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Sensitivity of proton NMR relaxation times in a HTPB based polyurethane elastomer to thermo-oxidative aging

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Abstract

Solid-state ^{1}H NMR relaxometry studies were conducted on a hydroxy-terminated polybutadiene (HTPB) based polyurethane elastomer thermo-oxidatively aged at 80 °C. The ^{1}H T_1, T_2, and $T_{1\rho}$ relaxation times of samples thermally aged for various periods of time were determined as a function of NMR measurement temperature. The response of each measurement was calculated from a best-fit linear function of the relaxation time vs. aging time. It was found that the $T_{2,\mathrm{H}}$ and $T_{1\rho,\mathrm{H}}$ relaxation times exhibited the largest response to thermal degradation, whereas $T_{1,\mathrm{H}}$ showed minimal change. All of the NMR relaxation measurements on solid samples showed significantly less sensitivity to thermal aging than the $T_{2,\mathrm{H}}$ relaxation times of solvent-swollen samples.

Keywords: Polyurethane elastomer; NMR relaxation; Thermo-oxidative aging

1. Introduction

Hydroxy-terminated polybutadiene (HTPB) based polyurethane elastomers are used extensively as binders in the manufacture of solid rocket propellants [1]. Unsaturation in the molecular backbone results in an increased susceptibility to oxidative aging, which has a direct impact on the material lifetime and mechanical integrity. Hence, understanding the thermo-oxidative aging of such materials is important. Recently, several reports investigating the various aspects of the oxidative degradation of this polyurethane rubber have been published [2–6]. Celina et al. [2] established that oxidation was the primary factor in the degradation mechanism of the material. Additional cross-linking and densification at elevated aging temperatures resulted in a loss of elasticity of the material.

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool in the study of polymer chain structure and dynamics [7,8]. A variety of NMR experiments have been applied in the examination of HTPB elastomers, investigating the effects of thermo-oxidative aging on the chemical structure [3,6], heterogeneity [3], and molecular dynamics [2–5]. For cross-linked elastomers, it has been well known for decades that NMR relaxation times are sensitive to the cross-link density. In one study, Assink and co-workers [5,9] used ^{1}H T_2 relaxation time measurements of thermally aged elastomeric polymers swollen in appropriate deuterated solvents to monitor the condition of those materials. These relaxation times showed an excellent correlation with mechanical properties such as tensile elongation at break and with the oxidation rates as a function of aging time and aging temperature. It was established that the solvent-swelled ^{1}H T_2 times are more responsive to the extent of thermal aging than solid ^{1}H T_2 times. However, swelling the polymer with solvents cannot be used to examine field samples in situ and limits the prospect of NMR analysis for nondestructive, comprehensive condition monitoring. Hence, ^{1}H NMR relaxation times of the HTPB rubber in the solid form must be considered.

Magnetic resonance imaging (MRI) has been utilized in the microscopic evaluation of solid polymers, especially elastomers [10,11]. Parameter-selective imaging, which entails the acquisition of images weighted by NMR relaxation times, is commonly employed. Sample images can be acquired that are dependent on changes in NMR relaxation times with thermal aging. MRI based on ^{1}H T_1, T_2, and $T_{1\rho}$ relaxation times has been used to analyze aged samples of natural rubber [12–15], styrene-*co*-butadiene rubber (SBR) [15,16], and nitrile rubber [17]. Portable, hand-held NMR instruments, specifically the NMR-MOUSE [18], have also been developed to probe

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and image NMR relaxation near the surface of samples, such as elastomers [19]. With these instruments, sample size and geometry are not a restriction. However, their usefulness depends on the sensitivity of the relaxation times to material changes, such as oxidation. HTPB elastomers exhibit NMR relaxation times with measurable sensitivity to thermo-oxidative aging [2,4,5], which makes them a good candidate for study by parameter-selective MRI and NMR surface probes. The nondestructive nature of MRI analysis and NMR surface probes would be ideal in evaluating the aging of the material in situ.

