

# Condition Monitoring of a Thermally Aged Elastomer by $^1\text{H-NMR}$ $T_2$ Relaxation Measurements of Solvent-Swelled Samples

Roger A. Assink,<sup>1</sup> Mathew Celina,<sup>1</sup> Leanna M. Minier<sup>2</sup>

<sup>1</sup>Organic Materials, Sandia National Laboratories,\* Albuquerque, New Mexico 87185-1453

<sup>2</sup>Explosive Materials, Sandia National Laboratories, Albuquerque, New Mexico 87185-1411

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**ABSTRACT:** The aging of polymers is often monitored by mechanical property measurements such as those of Young's modulus or tensile elongation at break; new methods are required, however, in situations where traditional mechanical methods cannot be employed. A hydroxy-terminated polybutadiene/isophorone diisocyanate elastomer is commonly used as a propellant binder. The thermal degradation of the binder is believed to be an important parameter governing the performance of the propellant. Classical mechanical methods cannot be used to monitor the condition of this material when it has been aged *in situ* as a highly dispersed binder. In this study, the  $^1\text{H-NMR}$  spin-spin relaxation times,  $T_2$ , of solvent-swelled samples decreased substantially as thermally induced oxidation led to addi-

tional crosslinking. A time-temperature superposition analysis of the relaxation times was performed on samples that had been aged at temperatures ranging from 50 to 125°C. The acceleration factors derived from the relaxation measurements agreed with those reported earlier for tensile elongation at break and oxygen consumption. The dependence of  $T_2$  on tensile elongation at break was independent of the temperature at which the sample was aged. A shortened version of the experiment, requiring only two spin-echo delay times, is presented. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3636–3641, 2002

**Key words:** ageing; polybutadiene; degradation; NMR; solution properties

## INTRODUCTION

Robust methods to monitor the condition of aged polymers are essential for the assessment of a polymer's suitability in high-stress environments and for the development of improved scientific aging models. In addition, there is often a need to characterize the condition of a polymer in an atypical form, such as a powder, film, or foam, for which classical mechanical approaches may not be readily applied. We had a particular need to monitor the condition of a hydroxy-terminated polybutadiene (HTPB) elastomer that is commonly used as a binder in solid rocket propellants. Because the backbone of the HTPB elastomer is unsaturated, it is highly susceptible to oxidation and the resulting loss in mechanical properties. A time-temperature superposition study of tensile elongation at break was completed for the pure HTPB elastomer.<sup>1</sup> Classical methods, however, cannot be used to monitor the condition of the elastomer after it has been aged *in situ* as a highly dispersed binder.

We recently reported a correlation between the  $^{13}\text{C}$  cross-polarization NMR time constant and the tensile elongation at break of the HTPB elastomer as a function of aging time.<sup>2</sup> This method was demonstrated on pure elastomers but has also been used to examine the binder of an ammonium perchlorate propellant from which the ammonium perchlorate has been removed by a simple water extraction. Although the correlation between the time constant and the elongation was excellent, this technique has several disadvantages. The experiment requires on the order of 200 mg of sample and takes several hours to complete. In addition, a spectrometer with solid-state capabilities is required. The measurement is best performed with a ramped-amplitude cross-polarization experiment, or else extreme care is required when setting the radio frequency power matching levels.

We have also used  $^{13}\text{C-NMR}$  and  $^{17}\text{O-NMR}$  spectroscopy to characterize the degradation products in oxidatively aged HTPB.<sup>3</sup> Alcohols were the dominant oxygen-containing degradation products with minor amounts of esters and acids. Again, these experiments were lengthy and, in the case of  $^{17}\text{O-NMR}$ , required special sample preparation involving  $^{17}\text{O}$ -labeled molecular oxygen. Although useful for understanding degradation pathways and mechanisms, these approaches do not provide a convenient method to monitor the condition of the polymer.

Correspondence to: R. A. Assink (raassin@sandia.gov).

