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Original contribution

Non-destructive analysis of polymers and polymer-based materials by compact NMR

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ABSTRACT

Low-field nuclear magnetic resonance (NMR) based on permanent magnet technologies is currently experiencing a considerable growth of popularity in studying polymer materials. Various bulk properties can be probed with compact NMR tabletop instruments by placing the sample of interest inside the magnet. Contrary to this, compact NMR sensors with open geometries give access to depth-dependent properties of polymer samples and objects of different sizes and shapes truly non-destructively by performing measurements in the inhomogeneous stray-field outside the magnet system. Some of the sensors are also portable being thus well suited for onsite measurements. The gain of both bulk and depth-dependent microscopic properties are important for establishing improved structure-property relationships needed for the rational design of new polymer formulations. Selected recent applications will be presented to illustrate this potential of compact NMR.

1. Introduction

In the last decades, polymers revolutionized the progress of our society due their excellent properties tailored towards specific applications [1–5]. Such properties are achieved through ingenious formulations on which a polymer is mixed with various additives such plasticizers, stabilizers, and fillers. The interaction among the various ingredients as well as the structure, dynamics, and morphology of the building blocks at different time and length-scales critically impact the short- and long-term properties of the final product [6–9]. Furthermore, the effect of external factors during production and usage such as temperature, pressure, and deformation needs to be taken into account while designing a polymer product for a specific application. If these relationships would be fully understood, any macroscopic property could be predicted and controlled through the design of a defined microscopic structure, a dream of any chemist. Despite of much progress towards this goal in the last years through the combined efforts of scientists from different fields of activities, it still remains a major challenge.

In the last decades, huge efforts were done towards the development and the implementation of sophisticated analytical tools which can offer a detailed analysis of complex polymer structures both in liquid and solid-state in state of the art laboratories with the aim of establishing reliable structure-properties relationships [10–12]. Yet, there are also great efforts in developing low-cost compact table-top as well as portable analytical tools for onsite characterization of in-service polymer products. Reasons behind are materials pre-screening, condition monitoring, real-time measurements to help make fast decisions. As an example, handheld portable sensors based on Fourier Transform Infrared Spectroscopy (FTIR) and RAMAN are already available to the market but their utilization in the field of non-destructive study of polymer materials is still rare [13–15].

Nuclear Magnetic Resonance is one of the analytical methods which substantially improved our understanding about the microscopic behavior of polymer materials and has largely contributed to current developments in polymer science [16–24]. While liquid-state NMR is the work horse of structural analysis of polymers in solution, its counterpart, solid-state NMR, is seen today as belonging to the top 10 newer analytical methods in polymer science [11]. Solid-state NMR measurements performed in a homogeneous and high-magnetic field delivers structural information with atomic resolution and enables characterizing the amplitude and the time scales of motions over broad ranges of length and time for both amorphous and semi-crystalline polymers [17–22]. The NMR techniques can overcome problems associated with various other analytical methods such as the need for long-range order as required by X-ray scattering. Moreover, depth- und lateral-dependent microscopic properties of a polymer product can be probed by NMR imaging technique while information about its interaction with liquid media is gained from diffusion studies [23–25]. As with other techniques, miniaturization also impacted the field of NMR [26]. As a consequence, table-top NMR sensors as well as portable NMR sensors with open and closed geometries and working at low magnetic

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fields are readily available today [26–28]. Such small and light compact sensors are an excellent alternative to the expensive and sophisticated high-field equipment for many applications as successful demonstrated by investigations ranging from chemical science to cultural heritage [26–33]. Such sensors are able not only to measure relaxation, as demonstrated in earlier work, but also diffusion, images and high-resolution spectra thereby greatly expanding the area of applications [26–34].

This work reviews some recent applications of compact NMR in the field of polymer science and illustrates how NMR measurements with open and closed sensors of different magnetic field homogeneities provide simple solutions to challenging questions. Furthermore, the reliability of the method is discussed by comparing its results with those delivered by other classical analytical techniques.

