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Surface UV aging of elastomers investigated with microscopic resolution by single-sided NMR

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Abstract

Depth profiles taken from the surface of UV irradiated natural rubber sheets have been measured with microscopic resolution using a Profile NMR-MOUSE®. An NMR observable related to the sum of the spin echoes in the Carr–Purcell–Meiboom–Gill pulse sequence was used to characterize the cross-link density changes produced by the action of UV radiation in each sheet. The aging process was investigated as function of irradiation time and penetration depth. An exponential attenuation law with a space dependent absorption coefficient describes the change in the NMR observable with penetration depth. An Avrami model is used to describe the dependence of the absorption coefficient on the aging time. The method can be applied to investigate the effect of various aging agents on the surfaces of elastomers.

Keywords: ^{1}H NMR; Transverse magnetization relaxation; NMR-MOUSE; Elastomers; UV aging

1. Introduction

The effect of UV light on polymers, and especially on elastomers is still not completely understood, although extensive data have been reported on the action of electromagnetic radiation on such materials [1–3]. Studying the interaction of UV irradiation with elastomer networks is an important topic in polymer science relevant to the polymer industry.

The interest in the transformation of organic polymers under the action of UV radiation relates to a number of reasons. First, polymer modification by ionizing radiation is an important technological means for functionalizing polymer surfaces [4]. The reaction mechanism is complex and involves the action of many primary particles. Second, an analysis of this process is important considering the material deterioration during processing and use in different environmental conditions. One example is the dry etching of polymer resists in microelectronics. Small structures require high resolution and thus short wavelength light. Furthermore, for a lifetime prediction, the natural exposure to UV radiation has to be considered. The UV component of sun light deteriorates many polymeric materials especially in the presence of oxygen. Understanding the long-term aging characteristics of elastomers is critical for performance assessment and lifetime prediction of such materials.

As the irradiation enters from the outside and is absorbed by the polymer, spatial heterogeneity develops in originally homogeneous objects. For this purpose, the development of new experimental techniques that can probe the spatial heterogeneity of aged polymers is important. NMR and especially magnetic resonance imaging (MRI) are experimental techniques that *have* seen an ever-increasing role in material science, particularly in the spatial analysis of heterogeneous polymers and composites [5–10, and references therein].

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MRI has been used in the past to investigate polymer aging and degradation. Over a decade ago Blümer and Blümich reported the T_2 maps of natural rubber thermally aged in air, which clearly reveal the growth of a surface layer which hardened with the aging time [11]. MRI has also been used to investigate the biodegradation of polymer films [12], the aging in nitrile rubber elastomers [13], the degradation of rubber and polystyrene [14], the oxidative aging of natural rubber [15,16], and radiation effects in polymer gels [17]. Recently, ^{1}H relaxation encoded NMR images were measured to investigate the thermo-oxidative aging in a hydroxy-terminated polybutadiene based elastomer [18] and to establish a correlation with Young's modulus. Changes in the transverse relaxation and double-quantum buildup curves due to ^{1}H residual dipolar couplings of polymers have been correlated before with the modulus and induced stress [19–22].

In the last few years, several NMR applications have been developed which operate in strong static magnetic field gradients [23,24]. A prominent and most practical example is the development of single-sided NMR devices like the NMR-MOUSE® [25,26] with applications to non-destructive material testing of arbitrarily large objects [27–30]. For example, the orientation dependence of NMR parameters can easily be investigated with single-sided devices for large, stretched samples [29]. Furthermore, mobile, one-sided NMR imagers have been designed and applied to material investigations [24,31,32].

The NMR-MOUSE® is characterized by strong inhomogeneities of the static and radio-frequency magnetic fields. But even in the presence of these field inhomogeneities, the NMR relaxation times and parameters of translational motion can be measured by spin echo techniques [5]. There are several advantages of working with such fields. The inhomogeneous polarization field $\boldsymbol{B}_0$ provides spatial localisation along the gradient direction. Knowing the gradient profile of the sensor, the image of the investigated object can be reconstructed without spatial distortions in terms of NMR relaxation and spin density parameters. In the ideal case of a constant gradient, the image reconstruction is trivial. Then the spatial resolution is proportional to the frequency resolution determined by the excitation and acquisition bandwidths (selective pulse length and acquisition time). For frequency selective excitation it is straightforward that the gradient strength determines the spatial resolution. By using strong constant gradients, separation of spatially identical intervals is possible with microscopic resolution [24].

The aim of this work is to investigate the effect of UV radiation upon cross-linked natural rubber. A special single-sided sensor with an improved magnetic field profile, the Profile NMR-MOUSE®, was used for this purpose [24]. High resolution ^{1}H NMR depth profiles have been obtained of a rubber sample after exposure to UV radiation for several days. An NMR observable related to the sum of the spin echoes in the Carr–Purcell–Meiboom–Gill pulse sequence was used to characterize the cross-link density changes produced by the action of the UV radiation. An exponential attenuation law with a linearly space dependent absorption coefficient was proposed to describe the measured space profiles at different irradiation times.

2. Experimental

2.1. Samples, UV irradiation, and NMR measurements

The investigated elastomer sample is from commercially available natural rubber (NR) SMR10 (Malaysia). The additives were 3 phr (*p*arts-per-*h*undred-*r*ubber) ZnO and 2 phr stearic acid. The sulfur and accelerator contents were 3 phr each. The accelerator is of the standard sulfenamide type (TBBS, benzothiazyl-2-*tert*-butyl-sulfenamide). After mixing the compound in a laboratory mixer at 50 °C, the sample was vulcanized at 160 °C in a Monsanto MDR-2000-E vulcameter.

For irradiation, a 300 W Osram Ultravitalux UV lamp with an emission spectrum in the 300–400 nm wavelength range was used. The total irradiation time was 8 days. The NMR measurements were done after 5 h, 1 day, 2 days, 4 days, and 8 days of irradiation. The distance between sample and radiation source was 20 cm.

To characterize the segmental dynamics of elastomers after irradiation, a setup consisting of the Profile NMR-MOUSE® [24] and a high precision lift was used. The Profile NMR-MOUSE® has a flat sensitive volume at a fixed distance of 5 mm above its surface, and the object is positioned on top of a lift which contains the NMR-MOUSE® (Fig. 1a). The lift changes the distance between the NMR-MOUSE® and the object with a precision better than 10 μm. In this way, the sensitive volume can be shifted through the object to acquire ^{1}H NMR parameters as a function of depth into the object (Fig. 1b). In the work reported below, depth profiles were measured in increments of 20 μm at a resonance frequency of 18.1 MHz in a uniform gradient of 22.3 T/m [24].

Carr–Purcell–Meiboom–Gill decays (CPMG) were acquired in the strongly inhomogeneous magnetic field of the sensor [24] to measure the transverse NMR relaxation. The nominal 90° and 180° pulses were 20 μs, exciting a frequency bandwidth of ca. 50 kHz, and the acquisition time per echo was set to 50 μs to achieve a frequency resolution of 20 kHz per acquisition step. For each echo 25 points were detected and averaged. The data are acquired in the linear region of the static polarizing magnetic field. Given a constant field gradient of ca. 950 kHz/mm the profiles were acquired by measuring the NMR signals from slices 20 μm thick and parallel to the scanner surface. Each sample was measured in 30 steps from the surface up to a depth of 0.6 mm. The dead time of the radio-frequency setup was 30 μs. The CPMG-train consisted of echoes acquired with echo times of 130 μs. The number of scans was 256 with a repetition time of 0.5 s. The NMR experiments were performed at 23 °C with a temperature stability of ±0.1 °C.