It is known that the choice of NMR relaxation time can affect the sensitivity and contrast in relaxation-weighted NMR imaging of elastomers [10,16,20]. NMR relaxation times, such as the spin–lattice relaxation time in the laboratory frame (T_1), the spin–lattice relaxation time in the rotating frame ($T_{1\rho}$), and the spin–spin relaxation time (T_2), are sensitive to molecular motions in the ranges of 10^7–10^9, 10^4, and $<10^9$ Hz, respectively, in modern spectrometers [8,20]. Under a specific set of environmental conditions (e.g. temperature, humidity), one NMR relaxation time may change more significantly with the level of aging than another, depending on the influence of those conditions on local chain dynamics. In this study, we examine the effects of thermal aging time and NMR measurement temperature on the ^{1}H T_1, T_2, and $T_{1\rho}$ NMR relaxation times for a HTPB based polyurethane elastomer. The relative sensitivities of these relaxation times with the level of aging will be evaluated as a function of NMR measurement temperature. A comprehensive comparison of these NMR parameters that could be utilized for condition monitoring of the HTPB elastomer in the solid form is presented.

2. Experimental

2.1. Materials

The polyurethane elastomer examined in this study is comprised of hydroxy-terminated polybutadiene (HTPB) cured with isophorone diisocyanate (IPDI). The uncured resins were provided by industry (Elf Atochem and Hüls America Inc.). The approximate hydroxyl group functionality of the HTPB is 2.1, which corresponds to a weight-average molecular weight $M_w \approx 2800$ g/mol. Cross-linking was obtained via an isocyanate/hydroxyl addition reaction yielding a simple polyurethane linkage. A ratio of HTPB to IPDI of ~12.1:1 (wt/wt) was used to achieve molar conversion of the HTPB with the IPDI. Thermal curing was carried out for 1 week at 65 °C. Further details about the chemistry and physical properties of the cured HTPB based rubber are given in the work of Celina et al. [2]. Sample strips (~6 mm wide and 150 mm long) were cut from sheets (~2 mm thick) of the cured rubber.

2.2. Thermal aging

Thermal aging of the HTPB rubber strips was performed at 80 °C in a temperature-controlled (±1 °C stability), commercial, air-circulating aging oven under ambient atmospheric conditions (~630 mmHg in Albuquerque). HTPB rubber samples were thermally aged in air up to 266 days.

2.3. NMR parameters

NMR experiments were conducted on a Bruker Avance 400 spectrometer at a ^{1}H resonance frequency of 400.16 MHz. A 4-mm magic-angle spinning (MAS) probe with variable temperature (VT) capability was used, although the samples were not spun. Aged rubber samples were cut into shreds about 1 mm in size and loosely packed into MAS rotors. Shreds were abstracted from slices made along the widths of the aged HTPB rubber strips. Hence, the NMR samples employed in this study were representative of the bulk average of the aged rubber strips, including limited contributions from surface hardening induced by diffusion-limited oxidation (DLO) at 80 °C [2]. NMR samples were allowed to equilibrate at the specific measurement temperature for at least 15 min.

^{1}H NMR relaxation experiments were performed using ^{1}H 90 and 180° pulses of 4 and 8 μs, respectively. T_1 relaxation times were determined using an inversion recovery pulse sequence, while T_2 relaxation times were measured with a Hahn spin-echo pulse sequence, $90°–\tau–180°–\tau$-acquire. $T_{1\rho}$ relaxation times were measured using spin-lock field strengths of $\gamma B_1/2\pi = 10$ and 25 kHz. T_1 inversion recovery curves fit well to a single exponential build-up function. $T_{1\rho}$ relaxation decay curves were slightly nonexponential, while T_2 relaxation decay curves showed significant deviation from a single exponential decay. ^{1}H T_2 and $T_{1\rho}$ relaxation times were, therefore, arbitrarily defined as the time to reach $1/e$ the initial intensity value, as done in recent ^{1}H NMR relaxometry studies from this laboratory [5,9].