2. Experimental methodology for polymer materials

Compressive reviews about compact low-field NMR instruments and measuring methods can be found, for example, in [27,28,34,35]. This minireview will highlight the instruments and experimental methods used in selected applications to polymer materials.

2.1. Compact NMR instruments

Fig. 1 depicts various compact low-field NMR sensors based on permanent magnet technologies which are currently used for the study of polymer materials. They include stray-field relaxometers with the Profile NMR-MOUSE being the most widely employed (Fig. 1a). With this sensor, the signal is acquired from a thin flat slice situated at a fixed distance above the surface of the magnet. It enables the measurement of a one-dimensional depth-profile by changing step by step the distance between the sensor and the object and with that the position of the sensitive slice inside the object. This is the best done automatically with the help of a high precision lift. A two-dimensional microscopic map of large polymer objects can be acquired by changing the lateral position of the sensitive slice. In combination with the depth-dependent information, a three-dimensional image can be obtained. Such sensors have an intrinsic strong static gradient somewhere between 10 T/m and 20 T/m enabling thus high-resolution depth-profiles and are in the most cases employed for relaxation and self-diffusion measurements. The lateral resolution is generally lower than the depth resolution as it is determined by the size of the radio-frequency coil. Polymer solutions as well as solid amorphous and semi-crystalline polymer materials in form of powder, pellets, or more complicated shapes and much larger sizes such as car tires and pipelines can be measured truly non-destructively by placing them near by the NMR sensor [29,30,36–38].

Simple Halbach sensors (Fig. 1b) can also be used for the study of polymer materials. They are cylindrical magnets with the direction of the magnetic field transverse to the axis of the borehole and a very low stray-field magnetic field outside the borehole. The magnetic field is much homogeneous than for the stray-field sensors and the volume of the sensitive slice higher. They enable bulk relaxation measurements of samples which are either small enough or need to be cut in small pieces in order to fit inside the radio-frequency coil placed inside the magnet. Both the stray-field and the Halbach NMR sensors have a much lower magnetic field homogeneity than the desktop Bruker Minispec, another low-field NMR device with closed geometry and largely used for the study of polymer materials [19,21]. Yet, their much smaller size and weight compared to the Bruker Minispec make them well suited for measurements done under place restriction such as under the fume hood and for investigations outside the laboratory.

The highly homogeneous magnetic field of a SpinSolve spectrometer (Fig. 1c) is well suited for spectroscopy measurements of liquid samples being of primary use for the structural analysis of small molecules [34]. Small size and low installation price compared with the high-field NMR liquid-state devices compensate for their medium resolution spectra and enable also, for example, to be used as online detector for Size-Exclusion Chromatography (SEC–NMR) of polymers such as polymethylmethacrylate (PMMA) and polystyrene (PS) [39].

2.2. Measuring methods

The used measuring methods with the low-field sensors strongly depend on the homogeneity degree of the magnetic field. Relaxation measurements are most widely used with the sensors depicted in Fig. 1a and b. Information about the molecular dynamics of amorphous and semi-crystalline polymers is often gained with the help of multi-echo techniques such as CPMG (Carr, Purcell, Meiboom, Gill) pulse sequence which enables acquiring the whole relaxation decay within a single shot [40,41]. Instead of a CPMG, a multisolid-echo train employing the OW4

