Rheology · Curing · Cross-linking · Molecular mobility · Permanent magnets · Rubber · NMR

A new design for an in-situ combination of NMR and rheological measurements is presented. The NMR instrumentation is based on a Bruker Minispec spectrometer with a home-built magnet system consisting of 64 permanent magnets in a so-called MANDHALA arrangement. This magnet reaches a flux density of about 0.23 T, corresponding to a ^{1}H NMR resonance frequency of about 9.5 MHz. The NMR apparatus is combined with a Scarabaeus SISV50 instrument with modified sample cells to allow synchronous in-situ rheological and NMR measurements. This unique instrument and first exemplary measurements of a curing epoxy resin and the vulcanization of a rubber sample are presented.

Kombinierte Messung von mechanischen Eigenschaften und NMR Relaxometrie

Rheologie · Vernetzung · molekulare Beweglichkeit · Permanentmagnete · Kautschuk · NMR

Ein neuartiges Design für kombinierte, in-situ NMR- und Rheologie-Experimente wird vorgestellt. Das NMR-Gerät besteht aus einem Bruker Minispec mit einem im Eigenbau entwickelten Magnetsystem, welches aus 64 Permanentmagneten in einer sogenannten MANDHALA Anordnung besteht. Damit wird eine magnetische Flussdichte von ca. 0.23 T erreicht, was einer NMR Resonanzfrequenz von 9.5 MHz für ^{1}H entspricht. Das NMR-Experiment ist mit einem Scarabaeus SISV50 Rheometer mit einer modifizierten Probenkammer kombiniert worden, um synchron und in-situ sowohl rheologische als auch NMR-Messungen vornehmen zu können. Dieses einmalige Gerät wird zusammen mit ersten exemplarischen Messungen eines aushärtenden Expoxiharzes und der Vulkanisierung einer Gummimischung vorgestellt.

Combination of NMR Relaxometry and Mechanical Testing During Vulcanization[1]

The first idea of combining NMR (nuclear magnetic resonance) together with measurements of rheological properties is described by Martins et al. in 1986 [1]. This idea, which was called "Rheo-NMR", allows unique investigation of complex systems and opens up a new field with large potential towards both, fundamental research and industrial applications.

Conventional rheology measurements such as viscosity, modulus etc. relate to the changes that occur on a macroscopic level in a sheared sample. However, such macroscopic parameters are linked to chemical and dynamic changes on a molecular level. As a consequence, only combined methods allow bridging of the largely different time and length scales for complex and time dependant systems.

Rheo-NMR, as one example, can simultaneously probe the molecular (few nm) and macroscopic dynamics of the sample. The benefit of using the in-situ combination of NMR and relaxation measurements under mechanical shear for rubber investigations is obvious: shear measurements provide information about the mechanical properties of a macroscopic sample, and NMR-relaxometry about the mobility of the protons on a length scale of 1 – 2 nanometers. If both methods are conducted within the same apparatus, and ideally synchronously, fast reactions which involve rheological changes, e.g. the time evolution of the curing process can be investigated.

This work is composed of two parts: In the first part we report the development and construction of a new Rheo-NMR instrument, and in the second part examples of in-situ investigations of resin curing and the vulcanization process in rubber within this instrument are shown.

Experimental

The instrumentation for the combined rheology and NMR apparatus was chosen with the aim to have the highest commercial availability of the components. Hence, it is built around an existing Bruker Minispec spectrometer (Bruker Biospin GmbH, Rheinstetten, Germany), additionally equipped by an home-built NMR-magnet to fit the commercial rheometer. The NMR magnet (Halbach dipole [2]) is constructed from two layers of permanent magnets (NdFeB N-45 alloy with a remanence of B_r ca. 1.33 Tesla) each arranged in an array of 32 forming a MANDHALA arrangement [3]. The NMR probe head, including the RF coil and the electrical circuit, is then centered between the two magnet layers. This "sandwich design" of magnet arrays and RF (radio frequency) probe head is shown in Fig. 1. The resulting magnetic flux density is about 0.23 T. This corresponds to a proton frequency of about 9.5 MHz. The observed magnetic field inhomogeneity is on the order of 0.5 % (5000 ppm). This corresponds to an inherent line width of about 50 kHz. Note that this resolution is not sufficient for spectroscopic measurements but allows for the excitation of the entire sample volume without any problems by reasonably short RF pulses (with the 300 W amplifier of the Bruker Minispec a 8 µs pulse was sufficient for full excitation). The achieved field

