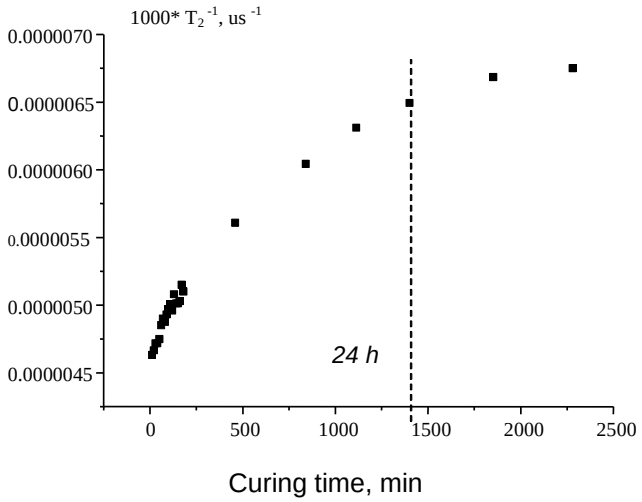

Fig. 7. Dependence of spin relaxation rate on curing time

7. Surface NMR in tire industry

Surface NMR sensor was used in tire industry to investigate a depth of forcing compound penetration into tire volume.

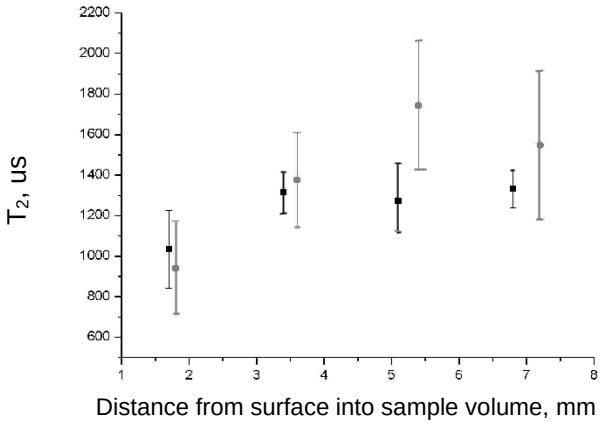

Fig. 8. T_2 dependence on penetration depth

Surface NMR sensors from Resonance Systems Ltd. have very high point of penetration, up to 10 mm. Operating by frequency is possible to shift resonance point into the sample and acquire relaxation decay.

[1] Molecular dynamics of elastomers investigated by DMTA and the NMR-MOUSE®/ Herrmann V., Unseld K., Fuchs H.-B., Bluemich B.// Colloid Pol Sci.-2002.-№280.-pp.758-764.

T_2 proportional proton mobility, but forcing compound reduces it. It should be concluded than T_2 gives possibility to obtain distribution of compound into the sample (Fig. 8).

8. Defect Identification in Trachea Tubes

Measuring of T_2 by the Hahn Echo Decay was used. Samples were cut to the small sizes to fit glass ampoule of NMR sensor. The T_2 of samples that is proportional to the molecular stiffness slightly goes down with the increase of amount of sterilization cycles.

The ”defect” sample has got the minimum mobility of internal hydrogen nuclei. This can be related to reduced elasticity. The T_2 of samples is proportional to the molecular stiffness slightly goes down with the increase of amount of sterilization cycles (table 4). The ”defect” sample has got the minimum mobility of internal hydrogen nuclei. This can be related to reduced elasticity. Results of measurements are critical to temperature changes. Accuracy of T_2 estimation is caused by the ”good” volume of statistical averaging.

Table 4

Sample:	New	1 cycle	10 cycles	defect
T_2, ms	1.31	1.27	1.28	1.19
	1.3	1.25	1.25	1.15
	1.27	1.26	1.24	1.19
	1.28	1.27	1.23	1.21
Mean T_2, ms	**1.29**	**1.2625**	**1.25**	**1.185**

9. 1-D imaging with surface NMR

Fig. 9. 1-D surface NMR imager

Complicated measurement system was developed to resolve a space distribution of armed fibers in amortization spring. Distance between fibers was exact and equals to 0.8 mm. The measurement system is shown at Fig. 9. It was supplied pulsed gradient system, step motor for sample rotation and driven by **Spin Track** NMR analyzer.

Standard phase encoding pulse sequence was used. The results are shown at Fig. 10. Peaks correspond to rubber base.

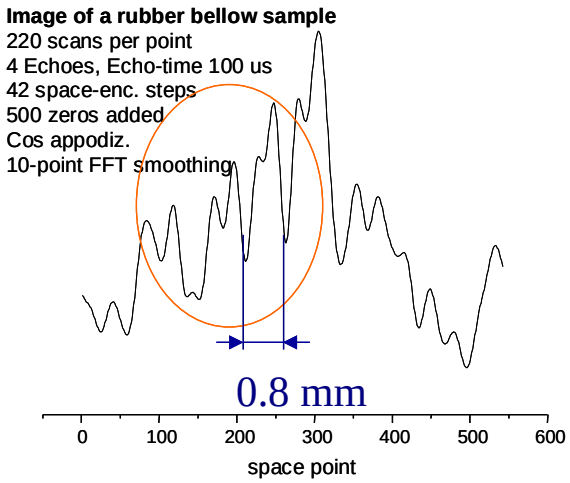

Fig. 10. Image of armed rubber spring

10. Software

NMR spectrometer is controlled by original software Relax developed by Resonance Systems Ltd.

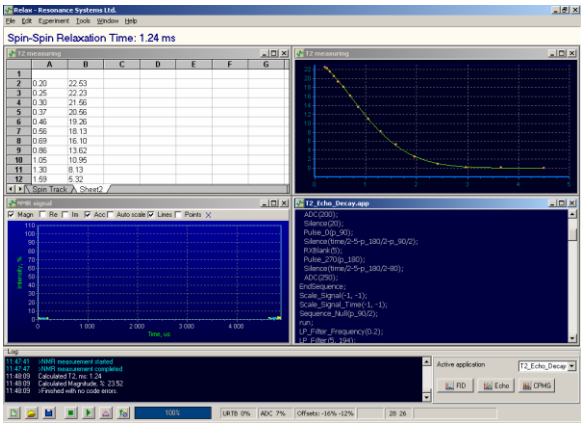

Fig. 11. **Relax** software

11. Contacts

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