3. Results and discussion

Oxidative aging of the HTPB based polyurethane elastomer at elevated temperatures causes additional cross-linking and material densification, which result in a loss of elasticity [2]. The continual reduction in ultimate tensile elongation with increasing oxidative aging time is one measure of this decrease in elasticity. As a result, tensile elongation is a sensitive condition monitoring parameter of the oxidative degradation of HTPB rubbers [2]. Tensile elongation data for HTPB rubber samples thermo-oxidatively aged at 80 °C for varying times are given in Fig. 1; these data are from the previous work of Celina et al. [2]. Based on the data in Fig. 1, three thermal aging times (0, 105, and 266 days) were selected so that the corresponding tensile elongation values differed significantly for the HTPB rubber samples aged at these times. The tensile elongation data were 305, 98, and 10% for the unaged sample, the sample aged 105 days (intermediate aged), and the sample aged 266 days (highly aged), respectively.

A reasonable objective in this study would be to detect significant differences in the solid ^{1}H NMR relaxation times of the three selected HTPB rubber samples, particularly between the unaged and 105-day aged samples. By 105 days of

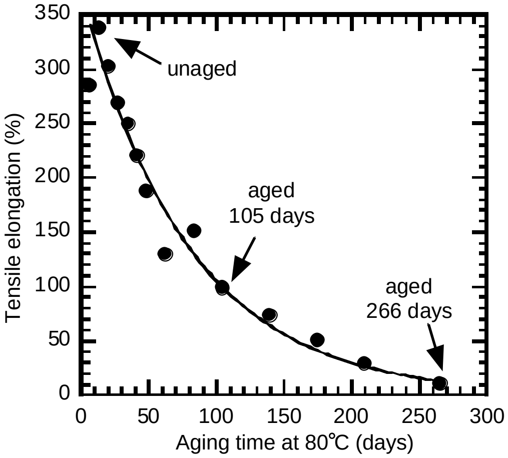

Fig. 1. Ultimate tensile elongation data (room temperature, 0.04 s^{-1} strain rate) of the HTPB based polyurethane elastomer plotted versus thermo-oxidative aging time at 80 °C. The elongation data of three selected thermal aging times analyzed with ^{1}H NMR relaxometry in Figs. 2–4 are indicated in the figure.

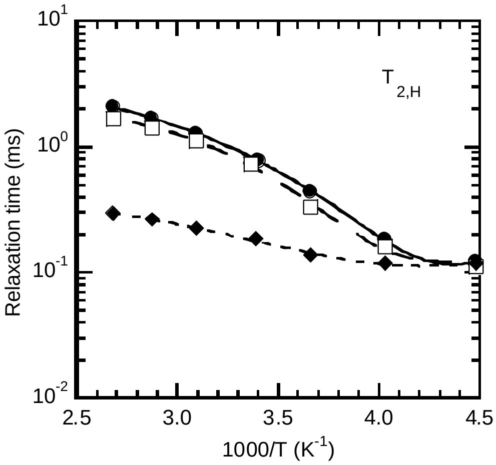

Fig. 3. ^{1}H T_2 relaxation times for solid HTPB rubber samples of three different thermal aging times at 80 °C plotted versus inverse NMR measurement temperature (in kelvins). (●) unaged (aged 0 days); (☐) aged 105 days; (◆) aged 266 days.

oxidative aging at 80 °C, the elasticity of the HTPB rubber has been severely reduced by oxidation, as indicated by the 68% decrease in tensile elongation. The sample aged for 266 days is well past its useful mechanical life but was included as an ‘end point’ to test the responsiveness of the relaxation measurements. ^{1}H T_1, T_2, and $T_{1\rho}$ relaxation times for the three solid HTPB rubber samples of different aging times are shown versus inverse temperature in Figs. 2–4, respectively. NMR relaxometry measurements were made at temperatures from −50 to 100 °C for each of the three relaxation times. The NMR measurement temperatures were varied in order to observe any temperature-dependent differences in relaxation time between samples of diverse aging time. The vertical axes were presented with the same number of decades for each relaxation time in Figs. 2–4 in order to compare such relative differences.