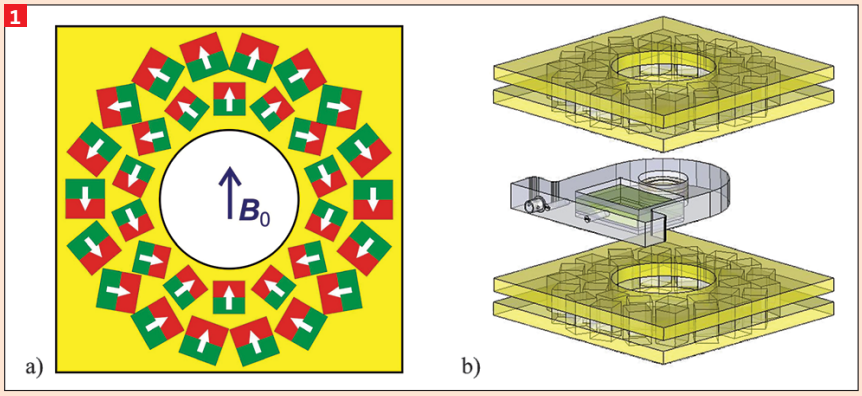
Authors

S. Kahle, W. Nussbaum, Langgöns, M. Hehn, H. P. Raich, M. Wilhelm, Mainz, P. Blümler, Jülich

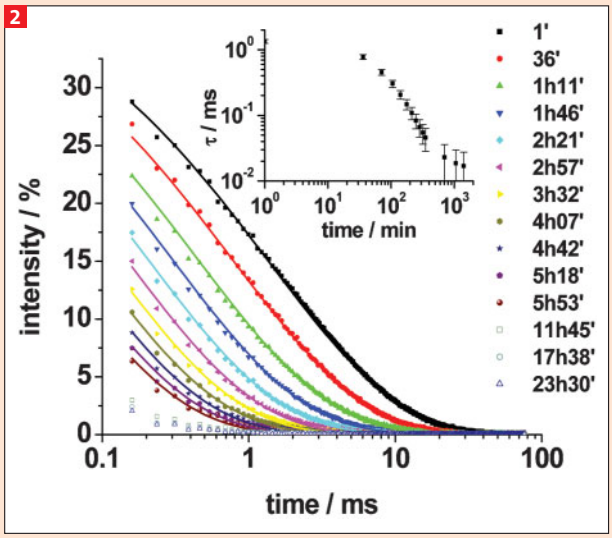
Corresponding author:
M. Wilhelm
Max-Planck Institute
for Polymer Science
55021 Mainz
www.mpip-ainz.mpg.de
Universität Karlsruhe
76131 Karlsruhe
www.polymer.uni-karlsruhe.de
E-mail: wilhelm@polymer.uka.de

[1] Lecture given at the International Seminar on Elastomers Freiburg (Germany), Sept. 23-27 (2007)

homogeneity and the sample excitation then allows for relaxation measurements with appropriate pulse sequences.
NMR relaxation measurements to quantify T_1 and T_2 were performed by using the inversion recovery [4] (for the determination of the spin-lattice relaxation time, T_1) and Carr-Purcell-Meiboom-Gill [5] (for the determination of the spin-spin relaxation time, T_2) pulse sequences. The length of the 180° pulse was determined to be 16 µs. The CPMG sequence is composed of 3000 to 6000 echoes, and 12 transients were typically accumulated. The recycle delay was determined individually for each sample by T_1 measurements prior the CPMG experiment. Typical T_1 times are in the range of 0.1 to 2 seconds, therefore the 12 transients are acquired within much less than 1 minute.



1 **Design of NMR magnet and RF-probe: The static magnetic field is provided by the magnet arrangement as sketched in a). The detailed structure of the probe is shown in b) It is comprised by two nested Mandhala-rings [3] of 14 and 18 magnets, respectively. Two of these magnet arrays are sandwiched by the central NMR-transmit and receive circuit, consisting of the RF-coil and the electrical components for matching and tuning the resonance frequency**



2 **NMR T_2 relaxation measurements of an epoxy resin at 14 different cross linking times. The inset shows the time dependence of the characteristic relaxation times T_2 (τ, see eqn. 1) versus the curing time**

Cell Geometry for Rheo-NMR

In order to test the reliability of the NMR-measurements, water and rubber samples were investigated (not shown). The T_1 and T_2 values observed were in agreement with literature values and didn't vary over the sample volume (tested with smaller samples at various spots, also not shown).
For the combined Rheo-NMR measurements a SIS V50 rheometer (Scarabaeus GmbH, Langgöns, Germany) was modified with the home-built NMR magnet and probe. Especially when the permanent magnets are combined with a rheometer, it is important to remove all materials that can be magnetized from the magnets' proximity. Therefore, the sample holder of the rheometer was completely redesigned, and all ferrous parts were replaced by non-magnetizable materials. Since the sample has to be excited by RF waves, it is also necessary to have no electrical conductors inside the NMR probe. Consequently, the sample holder was made from glass-fiber-filled PEEK material. With this high-temperature stable material it is possible to heat the samples higher than 200 °C.

