Nuclear magnetic resonance · NMR · product control · elastomers

NMR as a method has experienced continuous growth and development over the years and new fields of applications are steadily being explored. While progress in methods and applications of NMR to molecules in solution, solid materials, and medical imaging is reported in the scientific literature, developments in NMR with applications outside a laboratory often are encountered only occasionally, and some information can be retrieved from the internet. In the following some of the industrial applications of magnetic resonance are reviewed in an attempt to assess the current state of magnetic resonance in environments more demanding than a clean laboratory, and the possibilities of NMR for quality control of elastomer products are analyzed by example of the NMR-MOUSE®.

**NMR zur Produkt- und Qualitätssicherung von Elastomeren**

Magnetische Kernresonanz · NMR · Produktkontrolle · Elastomere

Im Laufe der Jahre hat sich das Verfahren der magnetischen Kernresonanz (NMR) kontinuierlich weiterentwickelt und neue Anwendungsfelder erschlossen. Während der Fortschritte bei Methoden und Anwendungen der NMR auf Moleküle in Lösung, feste Materialien, und bei der medizinischen Bildgebung in der wissenschaftlichen Literatur erfaßt wird, so werden Entwicklungen der NMR mit Anwendungen außerhalb eines Labors dort nur selten angetroffen, wobei jedoch einige Information darüber aus dem Internet erhalten werden kann. Im folgenden wird ein Überblick über einige industrielle Anwendungsfelder der magnetischen Resonanz gegeben, um den gegenwärtigen Stand des Verfahrens für Anwendungen außerhalb einer sauberen Laborumgebung zu bewerten und die Möglichkeiten der NMR für die Qualitätssicherung von Polymerprodukten am Beispiel der NMR-MOUSE® zu analysieren.

**Magnetic resonance outside a clean laboratory**

Magnetic resonance outside a clean laboratory is nearly as old as NMR itself [1]. Already in the fifties the question of characterizing geological formations of bore-holes was addressed first by earth-field NMR techniques and then with the help of polarizing magnetic fields [2]. Today this field has matured into a powerful industry, where NMR relaxometers are lowered down a bore-hole and relaxation maps are acquired which bear information about the fluid and gas content of the surrounding rock while the device is pulled up [3]. This principle of inside-out-NMR has been suggested for use also in medicine, material science, and process control [3, 4], and suitable devices for use of NMR in the production line appear to have been produced by Southwest Research [5, 6]. Based on the principles of inside-out-NMR, the NMR-MOUSE® [7] has been developed for soft matter analysis (see below) [8–11]. Mobile unilateral EPR devices have been built based on similar ideas for assessment of damage and pollution from nuclear radiation in Japan [12]. NQR detectors are used in airports for identification of plastic explosives [13] and narcotics in suspicious luggage [14, 15]. Current interest focuses on refinement of the technique for reliable detection of non-metallic landmines for different explosives including TNT [14, 16]. NQR devices do not require magnets for polarization of spins, only rf antennas for excitation and detection. Extra polarizing fields are discarded also in earth field NMR, where coils with diameters of up to 100 m are used to locate underground water reservoirs [17]. Smaller portable devices have been developed for in situ analysis of Antarctic sea ice, however, in combination with a pulsed polarization field for signal enhancement [18]. Dedicated NMR devices have also been developed for studies of nutrient transport in plants [19] and for water and ion transport in building materials [20]. Moreover, NMR spectrometers are used inline in oil refineries for control of reaction intermediates and products in liquids product-stream by recording the time-dependent signal intensities at particular chemical shifts which are characteristic of a critical component in the fluid product stream [21, 22]. Off-line analysis of polymer products and raw materials, elastomers, and various food stuffs can be characterized with high accuracy by low resolution NMR not only for water and fat content, but also for extend of curing, molecular weight or melt-flow index, cross-link density, and other material parameters [23–26]. In the dairy industry imagers have been installed with conveyor belts running through the magnet which carry boxes of packaged food. Integral relaxation signals from large voxels chosen at known positions of food containers in the boxes on the belt are compared for deviations from a running calibration reference to identify food spoilage [27]. A similar scheme has been proposed for quality control of raw rubber packs in the elastomer industry [28].