Analysis of the $T_{1,H}$ relaxation times (Fig. 2) shows that the maximum difference between the highly aged (266 days) and unaged (0 days) T_1 times occurs at approximately 50 °C (1000/T = 3.1 K^{-1}). At this temperature, which coincides with a minimum in the $T_{1,H}$ curve for the unaged and intermediate aged (105 days) samples, the highly aged T_1 is approximately 3.5 times greater than the unaged T_1. The T_1 minimum indicates a molecular motion that strongly influences T_1 and which has a rate near the characteristic frequency of the ^{1}H NMR relaxation rate [8]. Overall, the T_1 difference between samples of varying aging times changes little from low temperature to high temperature. Thus, keeping the sample at room temperature (~21 °C) would give near optimum T_1 contrast. The difference in $T_{1,H}$ times between the unaged and intermediate aged samples is minimal (<6%).

The $T_{2,H}$ relaxation times for the three HTPB samples are presented in Fig. 3 as a function of inverse NMR measurement temperature. Clearly, relaxation time contrast between the unaged (0 days) and the highly aged (266 days) sample

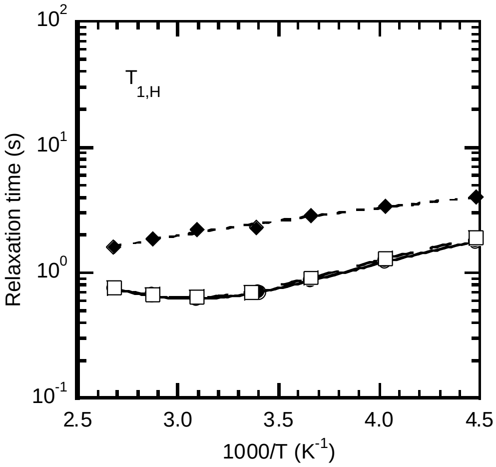

Fig. 2. ^{1}H T_1 relaxation times for solid HTPB rubber samples of three different thermal aging times at 80 °C plotted versus inverse NMR measurement temperature (in kelvins). (●) unaged (aged 0 days); (☐) aged 105 days; (◆) aged 266 days.

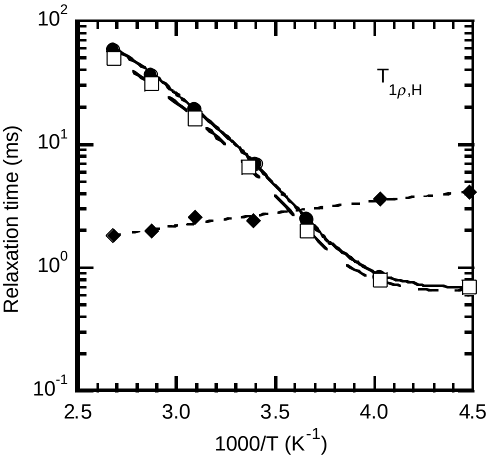

Fig. 4. ^{1}H $T_{1\rho}$ relaxation times (spin-lock field strength $\gamma B_1/2\pi = 10$ kHz) for solid HTPB rubber samples of three different thermal aging times at 80 °C plotted versus inverse NMR measurement temperature (in kelvins). (●) unaged (aged 0 days); (☐) aged 105 days; (◆) aged 266 days.

increases with temperature. At 100 °C ($1000/T=2.7\ \mathrm{K}^{-1}$), the unaged sample T_2 is about seven times larger than the highly aged sample T_2. From −25 to 100 °C, the difference between the unaged sample T_2 and the intermediate aged sample T_2 remains relatively unchanged. In general, $T_{2,\mathrm{H}}$ shows greater differences for samples of diverse aging times through most of the measured temperature range when compared to the $T_{1,\mathrm{H}}$.