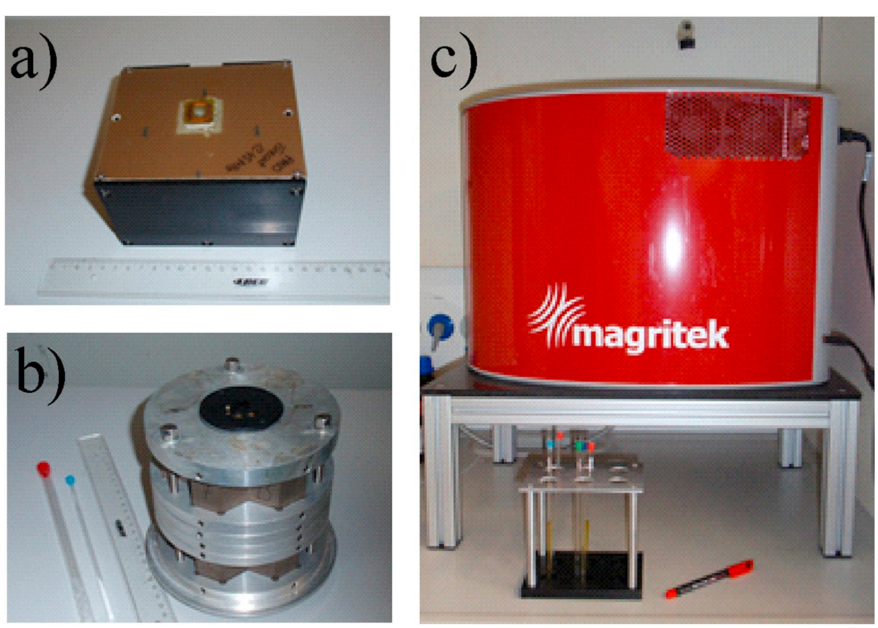

Fig. 1. Various compact low-field NMR sensors used for the study of polymer materials. (a) Profile NMR-MOUSE which enables non-destructive investigation of polymer samples and products with various shapes and size. (b) Halbach sensor. (c) SpinSolve spectrometer from Firma Magritek.

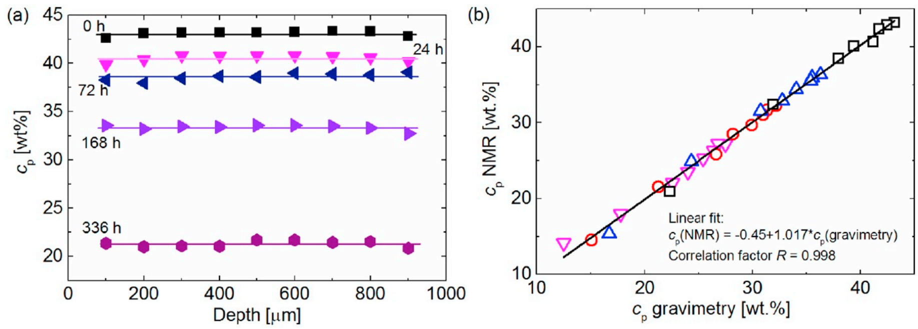

Fig. 2. (a) Local concentration c_p of ELATUR CH inside the PVC plates after different exposure times as quantified by NMR. The continuous lines serve as visual guide. (b) Correlation of the concentrations predicted by NMR with those directly determined by gravimetry. The NMR concentrations are the average of all concentrations across the plate thickness. The various symbols describe samples with different initial plasticizer concentrations and aged for various times under accelerated conditions. Adapted from [50].

(Ostroff-Waugh) pulse sequence is also sometimes employed [42]. The decay of the CPMG is characterized by an effective transverse relaxation time $T_{2\mathrm{eff}}$ which is a mixture of the transverse relaxation time T_2 and the longitudinal relaxation time T_1 [34,35]. The decay of the OW4 is characterized also by an effective transverse relaxation time $T_{2\mathrm{eff}}$ which in this case is a mixture of the transverse relaxation time T_2 and the longitudinal relaxation time in the rotating frame $T_{1\rho}$ [34,35].

The analysis of the experimental decays with analytical functions, usually exponential ones, delivers the values of the relaxation times $T_{2\mathrm{eff}}$. An alternative procedure uses the inverse Laplace Transform to extract details about the distribution of the relaxation times [34]. The obtained values give information about the molecular motion. The higher the frequency and/or amplitude of the molecular motion is, the longer is the $T_{2\mathrm{eff}}$. This dependency can then be used to quantify the molecular mobility of different regions in multiphase polymers given that the measurements are performed above the glass transition of the polymer under study. With this, also the proton fraction of each phase characterized by different mobility can be quantified giving thus information about the so called NMR phase composition. Identifying the most adequate NMR methodology and the best experimental conditions which provide the most accurate phase composition at low-field is still a field of intense research [43,44].