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This report describes  $^1\text{H}$ -NMR spin-spin relaxation time,  $T_2$ , measurements<sup>4</sup> of aged HTPB samples that were swollen in deuterated chloroform. The  $^1\text{H}$  nucleus was employed because of the greatly increased response of this nucleus compared to  $^{13}\text{C}$  and  $^{17}\text{O}$  nuclei. The  $^1\text{H}$  transverse relaxation was used by Simon et al.<sup>5</sup> to probe crosslinking in polymer networks at temperatures well above their glass-transition temperatures. Menge et al.<sup>6</sup> used similar experiments to study both solid and solvent-swollen poly(dimethylsiloxane) rubbers. Litvinov et al.<sup>7</sup> used  $^1\text{H}$ -NMR  $T_2$  experiments to measure the crosslink densities of ethylene-propylene-diene elastomers that had been prepared with various vulcanization conditions. In each of these studies, the relationship between  $^1\text{H}$ -NMR relaxation times and the state of crosslinking in the polymer was explored.

The number of crosslinks induced by the aging process determines the extent to which the elastomer can swell in a given solvent.<sup>8</sup> Additional crosslinks decrease the solvent-to-polymer ratio and stiffen the polymer network. Both effects reduce the mobility of the polymer chains and cause a reduction of the relaxation time. The  $^1\text{H}$   $T_2$  spin-spin relaxation times are reported for the HTPB elastomer aged for various periods of time at temperatures ranging from 50 to 125°C. Acceleration factors<sup>9</sup> derived from these measurements are compared to those derived from tensile elongation and oxygen consumption measurements.<sup>1</sup> In addition, the correlation between  $^1\text{H}$   $T_2$  spin-spin relaxation times and tensile elongation measurements were compared for samples aged at various temperatures to determine if a universal relationship between the two quantities existed for the HTPB elastomer. Because the sensitivity of the hydrogen nucleus is several orders of magnitude greater than that of the carbon nucleus, these experiments could be performed in minutes on milligram-size samples.

## EXPERIMENTAL

### Materials

The elastomeric binder was a cured HTPB/isophorone diisocyanate polymer. Samples of the uncured resins were provided by Atochem (Philadelphia, PA) and Thiokol (Brigham City, UT). Crosslinking was achieved via an isocyanate/hydroxyl addition reaction, yielding a simple polyurethane linkage. The HTPB resin had a relatively low concentration of reactive hydroxyl groups ( $\sim 0.74$  mequiv/g) that corresponded to an equivalent weight (EW) of about 1350 g. With an approximate functionality of 2.1, this corresponded to an average molecular weight ( $M$ ) of about 2835 g/mol. These values were very similar to those reported in other studies for the HTPB-type R45M with  $M \approx 2800$  g/mol and  $\text{EW} \approx 1370$  g<sup>10</sup> or  $\text{EW}$

$\approx 1300$  g.<sup>11</sup> Both components were mixed with equal molar reactivities and included 1% Vanox MBPC antioxidant [2,2'-methylene-bis(4-methyl-6-*t*-butylphenol)]. A sample containing no antioxidant oxidized approximately three orders of magnitude faster than the stabilized material, confirming the action of the antioxidant. We thermally cured the resulting resin for 1 week at 65°C to obtain sheets of 2 mm thickness with Teflon-coated molds to allow for removal after curing. The sheets were cut into strips 6 mm wide and 150 mm long.

### Thermal aging

Thermal aging of the rubber strips was carried out in temperature-controlled ( $\pm 1^\circ\text{C}$  stability), commercial, air-circulating aging ovens under ambient atmospheric conditions ( $\sim 630$  mmHg in Albuquerque, NM).

### Tensile testing

Tensile elongation tests were performed with an Instron (Canton, MA) table model testing machine (model 1000) equipped with pneumatic grips and an extensometer. The strain rate was 12.7 cm/min for an initial crosshead separation of 5.1 cm, and stress-strain data were determined up to failure.

