Quality Control with NMR: Selected Examples and Applications in Polymer Industry

In the polymer industry, the quality control of materials is an essential subject. Starting material, final products and various stages in between are to be tested in order to guarantee quality. The majority of test methods measures mechanical properties which often do not reveal the origin of possible deviations in quality. In polymer research, high resolution nuclear magnetic resonance (NMR) is often used for investigation of the molecular properties, which are essential for the macroscopic mechanical behaviour of a product [1–3]. However, high-end NMR equipment is often too expensive and requires scientists for operation. Thus there is a considerable need in analytical equipment which combines ease of handling by untrained personnel, small footprint and minimal service and maintenance requirement. One possibility is low-resolution (LR) or time domain (TD) NMR (Fig. 1, [4]). Unlike most of the mechanical testing methods, TD-NMR is a non-destructive and non-invasive method.

The method of nuclear magnetic resonance is based on the fact that a large amount of isotopes has a nuclear spin which has preferred orientations in a magnetic field, rather like a compass needle. This fact can be exploited to obtain some insight about material properties, as the nuclear spins “see” their surrounding by diverse nuclear interactions as for example the dipolar couplings. In this context, it is important that not only static interactions contribute to the NMR signal but also dynamic properties, as the interactions of nuclei with their surrounding are modulated by the molecular motions. Therefore, most TD-NMR applications in the field of polymer quality control and also polymer research are based on the fact that the molecular mobility of the polymer chains and their segments strongly influences the nuclear interactions and therefore the NMR parameters. Since TD-NMR yields low to no spectral resolution, the main parameters are relaxation times and their distributions, which are accessible by different pulse sequences, for example by the FID (Free Induction Decay) or CPMG (Sequence according to Carr, Purcell, Meiboom, and Gill). Several TD-NMR methods are well known, which depend on the polymeric samples to be measured and also on the question to be answered by the TD-NMR measurement. Different methods are discriminated: In case of absolute measurements, only signal amplitudes are measured at very well defined experiment time, reflecting specific material properties. An example is the elastomer content in hard plastics. The second method is a ratio method. Two signal amplitudes are measured again under well defined circumstances. Their ratio is used to obtain a quantitative information about a certain material property. An example is the determination of xylene soluble content in poly (propylene). Finally, relaxation time measurements have to be mentioned where amplitudes, their ratios or also relaxation times are correlated with material properties, for example the cross-link density. TD-NMR can assist in Quality Control and R&D in the following areas of interest: Characterisation of raw materials, characterization of recipes and their impact on the materials properties (e.g. additives, plastisers) and the quality control of final products. Here, we would like to give some insight by selected examples of TD-NMR quality control (QC) applications in the field of polymers nowadays.

The characterisation of polymers via TD-NMR starts with the raw material. These raw materials are often fractions of crude oil. In the mineral oil industry, an important question is the composition of the crude oil. Essentially the number of \(^{1}H\) spins determines the signal strength, and each substance in crude oil has a special ratio of \(^{1}H\) to the molecular weight. Thus, measuring the NMR signal very accurately characterizes the oil fractions. This method is an international standard (ASTM – D 3701, ASTM – D 4808 of the American Standardization of Technologies and Measurements (ASTM)), known as “Hydrogen Content in Hydrocarbons”. Apart from this application, also the oil content in wax can be addressed accurately by TD-NMR. An important question concerns the characterisation of raw polymer materials. It is

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well known, that the quality of the raw materials can fluctuate and that this has an impact on the quality of the final product. Here, TD-NMR can contribute to establish a defined quality via relaxation weighted measurements. Chain length and thus the molecular weight strongly influence the chain dynamics and therefore the NMR relaxation. These properties are therefore accessible by TD-NMR. The main applications are the measurement of xylene soluble content and tacticity in poly(propylenes), crystallinity and density of poly(ethylene), and measurements of the polymerisation degree e.g. in polymethacrylate. In Fig. 2 a typical signal decay is shown, which reflects material properties. Crudely speaking, the signal may be decomposed into a longer living signal, due to more mobile fractions, and a shortly living signal, due to the rigid parts of the sample. Following an one-time calibration of the NMR measurements against values obtained by a proper reference method allows the characterization of the material in quality or also process control.

An example of the application of TD-NMR in polymer research is the measurement of the polymerisation rate of styrene. In this case, the transverse relaxation decay is the correct NMR parameter, which can be measured by a multi-echo sequence. According to the underlying principle that the molecular mobility determines the NMR relaxation times, it is expected that the degree and rate of polymerisation can be measured by monitoring the transverse relaxation as function of time. The relaxation time will decrease as the chain length of the molecular species increases during the polymerisation process. After data processing, Fig. 3 is obtained, where the conversion of the styrene to polystyrene is plotted as function of time. Obviously, the polymerisation rate depends on several factors, such as the initial concentration of the initiator, intrinsic rates of polymerisation steps, concentration of the monomer as well as environmental parameters. In Fig. 3, the initiator concentration is varied and the effect on the conversion process is shown. Clearly, TD-NMR provides clear-cut information about the polymerisation rate and the influence of the various reaction conditions.