**Low-field NMR**

In all of these cases simple NMR techniques are employed, which consist of few pulses only, and stripped down NMR spectrometers and imagers are employed in robust cases which can be operated by technicians. PC-based spectrometers are produced by a variety of small and large NMR companies [22, 24–26, 29]. In addition to lower-cost spectrometers, also lower-cost
magnets often are employed with degraded magnetic field homogeneity. Although such fields may prohibit spectroscopic resolution of spin-1/2 nuclei by established techniques, relaxation times, diffusion coefficients, and parameters of coherent translational motion can still be measured, and NMR images can be generated by single-point imaging techniques.

Low-cost polarizing magnetic fields are often generated by permanent magnets, so that Larmor frequencies for $^1$H are less than 30 MHz. Depending on the magnet arrangement, weakly and strongly inhomogeneous magnetic fields need to be discriminated. In weakly inhomogeneous magnetic fields the bandwidth of rf excitation pulse still covers the spread in Larmor frequencies caused by the field inhomogeneities. In strongly inhomogeneous magnetic fields every rf pulse is selective. The former situation is typically encountered in low-resolution NMR, where a sample of the object under investigation is positioned somewhere inside a magnet arrangement. Apart from flow-through geometries the measurement is destructive and not suitable for in-line analysis. In the latter situation the magnetic field may be applied in a unilateral fashion, where field homogeneity is harder to achieve in a larger volume. Nevertheless such strongly inhomogeneous magnetic fields can be quite useful also for NMR in an industrial environment as is demonstrated by the NMR-MOUSE® [7–10, 30].

Unilateral NMR: quality and product control

Very interesting applications of unilateral NMR are in soft-matter analysis, where signals from liquid components are readily attenuated by fast molecular diffusion and only the cell structure of plants, the network of latex particles in a liquid, or of rubber in a finished product produces readily detectable signals. The use of echoes is a condition sine qua non to overcome unwanted signal dephasing by the magnetic field inhomogeneity and different types of echoes can be exploited for better discrimination of material properties. Although the echo decay is influenced by the magnetic field inhomogeneity, the distribution of the rf excitation amplitude in the sample, and the NMR pulse sequence parameters used [30], standard sequences can be developed for particular objects and geometries, so that apparent experimental relaxation times after all provide a measure for material properties and product quality. Because the instrumentation is mobile, investigations can be carried out at the site of interest (Figure 1, Figure 2). When reducing the receiver dead-times to less than 20 $\mu$s, rigid polymer materials can be investigated as well.

Unilateral NMR: fluid flow and imaging

By the judicious manipulation of moments of the magnetic field profile across the object, also translational flow of complex fluids can be assessed through phase-encoding schemes based on multi-echo sequences similar to the CPMG sequence which is often analyzed for a space-linear variation of the magnetic field. The NMR-MOUSE® produces a quadratic field profile and a theory for NMR pulse sequences sensitive to flow can be worked out similar to that known for linear field profiles, so that in principle, flow can be characterized noninvasively in a quantitative fashion by that device. In weakly inhomogeneous fields spatial resolution can be achieved by phase-encoding techniques like single-point imaging [31]. Such single-sided NMR imagers have first been conceived in the health industry [32], but applications for
product and quality control can also be envisioned in the polymer and elastomer industry, where the use of x-rays may be unsuitable less for reasons of contrast than for limitations in the operation of ionizing radiation in a factory implementation with access to different personnel.

Conclusions

Given the known sensitivity of the NMR-MOUSE\textsuperscript{®} with regard to discrimination of different properties of soft matter products and the possibility to perform imaging with unilateral NMR, low resolution NMR on the factory floor is indeed conceived feasible for product and quality control of elastomers. A drawback is the duration of measurement times, which may be shortened by a larger sensitive volume and an adapted coil geometry, so that useful data can be obtained in a matter of seconds instead of minutes for a variety of elastomers. Improvements in instrument dead-time will extend the range of applications of NMR on the factory floor from elastomer products to rigid and glassy polymer products including glass and carbon fiber reinforced materials.

References


[7] NMR-MOUSE\textsuperscript{®} is a registered trademark of RWTH, P. Blümner, and B. Blümich.


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