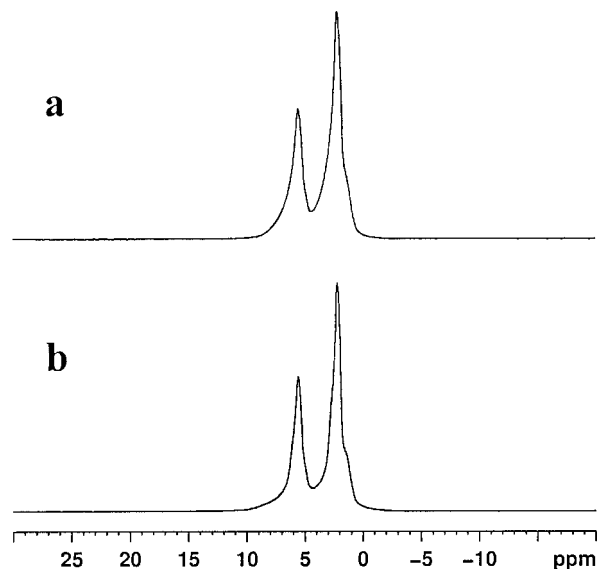
### NMR experiments

The  $^1\text{H}$  relaxation times were measured on a Bruker (Billerica, MA) DRX spectrometer at 399.9 MHz with a 5-mm broadband solution probe. The  $T_2$  relaxation times were measured with a spin-echo pulse sequence consisting of  $\{90^\circ - \tau - 180^\circ - \tau - \text{acquire}\}$  with a  $90^\circ$  pulse width of  $7.5 \mu\text{s}$ . The  $\tau$  values ranged from 0.1 to 20 ms. The relaxation delay was 4 s, and eight scans were accumulated for each  $\tau$  value. The ratio of polymer to  $\text{CDCl}_3$  for the solvent swelling experiments was 1:9 (w/v). The samples were allowed to equilibrate overnight.

## RESULTS AND DISCUSSION

### Experimental approach

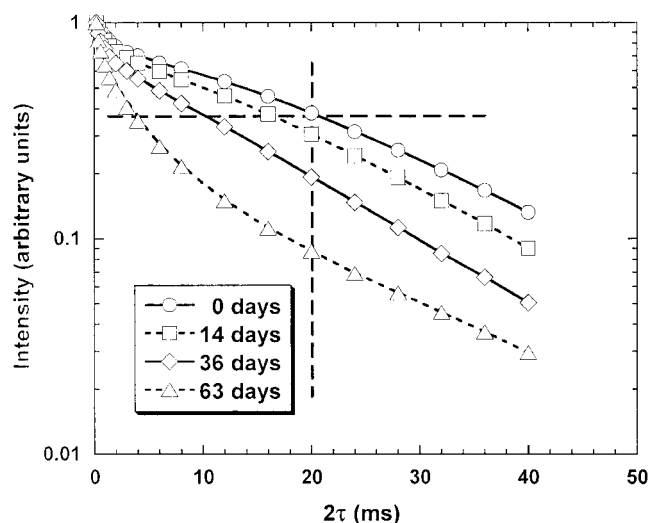
The  $^1\text{H}$  spectra of unaged HTPB and HTPB aged for 36 days at 95°C are shown in Figure 1. The latter condition corresponds to significant aging as the tensile elongation dropped to less than 70% from its initial value of 305%. Each of the 10 mg samples was placed in 90  $\mu\text{L}$  of  $\text{CDCl}_3$  and allowed to equilibrate overnight. The spectrum consisted of two broad overlapping resonances corresponding to the  $\text{sp}^2$  (6 ppm) and  $\text{sp}^3$  (3 ppm) hybridized carbons. The spectral features appeared to be similar for the unaged and aged sam-



**Figure 1**  $^1\text{H}$ -NMR spectrum of the HTPB elastomer swollen in  $\text{CDCl}_3$ : (a) unaged and (b) aged for 63 days at  $95^\circ\text{C}$ .

ples. Although aging was expected to cause some broadening of the resonances, the line width in each instance was dominated by magnetic field inhomogeneities due to the short and asymmetrical samples. The total intensity of each of the spectra could easily be measured by normal integration techniques.