Both sensors enable also the quantification of proton longitudinal relaxation time T_1 usually with the help of the saturation recovery pulse sequence. The detection is in many cases done with an echo-train in order to improve the signal to noise. Also here an analysis using exponential functions or inverse Laplace Transform can be performed.

The strong and constant static field gradient of the Profile NMR-MOUSE allows as well probing the slow translational self-diffusion of small protonated penetrants in amorphous and semi-crystalline polymers [34,35,45,46]. For this, a constant gradient stimulated echo or a constant gradient Hahn-echo in conjunction with a CPMG echo-train for detection can be used [34,35,45,46]. The analysis of the diffusion curves can be done in terms of exponential functions or with the help of inverse Laplace Transform.

SpinSolve devices enable in most cases one-dimensional ^{1}H and ^{13}C spectra, 2D NMR measurements such as COSY and HETCOR and proton T_2 and T_1 relaxation measurements of samples in liquid-state [34]. One-dimensional ^{1}H NMR spectroscopy is often the method of choice for structural investigations due to its higher sensitivity. Such spectra are generally well suited for the structural analysis of small molecules and reaction monitoring [34]. Yet, their appearance increases in complexity for larger and more complicated molecules such as polymers and therefore one needs to make use of ^{13}C spectroscopy in the view of the larger chemical shift range. However, these measurements require much longer measuring times because of the low abundance of ^{13}C. For quality control purpose, a good alternative is the combination of proton spectra with chemometrics [47].

3. Applications

3.1. Quantification of local plasticizer concentration in PVC

Today, poly(vinyl chloride) (PVC) is frequently used in a large variety of applications including medical devices and packaging [48,49]. In most cases, PVC is used in a plasticized form with plasticizers making up to 80% of the mass. The content and type of plasticizer strongly control the macroscopic properties of the PVC product. As external plasticizers are used in most PVC products, their amount will diminish with increased usage time due to migration, a process which fails to be properly described by existing mathematical models. Furthermore, the loss of certain plasticizers raises questions about their impact on health and environment [48,49]. Moreover, there are studies pointing out the impact of the heterogeneous plasticizer distribution in a product on its properties, making thus the prediction of the long-term properties even more challenging. This complexity around the plasticized PVC products clearly demonstrates the need of analytical tools which can provide information about not only about the structure of the plasticizer but also about the bulk plasticizer content and its distribution.

In this context, a novel methodology using low-field NMR relaxometry was recently proposed for the non-destructive quantification of the local plasticizer concentration in PVC products within some couple of minutes [50]. The introduced approach makes use of correlation curves established between the transverse relaxation parameters measured with a profile NMR-MOUSE and the known bulk concentrations of plasticizer in fresh PVC plates with a homogeneous distribution of plasticizer. Slice-selective relaxation measurements at different depths inside a PVC sample with a known type of plasticizer enables the quantification of the local plasticizer content using the apriori established correlation curves, as demonstrated on samples with different aging times (Fig. 2a). The predicted concentrations from NMR show excellent agreement with those measured by gravimetry (Fig. 2b).

Furthermore, this study highlights the possibility of chemical identification of various plasticizers without the need of spectroscopic techniques using solely the above mentioned correlation curves [50]. Therefore, the proposed method has distinct advantages over other analytical tools currently applied in the study of plasticized PVC, including standard NMR, which either can probe only bulk or surface properties or need to extract the plasticizer for chemical identification and concentration quantification [51–53].

3.2. Solvents and polyethylene

The interaction between solvents and polymers plays a critical role in many applications including membrane technologies, pipeline transportation, packaging, coatings, and medical devices. Residual solvent can be trapped in the finished polymer products or the polymer products come into contact with solvents during many applications. The presence of the solvent can induce changes in the microscopic structure of the polymer including the molecular dynamics and morphology through plasticization and solvent-induced crystallization and can cause an extraction of additives [6,8,54–56]. As a consequence, the macroscopic properties are altered. One the other hand, various polymer microstructure characteristics including crosslinking and morphology influence also the solvent uptake and evaporation [54–56]. This interplay is even more complex for semicrystalline polymers due to the presence of both crystalline and non-crystalline regions with the crystalline regions being normally not accessible to the solvent [57].