The $T_{1\rho,\mathrm{H}}$ relaxation times reveal an interesting behavior (Fig. 4). At high NMR measurement temperatures, $T_{1\rho,\mathrm{H}}$ decreases with increasing aging time. The trend at temperatures below 0 °C ($1000/T=3.7\ \mathrm{K}^{-1}$) is reversed. These observations suggest a minimum in the $T_{1\rho,\mathrm{H}}$ curve that shifts dramatically to higher NMR measurement temperatures with increased thermal aging time. As seen with $T_{2,\mathrm{H}}$ times, the $T_{1\rho,\mathrm{H}}$ relaxation times show the largest contrast at 100 °C ($1000/T=2.7\ \mathrm{K}^{-1}$) in the range of sample temperatures examined. At this temperature, the $T_{1\rho}$ of the unaged sample (0 days) is about 32 times greater than the $T_{1\rho}$ of the highly aged (266 days) sample. From 0 to 100 °C, the difference between the unaged sample $T_{1\rho}$ and the intermediate aged (105 days) sample $T_{1\rho}$ remains relatively unchanged. The effect of thermo-oxidative aging time on $T_{1\rho,\mathrm{H}}$ is comparable to the effect on $T_{2,\mathrm{H}}$ and greater than the effect on $T_{1,\mathrm{H}}$.

It has been observed that the spin-lock field strength $\gamma B_1/2\pi$ can affect the contrast in $T_{1\rho}$ weighted imaging [14]. Hence, in order to see any effects from a variation in spin-lock field strength on the sensitivity of $T_{1\rho,\mathrm{H}}$ relaxation times to oxidative degradation, $T_{1\rho,\mathrm{H}}$ times were acquired for solid HTPB samples aged to different thermal aging times at two different spin-lock field strengths, $\gamma B_1/2\pi=10$ and 25 kHz (Fig. 5). For thermal aging at 80 °C up to 210 days, the magnitude of the $T_{1\rho,\mathrm{H}}$ times measured at 25 kHz are consistently about 36% greater than the corresponding times measured at 10 kHz. For the highly aged material (aged 266 days), the $T_{1\rho,\mathrm{H}}$ measured at 25 kHz was approximately two times the $T_{1\rho,\mathrm{H}}$ measured at 10 kHz. Overall, however, the variation in field strengths measured had negligible effect on the sensitivity of $T_{1\rho,\mathrm{H}}$ relaxation times to thermal aging time, as indicated by the similar rates of change of $T_{1\rho}$ with aging time (Fig. 5).

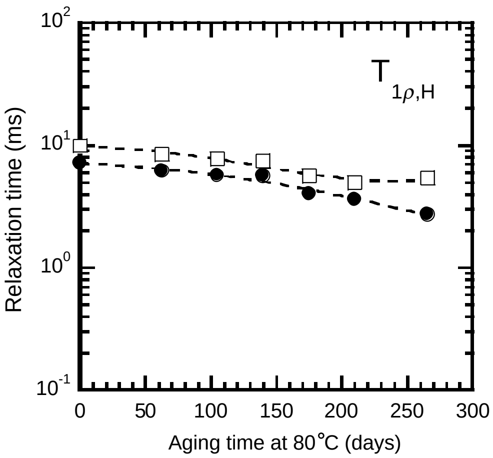

Fig. 5. Variation of ^{1}H $T_{1\rho}$ relaxation times with thermal aging time at 80 °C for solid HTPB rubber samples. $T_{1\rho,\mathrm{H}}$ times were measured at room temperature (∼21 °C) using two different spin-lock field strengths, $\gamma B_1/2\pi$. (●) $\gamma B_1/2\pi=10$ kHz; (☐) $\gamma B_1/2\pi=25$ kHz.

^{1}H T_2 and $T_{1\rho}$ relaxation times are plotted versus thermal aging time at 80 °C in Fig. 6. All three ^{1}H relaxation times examined in this study were measured at two different temperatures, room temperature (21 °C) and 75 °C. $T_{1,\mathrm{H}}$ times displayed less sensitivity to thermal aging than the $T_{2,\mathrm{H}}$ and $T_{1\rho,\mathrm{H}}$ times and are not presented in Fig. 6 for brevity. Overall, no dramatic change in the $T_{2,\mathrm{H}}$ and $T_{1\rho,\mathrm{H}}$ relaxation times was observed until the highest level of aging at 266 days, which agrees with the trends noted previously in this paper. Up to 210 days of aging, the $T_{2,\mathrm{H}}$ and $T_{1\rho,\mathrm{H}}$ times decreased in an approximately linear fashion with increasing thermal aging time (Fig. 6). Likewise, it was found that the $T_{1,\mathrm{H}}$ times increased in a roughly linear fashion with aging time.