The spin-echo decay curves of unaged HTPB and HTPB aged for various periods of time at  $95^\circ\text{C}$  are shown in Figure 2. As described in the previous paragraph, each of the samples was swollen in  $\text{CDCl}_3$ . Aging caused significant changes in both the shape of the spin-echo curve and the rate with which it decayed. These results are in sharp contrast to those reported earlier (Fig. 3 of ref. 2) for the  $^1\text{H}$  spin-lattice,



**Figure 2**  $^1\text{H}$  spin-echo decay curves for the swollen HTPB elastomer that had been aged for 0, 14, 36, and 63 days at  $95^\circ\text{C}$ .

**TABLE I**  
Relaxation Times (ms) of the HTPB Elastomer in Various Solvents and of the Solid Elastomer for Representative Aging Times (ms) at  $80^\circ\text{C}$

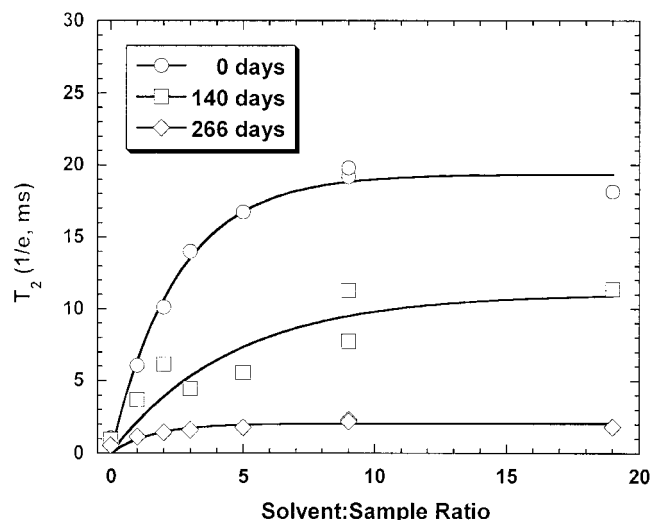
Time at $80^\circ\text{C}$ (days)	$\text{CCl}_4$ $\delta = 17.6^a$	$\text{CDCl}_3$ $\delta = 19.0^a$	DMSO $\delta = 24.6^a$	Solid
0	18.9	19.7	1.40	1.04
140	11.7	9.5	1.36	0.97
266	1.9	2.2	0.99	0.55

<sup>a</sup>  $(\text{J}/\text{m}^3)^{1/2} \times 10^3$ . Ref. 14.

$T_1$ , and  $T_2$  measurements of the solid polymer, where little change was observed for the first 52 days of exposure and  $T_2$  decreased only 40% after 63 days. The spin-echo decays were not a simple exponential function of time. To extract a quantitative measure of the relaxation time that was model independent and did not require extensive analysis, we arbitrarily defined  $T_2$  as the time it took for the spin-echo intensity to decay to  $1/e$  of its initial value. This definition is denoted Figure 2 by the horizontal dotted line and is used throughout the remainder of this article.

Swelling obviously increased the response of the  $^1\text{H}$  spin-echo decay to aging of the HTPB elastomer, and we expected the maximum response when the polymer was swollen to the maximum extent possible.  $\text{CDCl}_3$  was initially chosen because it is an inexpensive solvent commonly used for NMR samples. In addition, the solubility parameter of  $\text{CDCl}_3$  [ $19.0 (\text{J}/\text{m}^3)^{1/2} \times 10^3$ ] was reasonably close to that of the polybutadiene (17.4), the primary constituent of the polymer. Table I shows the relaxation of unaged HTPB and HTPB aged at  $80^\circ\text{C}$  measured as a solid and in various solvents along with the solubility parameter of the solvents.  $\text{CCl}_4$  was chosen because its solubility constant of may have been a slightly better match than that of  $\text{CDCl}_3$ , although the polar urethane linkage was expected to increase the solubility parameter of HTPB compared to that of pure polybutadiene. Dimethyl sulfoxide (DMSO) was chosen to demonstrate the effect of a poor match between the solubility factor of the solvent and that of the polymer.