Low-field NMR provides fast and precise methodologies to online monitor the solvent ingress or its evaporation and to quantify the distribution of the solvent inside various polymer materials as well as the associated microscopic changes [58–63]. Furthermore, another great feature of NMR is its ability to directly measure the self-diffusion coefficients of the confined solvent inside the polymer materials [27,28,45,46]. This gives in turn a reliable way to identify microscopic properties controlling the diffusion behavior which is of key importance in improving the existing diffusion models [57].

In a recent study it was shown that low-field NMR relaxometry performed with a Halbach sensor (Fig. 1b) is an apt method to detect swelling-induced morphological changes in semicrystalline polymers with demonstration on polyethylene (PE) [64]. For this, the morphological changes of three commercial-brand PE grades, low-density polyethylene (LDPE), high-density PE (HDPE), and linear low-density PE (LLDPE), induced by swelling after different exposure times in n-hexane, chloroform, and xylene were investigated. All three solvents have been chosen due to their solubility parameters which are closed to the solubility parameter of PE. It could be shown that the chain dynamics of the amorphous phase (Fig. 3a) decreases upon swelling and subsequent drying of the samples as a consequence of morphological arrangements leading to an increase in the degree of crystallinity. The extent of solvent-induced crystallization strongly depends on the type of solvent and PE grade and it is faster at higher temperatures. It seems to be determined by a complex interplay between the solubility parameters and the self-diffusion coefficients of the confined solvents. The low-field NMR observations could be confirmed by NMR measurements performed in a high-magnetic field and by Differential Scanning Calorimetry (DSC) results and are in agreement with literature findings on other polymer systems [65,66].

An improved understanding of the observed phenomena could also benefit from the existing fast and simple low-field NMR approach for the quantification of self-diffusion coefficients of small penetrants in semicrystalline polymers [46]. The extracted self-diffusion coefficients depend on the crystallinity of the samples and can also deliver information about the tortuosity of the samples [46].

The presence of oligomers in the final polymer product is reported to impact their thermo-mechanical properties [67,68]. Being preferentially localized in the non-crystalline regions of semicrystalline polymers, they can be easily extracted by the surrounding solvent and as a consequence their amount will change with increasing exposure time leading thereby to changes in various properties.

In this context, proton low-field NMR spectra acquired using SpinSolve (Fig. 1c) has been for the first time employed to monitor and quantify the leaching of wax from LDPE pellets into n-hexane at room temperature [69]. Wax stands for the low-molecular weight fractions generated in any polymerization process. For the NMR study, the pellets were exposed to a defined amount of n-hexane. After different periods of time, the pellets were removed and dried at 70 °C until reaching the equilibrium in mass. Given that no solvent remains trapped in the dry samples, the change in their mass compared to the non-exposed pellets corresponds to the lost wax content. Parallel to this, ^{1}H spectroscopy in combination with the standard addition method was used to measure the wax content in remaining n-hexane/wax mixture. It was found out that the wax content increases with the swelling time and reaches the equilibrium after about 6 days of exposure (Fig. 3b). The NMR results show fairly good agreement with the results from gravimetry yet offering a much faster way of quantification.

3.3. Aging of semicrystalline polymers

During their lifetime, the properties of polymer products will degrade under the impact of various external factors such as temperature, UV-light, pressure, or solvents and this will eventually lead to their failure. It becomes thus clear that reliable predicting the safe working time is the key for their successful use in any application. While different technologies and solutions have been developed over the years to overcome limitations in lifetime, core challenges for specialists working today in the field of polymer aging are: the prediction of the lifetime, the understanding and identification of microscopic properties responsible for the failure of the polymer product, and the development and the implementation of portable analytical techniques for onsite condition monitoring [70–73].