The response of each relaxation time was approximated with a best-fit linear function up to 210 days aging, as shown with the thick, solid lines in Fig. 6. The slope of each best-fit line was then normalized by the relaxation time of the unaged (0 days) sample for comparison purposes. These normalized slopes, as given in Table 1, represent response rates of the solid HTPB NMR relaxation times to thermal aging time. In other words, they reflect the dynamic sensitivity of the NMR relaxation times to aging-induced material changes. The greater the absolute value of the normalized slope, the more sensitive the relaxation time is to thermo-oxidative aging. This sensitivity would be important in relaxation-weighted NMR imaging and depth profiling using relaxation times.

Overall, $T_{1\rho,\mathrm{H}}$ showed the greatest response rate at both NMR measurement temperatures, although its rates were only

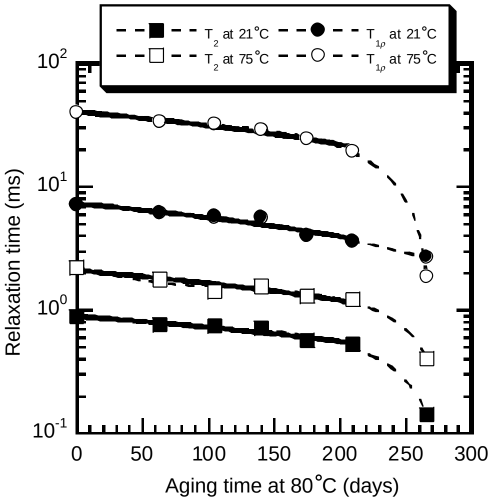

Fig. 6. Variation of ^{1}H T_2 and $T_{1\rho}$ relaxation times with thermal aging time at 80 °C for solid HTPB rubber samples at two different NMR measurement temperatures, room temperature (21 °C) and 75 °C. Solid lines represent the responses of the various relaxation times as approximated with a best-fit linear function up to 210 days aging. The normalized slopes of these linear responses, which are indicative of the dynamic relaxation time sensitivity to aging, are given in Table 1.

Table 1
HTPB based polyurethane elastomer: response rates of ^{1}H NMR relaxation times to aging time at 80 °C up to 210 days

^{1}H NMR relaxation time	Rate at 21 °C (10^3/day)	Rate at 75 °C (10^3/day)
T_1 (solid)	$+1.4\pm0.4$	$+0.9\pm0.3$
T_2 (solid)	-1.9 ± 0.2	-2.0 ± 0.4
$T_{1\rho}$ (solid)	-2.4 ± 0.3	-2.3 ± 0.2
T_2 (solvent-swollen)	-3.6 ± 0.1	–

modestly larger than the corresponding rates of $T_{2,\mathrm{H}}$. In fact, within measurement errors, the response rates of the $T_{2,\mathrm{H}}$ and $T_{1\rho,\mathrm{H}}$ relaxation times are comparable, particularly at 75 °C. Increasing the NMR measurement temperature had little or no effect on the response rates for $T_{2,\mathrm{H}}$ and $T_{1\rho,\mathrm{H}}$. As observed previously, $T_{1,\mathrm{H}}$ showed the smallest response to thermal aging time. A similar trend in ^{1}H NMR relaxation time sensitivity to thermal oxidation was observed by Blümich and co-workers [16,20] by comparison of NMR imaging profiles of an unaged and a thermo-oxidatively aged SBR sample. The changes in molecular dynamics induced by thermal oxidation in these elastomers are more readily detected by the T_2 and $T_{1\rho}$ relaxation times, which probe the slow-motion regime.

