

# Condition Monitoring of a Thermally Aged Hydroxy-Terminated Polybutadiene (HTPB)/Isophorone Diisocyanate (IPDI) Elastomer by Nuclear Magnetic Resonance Cross-Polarization Recovery Times

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**ABSTRACT:** A hydroxy-terminated polybutadiene (HTPB)/isophorone diisocyanate (IPDI) elastomer is commonly used as propellant binder material. The thermal degradation of the binder is believed to be an important parameter governing the performance of the propellant. The aging of these binders can be monitored by mechanical property measurements, such as modulus or tensile elongation. These techniques, however, are not easily adapted to binder agents that are dispersed throughout a propellant. In this paper we investigated solid-state nuclear magnetic resonance (NMR) relaxation times as a means to predict the mechanical properties of the binder as a function of aging time. Proton ( $^1\text{H}$ ) spin-lattice and spin-spin relaxation times were insensitive to the degree of thermal degradation of the elastomer. Apparently, these relaxation times depend on localized motions that are only weakly correlated with mechanical properties. A strong correlation was found between the  $^{13}\text{C}$  cross-polarization (CP) NMR time constant,  $T_{\text{cp}}$ , and the tensile elongation at break of the elastomer as a function of aging time. A ramped-amplitude CP experiment was less sensitive to imperfections in setting critical instrumental parameters for this mobile material. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 453–459, 2001

**Key words:** hydroxy-terminated polybutadiene (HTPB); ramped-amplitude cross-polarization NMR; elongation; polymer degradation; VACP

## INTRODUCTION

Hydroxy-terminated polybutadiene (HTPB)-based elastomers are commonly used as the polymeric binder matrix in solid rocket propellants.<sup>1</sup> Because of considerable unsaturation of their polymer structure, they are highly susceptible to oxidation. Oxidation of the binder is associated with a loss in its mechanical properties that can adversely affect the performance of the propellant. The aging and deg-

radation of these elastomers and the property changes that these processes bring about are genuine concerns.

The aging behavior of polymeric materials is usually studied by measuring 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 often used to predict behavior at low environmental stress (low temperature). The relationship between high and low temperature behavior is established by an Arrhenius plot or, in the more general case, by acceleration factors determined by a time-temperature

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superposition.<sup>2</sup> The tensile elongation at break of the binder is believed to be an important parameter related to the performance of a propellant and has proven to be a mechanical property that is sensitive to aging. A time–temperature superposition study of tensile-elongation at break has been completed for a pure HTPB/isophorone diisocyanate (IPDI) elastomer.<sup>1</sup>

To predict the performance of a propellant, however, one must understand how the binder ages when incorporated in the propellant. The binder comprises ~10% of the propellant by weight. Binder aging may be influenced by chemical interactions between the propellant components and by the effect of the propellant grains on the diffusion of oxygen to the interior of the sample. The intrinsic properties of the elastomer dispersed in the propellant are difficult to measure by conventional mechanical measurements. Although the energetic oxidizer component of the propellant can be extracted, the remaining binder is difficult to characterize. In this study, we examine several approaches to develop a correlation between the mechanical properties of the binder and nuclear magnetic resonance (NMR) relaxation parameters. These NMR relaxation parameters can be measured on samples of arbitrary form. If such a correlation can be established, then the mechanical properties of the binder, either incorporated into a propellant or remaining after extraction, can be predicted by these relaxation parameters.

Most common NMR relaxation times are related to the complex molecular motions occurring in the sample. These molecular motions are in turn related to the mechanical properties of the material.<sup>3</sup> Perhaps the most common relaxation times are the <sup>1</sup>H spin–lattice,  $T_1$ , and spin–spin,  $T_2$ , relaxation times. In this study, we found that these relaxation times of the solid material, when measured at 400 MHz, were relatively insensitive to age-induced changes of the mechanical properties of the binder. Evidently, these relaxation times are dominated by high-frequency local motions that are not strongly coupled to mechanical properties.

Parker et al.<sup>4</sup> and Marcinko et al.<sup>5, 6</sup> have shown that the <sup>13</sup>C cross-polarization (CP) time constant,  $T_{cp}$ , can be a sensitive probe of mechanical properties for a wide range of polymers.  $T_{cp}$  is a function of the low frequency motions that characterize long-range cooperative processes that are closely related to the mechanical properties of the polymer. In this study, we show that changes in

$T_{cp}$  are correlated to age-induced changes in tensile elongation at break of the HTPB binder. We also show that a ramped-amplitude CP experiment<sup>7</sup> is less sensitive to imperfections in setting critical instrumental parameters for this mobile material.