As noted previously, the relaxation time of the solid polymer was not affected until very late in the aging process. The relaxation trends of HTPB in  $\text{CCl}_4$  and  $\text{CDCl}_3$  were similar throughout the aging range. This similarity was encouraging and demonstrated that the method was not extremely sensitive to experimental details. The response of the relaxation time of HTPB in DMSO was markedly different, however. The relaxation time of the unaged sample was only 1.40 ms, which was not far removed from the 1.04 ms relaxation time of the solid unaged sample. This low value was attributed to the poor solvent quality of DMSO for the unaged HTPB. The relaxation time of HTPB in DMSO remained relatively constant through the mid-



**Figure 3** Dependence of  $T_2$  relaxation times on the solvent-to-sample ratio for the HTPB elastomer aged for various periods of time at  $80^\circ\text{C}$ .

stage of aging and only showed a significant decrease very late in the aging process. The results in Table I show that it is important to select a solvent with a solubility constant near that of the polymer, but a precise match is not critical. The remaining measurements were performed with  $\text{CDCl}_3$  as the solvent.

The effect of  $\text{CDCl}_3$  concentration is shown in Figure 3. The relaxation times increased as the solvent : sample ratio increased for unaged samples and for samples aged 140 and 266 days at  $80^\circ\text{C}$ . The relaxation times appeared to approach a maximum as the solvent : sample ratio approached a value of 9. Additional solvent was ineffective because the swelling had reached a maximum, and the excess solvent did not interact with the polymer. A ratio of 9 was chosen for the remaining measurements described in this article. This value provided maximum sensitivity to aging while being relatively insensitive to slight deviations in sample preparation. Duplicate samples were prepared and measured with a solvent : sample ratio of 9. The two data points for HTPB aged 140 days showed significant scatter, whereas those for the unaged samples and samples aged for 266 days agreed quite well. The occasional scatter was attributed to minor variations between these 10-mg samples. Repeat measurements on the same samples provided nearly identical results as those shown. The deviation, which looked rather large, actually had very little effect on the value of acceleration factors because they were derived from all of the data points in the rapidly decreasing time-temperature aging curve.

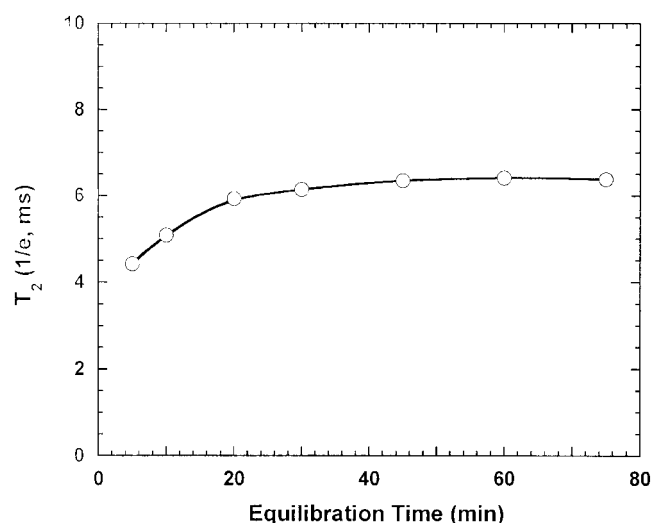
Figure 4 shows the relaxation time as a function of time after the solvent was added to a sample aged for 52 days at  $95^\circ\text{C}$ . The 10-mg samples had dimensions of approximately  $0.1 \times 0.2 \times 0.5 \text{ cm}^3$ . The relaxation time appeared to reach an equilibrium value after 1 h and

remained constant for up to 3 days after that time. The measurements reported in this article were performed on samples that were exposed to  $\text{CDCl}_3$  for a nominal 16 h.