Cross-link density is another very important parameter which determines, together with fillers and additives, the mechanical properties of the material. Its an important material parameter and often not known in detail. Established methods are swelling methods and rheometric experiments. Their major drawback is that they are time consuming and the samples of interest are destroyed. TD-NMR, on the other hand, overcomes these limitations of the established methods. For instance, the measurement time amounts to only about 5 min., whereas the established methods take up to weeks until the analysis is completed. In TD-NMR, it has been shown that mainly the transverse relaxation time, T2, reflects the cross-link density (CLD). This is due to the fact, that T2 is sensitive to molecular fluctuations in the proper time scale of several 10 µs up to ms. In case of natural rubber (NR), a quantitative determination via a CLD-fit was established [5-7]. The basis of this method is the modelling of the transverse relaxation according to the formulations in [5-7]. The fitting parameters, as for example the degree of motion, are consecutively used for determination of the cross-link density within this model. The comparison of the established methods as Mooney-Rivlin or swelling experiments shows a good agreement with the NMR method (Fig. 4). The difference between the established methods is of the same order of magnitude as the deviations of the minispec measurements. The method worked out in [5-7] is primarily restricted to NR and SBR because some of the physical constant entering the equations for the cross-link density are unknown in case of other polymers. In those cases, a calibration with known samples can be made, for example by implementing a data base where the relaxation prop-

Fig. 1. Bruker’s “the minispec” mq-series TD-NMR instrument. The minispec is a table-top NMR instrument tailored for QC and R&D analysis. It consists of an electronic unit and a magnet unit which houses the permanent magnet and the probe. Control and data analysis is done conveniently via the Windows based minispec program tailored for ease-of-operation. Sample diameters from 7.5 mm up to 50 mm are possible, the 1H-NMR frequency is in the range from 7.5 MHz to 60 MHz. Several accessories, such as temperature control or gradients can be added.

Fig. 2. Typical Free Induction Decay (FID) of a polymer sample. The FID consists of two components: A faster and a slower decaying part which correspond to the crystalline fractions and the monomers as well as additives, respectively.
Properties of defined compounds are listed. A comparison of measured values of unknown samples of the same chemical composition allows then the determination of the cross-link density. Also correlations with the glass transition temperature can be established, thus circumventing intricate mechanical or chemical testing methods. It should be mentioned that the chemical nature of the cross-linking as such doesn’t influence the NMR measurements. Thus, sulphur or peroxide cross-linking can be observed as can cross-linking by irradiation. Several examples show that the underlying principle, the change in the transverse relaxation, can be successfully exploited in order to quantify the cross-link density in a given compound.

In addition to global parameters such as cross-link density, spatially resolved information can be obtained by minispec measurements. Some products (e.g. tyres) require that several layers of different polymer mixtures are co-vulcanised in order to create the desired overall product property. The question of interest concerns the interfaces between the different mixtures. \( T_2 \) parameter profiles can be measured to reveal e.g. diffusive processes during vulcanisation.

Quality control in each stage but especially on the final product should be non-destructive and reliable. Most of the mechanical testing methods need to find a breaking point of the material or allow the examination of a small part of the sample only, and are therefore destructive. In addition, possible material inhomogeneities are not recognized.

As long as the products to be tested are small in size they can be analysed in a standard TD-NMR equipment. If required, the sample’s temperature can be easily controlled within the minispec TD-NMR system. Probes – essentially the measuring cell and the core element of a TD-NMR system – are available for sample sizes up to about 50 mm.

A dedicated NMR sensor, the MOUSE (MOBILE Universal Surface Explorer, Fig. 5), allows NMR measurements in the vicinity of the samples surface. Samples larger...
than 50 mm are therefore also accessible to NMR measurements. In contrast to conventional NMR devices, the MOUSE is not very susceptible to the presence of ferromagnetic parts in the sample, as is the case of steel-belted tyres. As in the case of conventional minispec measurements, the magnetization decay can be correlated to physical properties. The MOUSE therefore provides a method of quality control in the final product which is fast and totally non-destructive. Several publications describe the technical details, the NMR methods and the correlation with specific material properties as for example the cross-linker content, the glass transition or tan delta and the polymer matrix [8–12]. It should be pointed out that the measurement is completely non-destructive but restricted to measurement depth of less than 1 cm. A certain spatial resolution is inherent, as the MOUSE exhibits strong internal gradients.

In summary, TD-NMR can be applied at basically every stage in QC and R&D of polymer industry. With TD-NMR it is possible to correlate the microscopic properties like molecular chain dynamics to the macroscopic properties of the product like mechanical properties. The microscopic properties are pinned down in tailored NMR methods, mainly relaxation weighted experiments. Eventually, the TD-NMR method will replace labour intensive mechanical testing procedures for dedicated problems due to its superior properties, like fast analysis times, accurate results, simple measurement procedures and the fact that measurements are non-destructive.

References