Results and Discussion

Relaxation time measurements

To test the new NMR magnet and RF probe the cross link kinetics of an epoxy resin were determined. Fig. 2 displays CPMG measurements of the transverse relaxation time, T_2, after different curing times. We observe that the magnetization decays faster with increasing curing time. This corresponds to the reduced molecular mobility of the sample. The inset of this figure shows the characteristic relaxation times, determined by fitting the different NMR intensities by using a stretched exponential function:

$$I(t) = I_0 \exp\left[(t/\tau)^{\beta}\right]. \qquad [1]$$

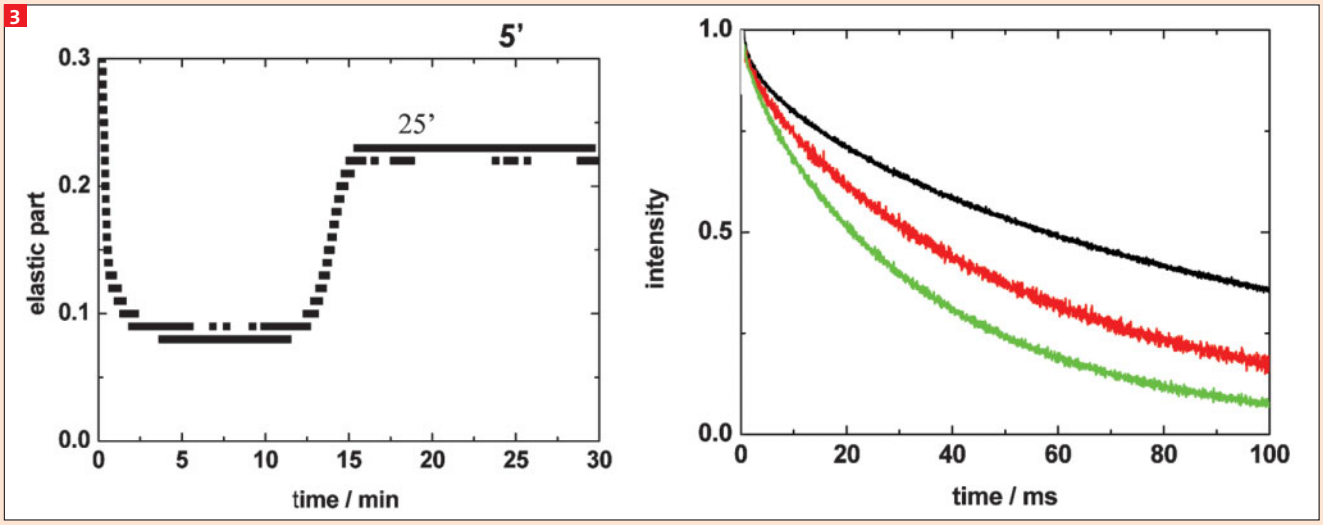
In this equation τ is the characteristic T_2 relaxation time, I_0 the intensity at $t = 0$, and β the stretching parameter.
Note that in contrast to common relaxation measurements (dynamic mechanic measurements, dielectric spectroscopy, etc.) the NMR measurements show opposite behavior, i.e. longer relaxation times T_2 are related to higher mobility.

In-situ Rheo-NMR Measurements

For the first combined tests the lower part of the rheometer cell was filled with the sample and the cell was closed. After certain times (5, 14, 25 minutes) the rheometer was opened again, and the NMR T_2 detected. This procedure became necessary due to the remaining large influence of magnetizable rheometer parts in the vicinity of the NMR apparatus (their replacement is under construction). The NMR T_2 parameter was recorded in less than one minute. The rheometer cell was closed again and the rheological measurements continued. The reduction of molecular mobility is reflected in a faster decay of the magnetization as depicted in Fig. 3.

Conclusions

An apparatus to perform in-situ Rheo-NMR experiments was developed and first tests were conducted. The NMR instrument was implemented in a SIS V50 rheometer from Scarabaeus by using permanent magnets in



3 Left: Time dependence of the elastic part of the shear modulus during vulcanization. The rubber mix consists of natural rubber, sulfur, oil, and accelerator CB. The shear frequency is 1 Hz, the strain amplitude 0.2 %, and the temperature is 150 °C.
Right: Corresponding NMR T_2 measurements after 5 (black), 14 (red), and 25 (green) minutes

the MANDHALA arrangement. This allows quantifying of the T_1 and T_2 NMR relaxation parameters within 1 minute during curing. Thus macroscopic and microscopic information, the shear modulus and local molecular motion, are combined.

Both experiments, NMR and rheological measurements, can be performed in the same instrument simultaneously. Focus was given to commercial availability of the different components. To further improve the performance of this instrument, residual magnetic materials within or close to the NMR magnets need to be replaced by non-magnetizable materials.

Acknowledgements

We would like thank Prof. H. W. Spiess, Dr. M. Parkinson, Dr. P. Minkin and Dr. G. Guthausen for helpful discussion.

References

[1] A. F. Martins. P. Esnault, F. Volino, *Phys. Rev. Letters* **57** (1986) 1745.
[2] K. Halbach, *Nucl. Instr. Meth.* **169** (1980) 1.
[3] P. Blümler, H. P. Raich, *Concepts in Magn. Reson. B: Magn. Reson. Eng.* **23 B** (2004) 16.
[4] R. L. Vold, J. S. Waugh, M. P. Klein, D. E. Phelps, *J. Chem. Phys.* **48** (1968) 3831.
[5] (a) H. Y. Carr, E. M. Purcell, *Phys. Rev.* **94** (1954) 630. (b) S. Meiboom, D. Gill, *Rev. Sci. Inst.* **29** (1958) 688.