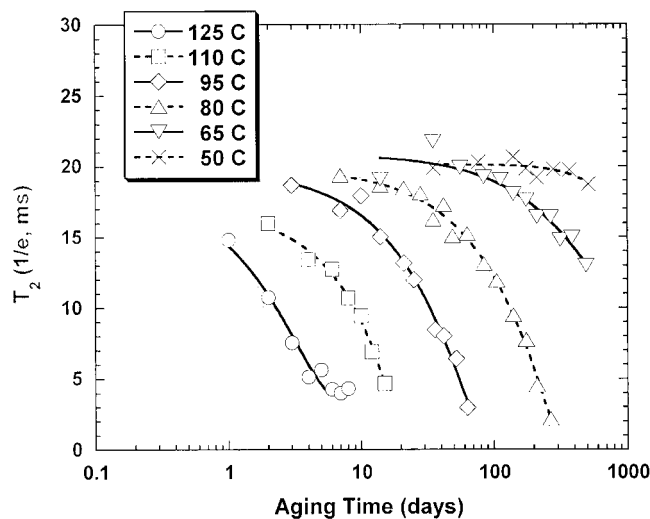
### Time-temperature superposition

The aging behavior of polymeric materials are often studied by the measurement of the property of interest as a function of aging time and conditions. To complete the study in a reasonable period of time, results at high environmental stress (e.g., high temperature) are used to predict behavior at low environmental stress (low temperature). The relationship between high- and low-temperature behavior can sometimes be established by an Arrhenius plot.<sup>12</sup> In the more general case, acceleration factors are determined by time-temperature superposition methods.<sup>9,12</sup> Acceleration factors were derived from the relaxation measurements and compared to acceleration factors derived from tensile elongation at break, a mechanical measurement, and from oxygen consumption data, a chemical measurement that can be performed over a wide temperature range.

The  $^1\text{H}$   $T_2$  relaxation times are shown in Figure 5 as a function of aging time and temperature. The longest aging times for temperatures of 80, 95, 110, and  $125^\circ\text{C}$  represented total degradation of the material given that the original elongation of 305% was reduced to less than 15% in each instance. The elongations for the longest aging times at 65 and  $50^\circ\text{C}$  were reduced to 126 and 213%, respectively. The relaxation times showed a significant response at each temperature with the exception of the sample aged at  $50^\circ\text{C}$ . Each of the curves was reasonably smooth and exhibited similar curvature when plotted on a logarithmic time



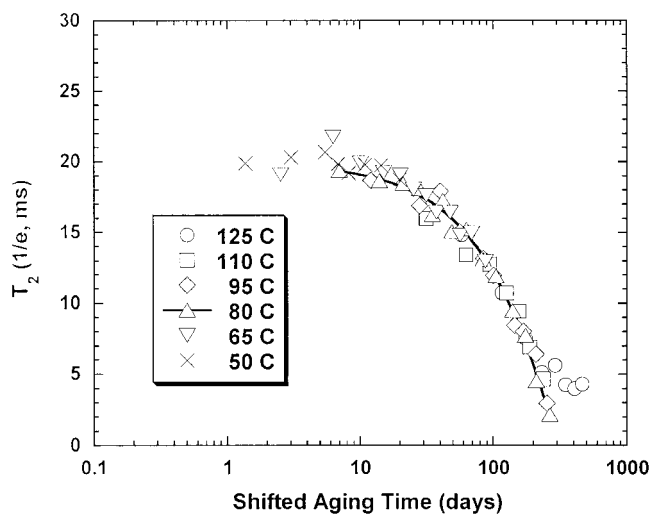
**Figure 4** Dependence of  $T_2$  relaxation times on the equilibration time in  $\text{CDCl}_3$  for the HTPB elastomer aged for 52 days at  $95^\circ\text{C}$ .