Low-field NMR methods gained over the years in popularity for studying the aging of polymer materials due to its ability to characterize in detail the molecular network of both amorphous and semicrystalline polymers [74–80,82]. While structural changes can be only probed at high-field so far, various other microscopic details can also be gained using low-field NMR. In addition, sensors like the NMR-MOUSE (Fig. 1a) are of particular interest for onsite studies due to their portability and ability to perform truly non-destructive measurements.

The potential of single-sided NMR for condition monitoring of polymer materials has been, for example, evaluated by investigating the aging kinetics of silane crosslinked polyethylene (PEX) up to six months upon exposure to aggressive media used during oil and gas production and transportation [83]. To validate the NMR method, the same samples were investigated also by conventional condition monitoring tools including gravimetry, mechanical measurements, and DSC. All investigated properties show complicated changes with the aging time and exposure medium due to a complex morphological reorganization induced by a combination of effects including annealing, solvent-induced crystallization, and chain scissions and crosslinking. The mobility of the amorphous phase, as quantified with the help of the NMR relaxation measurements, shows the highest sensitivity to the aging

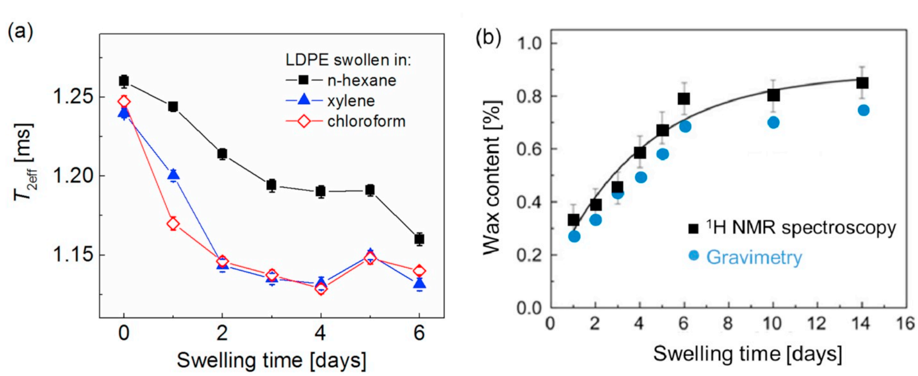

Fig. 3. (a) Changes in the proton relaxation times T_{2eff} of the amorphous phase of LDPE pellets swelled for various times in three different solvents measured by low-field NMR relaxometry. Before being investigated by NMR, all samples were dried until no changes in the mass of the samples could be detected. The small differences in the relaxation times of the non-exposed samples can be attributed to small morphological differences among the studied pellets. Adapted from [64]. (b) Evaluation of the wax leaching from the same LDPE pellets by low-field ^{1}H spectroscopy. The wax content from gravimetry is shown for comparison purposes. Adapted from [69]. The lines serve in both figures as visual guide.

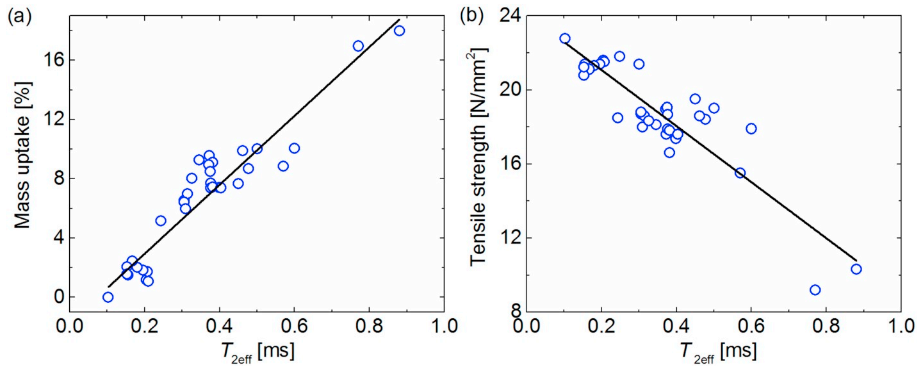

Fig. 4. Universal correlation curves of the proton relaxation time $T_{2\mathrm{eff}}$ describing the mobility of the amorphous phase with the mass uptake (a) and tensile strength (b). The results obtained for all exposure times up to six months and all six exposure media are included. The correlation coefficient for the linear fits is higher than 0.8 despite of the fact that new pieces were used to generate the samples for each exposure condition.