The aging time response of each of the solid HTPB ^{1}H NMR relaxation times are compared in Fig. 7 to the corresponding response of $T_{2,\mathrm{H}}$ relaxation times of solvent-swollen HTPB samples from the earlier work of Assink et al. [5]. The relaxation times are normalized to a value of 1.00 for the unaged (0 days) sample, and the inverse of $T_{1,\mathrm{H}}$ is presented so that all plotted relaxation measurements decrease with increasing thermal aging time. The response of each normalized measurement in Fig. 7 was approximated with a linear function up to 210 days aging at 80 °C, as done for the data presented in Fig. 6. The linear response rate of the $T_{2,\mathrm{H}}$ of the swollen samples is compared to the response rates of the solid measurements in Table 1 (rates at 21 °C). The $T_{2,\mathrm{H}}$ relaxation times of solvent-swollen HTPB rubber exhibit the largest response to thermal aging. Indeed, if very small samples are extractable from materials in the field, the solvent-swollen relaxation time method [5,9] is the most advantageous for condition-monitoring purposes. However, for in situ sampling or imaging of field materials, $T_{1\rho,\mathrm{H}}$ provides a modest increase in sensitivity over $T_{2,\mathrm{H}}$. The ultimate choice between these two relaxation times would depend on the relative accuracy with which each can be measured.

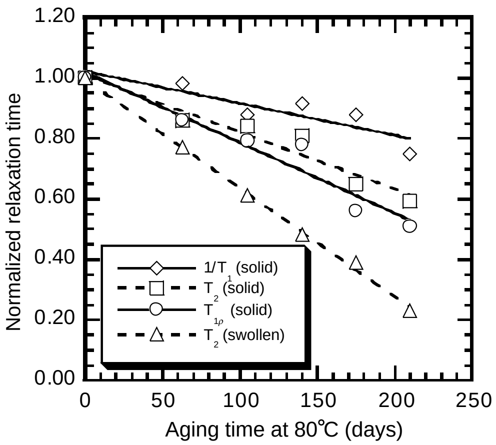

Fig. 7. Response of different ^{1}H NMR measurements of HTPB rubber samples (either solid or solvent-swollen, as indicated in the figure) to thermal aging time at 80 °C. Relaxation measurements are normalized to a value of 1.00 for the unaged sample. All NMR measurements were made at room temperature (21 °C). The $T_{2,\mathrm{H}}$ times of solvent-swollen HTPB rubber (from the work of Assink et al. [5]) were measured with samples allowed to equilibrate ~16 h in $CDCl_3$. Lines (both solid and dashed) represent best-fit linear responses of each relaxation measurement to aging time. The slopes of these lines are given in Table 1.

4. Conclusions

The ^{1}H T_1, T_2, and $T_{1\rho}$ relaxation times of a solid HTPB based polyurethane elastomer thermo-oxidatively aged at 80 °C for various periods of time were analyzed as a function of NMR measurement temperature. It was found that the $T_{2,\mathrm{H}}$ and $T_{1\rho,\mathrm{H}}$ relaxation times, which probe the slow-motion regime, exhibited the greatest sensitivity to thermal aging time, whereas the $T_{1,\mathrm{H}}$ relaxation time, which probes intermediate to fast motions, showed minimal change. Overall, $T_{1\rho,\mathrm{H}}$ was slightly more sensitive than $T_{2,\mathrm{H}}$. Spin-lock field strength had a negligible effect on the $T_{1\rho,\mathrm{H}}$ sensitivity to thermal aging. Elevated NMR measurement temperatures significantly increased the difference between the $T_{1\rho,\mathrm{H}}$ relaxation times of the unaged and highly aged samples. However, higher measurement temperatures had little or no effect on the response rate of $T_{2,\mathrm{H}}$ and $T_{1\rho,\mathrm{H}}$ for moderate thermal aging times. The $T_{2,\mathrm{H}}$ relaxation times of solvent-swollen HTPB rubber samples exhibit the largest, most effective sensitivity to thermal oxidation. However, if a nondestructive analysis of solid HTPB samples is required, then the $T_{2,\mathrm{H}}$ and $T_{1\rho,\mathrm{H}}$ relaxation times are recommended.

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