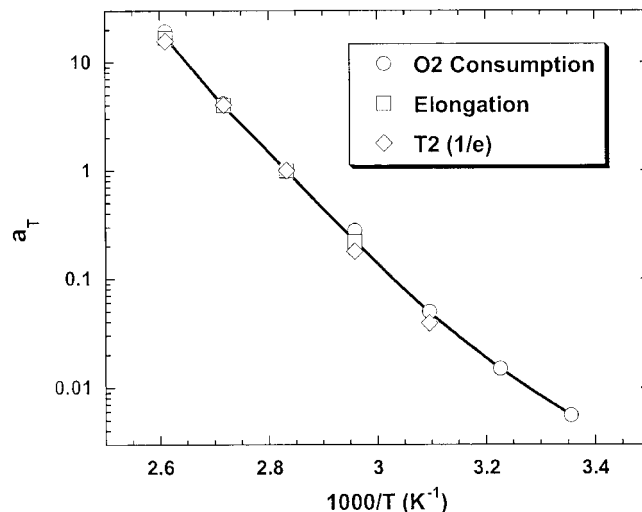
**Figure 5** Complete  $T_2$  relaxation time measurements of the swollen HTPB elastomer that had been aged for the times and temperatures shown.

scale. The relaxation times of samples aged at 125°C for the longest two or three aging times appeared to reach a lower limit. We believe that this effect may have been due to diffusion-limited oxidation in which rapid oxidation at the surface prevented oxygen flow to the center of the material. This effect has been discussed previously<sup>1,13</sup> and was evident by a “skin” effect on the samples. Because the NMR measurement probed the entire sample, much of the signal could be attributed to portions of the sample interior that could not age as rapidly as expected.

Figure 6 shows the superposition of the time–temperature data for HTPB. The time scale of the 80°C sample was assigned a value of 1.0, and the aging times at the other temperatures were multiplied by an appropriate factor so that their curves superimposed.



**Figure 6** Time–temperature superposition of the  $T_2$  relaxation time measurements of the swollen HTPB elastomer.



**Figure 7** Comparison of the acceleration factors for oxygen consumption, tensile elongation at break, and  $T_2$  relaxation time measurements of the swollen HTPB samples.

The agreement was particularly satisfying over the rapidly changing portion of the curve and enabled reasonable acceleration factors to be derived. Note that the acceleration factor for 50°C was subject to considerable uncertainty because the extent of degradation was modest. Also, note that the data corresponding to the longest aging times at 125°C deviated from the other curves. This deviation was attributed to diffusion-limited oxidation discussed in the previous paragraph, and these data were ignored when acceleration factors for the 125°C curve were calculated.

The acceleration factors for  $^1\text{H}$   $T_2$ , along with those for tensile elongation and oxygen consumption, are shown in Figure 7. Tensile elongation is often a very good measure of the mechanical integrity of a polymer, whereas the oxygen consumption technique measures the extent of oxidation of the sample. Oxygen consumption is particularly useful because these measurements are very sensitive and can be completed at low temperatures in a reasonable period of time. Thus, acceleration factors for ambient temperatures can be derived without the need for extrapolation. The acceleration factors for each of the techniques were normalized to 1.0 at 80°C ( $1000/T(\text{K}) = 2.83$ ). The acceleration factors for each measurement tracked each other over the temperature range that they were measured. Thus, we are confident that the  $^1\text{H}$  relaxation measurements provided a useful indicator of both the mechanical and chemical state of the polymer during its aging process.