conditions, in agreement with other aging studies [76,84]. Furthermore, it could be also demonstrated that the NMR results of all investigated samples correlate quasi linear with the results from mass uptake and mechanical measurements (Fig. 4), two classical destructive condition monitoring methods. This result is very important because of the current lack of analytical methods with can gain onsite information about the mechanical status of a polymer product and highlight the possibility of condition monitoring by simple non-destructive NMR relaxation measurements.

An improved understanding of the observed complex morphological reorganization in the presence of temperature and solvents is necessary to properly describe changes in the macroscopic properties. This would strongly benefit from disentangling which type of exposure is responsible for what change and how their effects combine. A comparison of the induced morphological changes in the same type of samples by either type of exposure is the way chosen in Ref. [69] using data primarily collected by NMR. The samples exposed to solvents were dried prior to the measurements in order to remove the effect of the solvent on the chain mobility of the amorphous phase as this microscopic parameter was also used for comparison in the view of its high sensitivity towards exposure conditions. Morphological changes including an increase in the fraction of the rigid domain at expense of the semi-rigid and mobile amorphous phases and a reduction in the chain mobility of the amorphous phase were detected for LDPE samples for both types of exposure. For thermal aging, these changes happen because of annealing and chemi-crystallization induced by chain scission. The observed morphological changes in the presence of solvents are of physical nature due to the solvent-induced crystallization as no chemical aging took place. Within the employed experimental conditions, the morphology changes induced by swelling and by elevated temperatures happen on different time scales with solvent-induced crystallization being much faster than temperature-induced crystallization.

Interpreting the changes in morphology of polymer products invoked by thermo-oxidation is further complicated by diffusion-limited oxidation (DLO) [71,85,86]. DLO induces depth-dependent morphological variations which in turn lead to depth-dependent variations of the macroscopic properties [71,85,86]. As an example, a thin oxidized layer, with a thickness of only few percent of the whole polymer thickness, significantly reduced the strain-at-break [86].

Non-destructive depth-dependent relaxation measurements with open NMR sensors such as the NMR-MOUSE gained in popularity for studying aging of polymer materials [87–89]. They offer an improve understanding of the local changes in the polymer network responsible for measured reduction in the mechanical properties [87–89].

For example, it was applied to investigate the depth-dependent changes during the thermo-oxidative aging at elevated temperatures of stabilized and non-stabilized polyamide 12 (PA12) plates [90]. It was found out that the morphological changes, which are due to a combination of annealing and chemical aging, are faster for the non-stabilized sample as for the stabilized one. They are the highest at surface and diminish than towards the middle of the plates. The interpretation of the detected trends took advantage of the results from high-field NMR and could be confirmed by FTIR and viscosimetry. This highlights also the need of a multi-experimental approach to facilitate the understanding of the aging process.

4. Conclusions and outlook

Quantification of local plasticizer concentration in plasticized PVC, study of the interaction of semicrystalline polyethylene with solvents together with the characterization of the solvent-induced morphological changes, and aging induced bulk and depth-dependent changes of the molecular network are just few selected successful applications of compact NMR in polymer science. The excellent correlation of the reported NMR data with the results from classical analytical techniques including gravimetry and mechanical measurements is an additional confirmation of the great potential of the method to answer questions from fundamental and applied polymer research. On the other side, depending on the application, a combination of NMR with other analytical tools is highly desired for a deeper understanding of the observed microscopic and macroscopic behavior and for establishing structure-property relationships [87–91]. Furthermore, measurements with compact NMR would also strongly benefit from methods to increase the sensitivity. This could be achieved with the use of hyperpolarization methods such as DNP (Dynamic Nuclear Polarization) or parahydrogen [92–96], or with the help of multi-coil arrays [97].

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