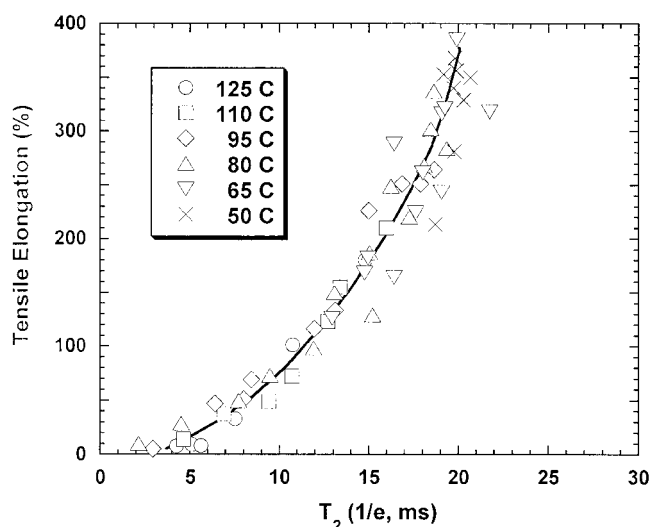
The relationship between elongation and  $^1\text{H}$  relaxation is shown directly in Figure 8 for each of the aging temperatures. An excellent correlation between these two quantities was observed, especially over the central region of the curve where the properties were changing most rapidly with time. This figure demon-

states that a given  $^1\text{H}$  relaxation time corresponded to a unique tensile elongation for the HTPB elastomer when it was thermally aged.

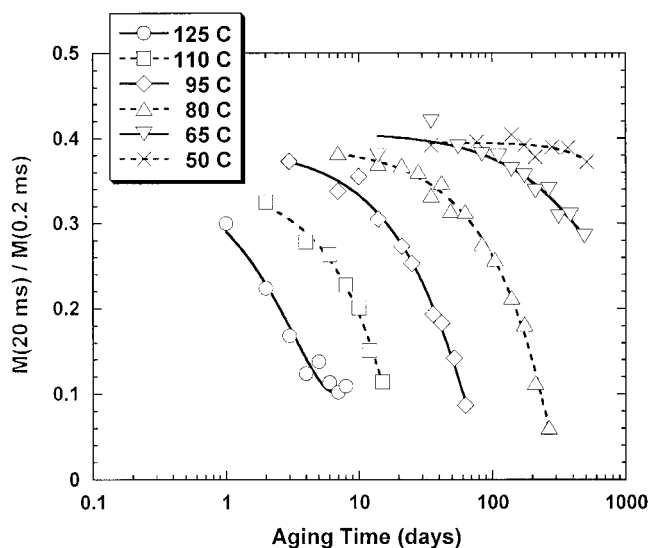
The  $^1\text{H}$  relaxation time experiments were rapid and required approximately 6 min to accumulate eight scans for each of the 18 delay times. We examined methods to further reduce this time for situations where time was critical or when a very small sample or a low-field instrument may require significantly more scans for sufficient signal to noise. The intercept of a spin-echo decay with the vertical dashed line in Figure 2 represents the intensity of the decay at a fixed delay time of 20 ms. The intensity of the decay at 20 ms decreased in a manner similar to that with which the delay time decreased for a constant spin-echo intensity (e.g., the  $1/e$  that we chose for this study). The advantage of choosing the intercept at a fixed time was that only two delay times needed to be measured: a short delay at 0.2 ms and a long delay at 20 ms. Thus, the experimental time was reduced by nearly an order of magnitude. Figure 9 shows the results of this intercept analysis. The general features of the time-temperature data were similar to those shown in Figure 5 with the time for the spin echo to decay to  $1/e$  of its initial value. Time-temperature superposition analysis provided nearly identical acceleration factors for the two approaches.

### CONCLUSIONS

The  $^1\text{H}$ -NMR  $T_2$  relaxation times of HTPB elastomer swollen in  $\text{CDCl}_3$  were much more responsive to thermal aging than those of solid samples. The acceleration factors derived from relaxation time measure-



**Figure 8** Dependence of tensile elongation on the  $T_2$  relaxation time of the swollen HTPB samples.



**Figure 9** Relative spin-echo intensity at 20 versus 0.2 ms of the swollen HTPB elastomer that had been aged for the times and temperatures shown.

ments agreed with those derived earlier from tensile elongation at break and from oxygen consumption measurements. This approach provides a rapid and convenient method with which to monitor the condition of aged elastomers on a conventional high-resolution NMR spectrometer. These relaxation measurements can be performed on very small samples of arbitrary form for which traditional mechanical methods are not suitable.

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