## EXPERIMENTAL

### Materials

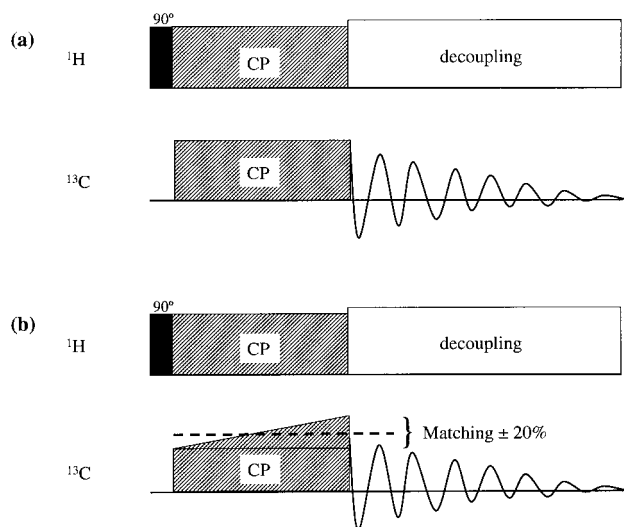
The elastomeric binder investigated is a cured HTPB/IPDI polymer. Samples of the uncured resins were provided by industry (Elf Atochem and Hüls America Inc.). Cross-linking is achieved via an isocyanate/hydroxyl addition reaction yielding a simple polyurethane linkage. The HTPB resin has a relatively low concentration of reactive hydroxyl groups (~0.74 meq·g<sup>-1</sup>) that corresponds to an equivalent weight (EW) of ~1350 grams. With a functionality of ~2.1, this EW corresponds to an average molecular weight,  $M$  of  $M \sim 2835$  g mol<sup>-1</sup>. These values are very similar to those reported in other studies for the HTPB type R45M, with an  $M$  of ~2800 g mol<sup>-1</sup> and EW values of ~1370 g<sup>8</sup> or ~1300 g.<sup>9</sup> Both components were mixed with equal molar reactivities and include 1% Vanox MBPC antioxidant (2,2'-methylenebis(4-methyl-6-*t*-butylphenol)). A sample containing no antioxidant oxidizes ~3 orders of magnitude faster than the stabilized material confirming the action of the antioxidant.<sup>1</sup> The resulting resin was thermally cured for 1 week at 65 °C to obtain sheets of 2 mm thickness using 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 ( $\pm 1$  °C stability), commercial, air-circulating aging ovens under ambient atmospheric conditions (~630 mmHg in Albuquerque, NM).

### Tensile Testing

Tensile elongation tests were performed with an Instron 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.



**Figure 1** CP pulse sequences for both (a) single- and (b) ramped- amplitude experiments. In the single-amplitude CP experiment, the amplitude of both the  $^{13}\text{C}$  and  $^1\text{H}$  channel remain constant during the CP transfer time, whereas in the ramped-amplitude CP experiment, the carbon field strength is increased linearly during the contact period.

### NMR Experiments

The  $^1\text{H}$  relaxation times were measured on a Bruker DRX spectrometer at 399.9 MHz using a 5-mm broadband solution probe. The  $T_1$  relaxation times were measured using an inversion recovery pulse sequence whereas the  $T_2$  relaxation times were measured using a spin-echo pulse sequence. Static, single-amplitude  $^{13}\text{C}$  cross-polarization (CP) spectra (Figure 1a) were recorded using variable contact times on a Bruker AMX spectrometer, equipped with a 7-mm MAS probe, at 100.6 MHz. Ramped-amplitude CP experiments<sup>7</sup> were performed by monotonically increasing the amplitude on the  $^{13}\text{C}$  channel from  $-20$  to  $+20\%$  of the amplitude of the standard, single-amplitude CP experiment (Figure 1b); the spin-lock amplitude of the  $^1\text{H}$  channel was kept constant during the experiment. The 'ramping function', which was programmed using *xshape*, a program supplied within Bruker's *xwinnmr* software package, consists of a number of discrete, uniformly sized steps that increase the power on the  $^{13}\text{C}$  channel over the duration of the CP contact time. Contact times for both the single- and ramped-amplitude CP experiments ranged from 0.05 to 6.0 ms. A total of 256 scans with a 2-s delay were accumulated at each contact time. Additional  $^{13}\text{C}$  CP experiments, using a single con-

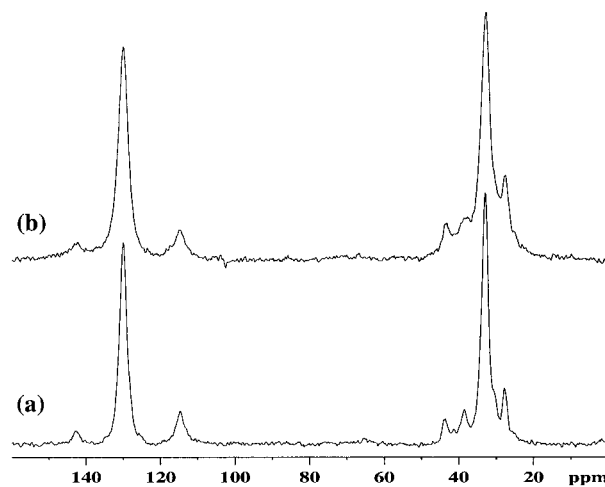
tact time of 2 ms and  $\sim 1$  kHz magic-angle spinning (MAS) were performed on the unaged sample and a sample aged for 52 days at  $95^\circ\text{C}$ . Although the MAS spectra had somewhat improved resolution compared with static spectra, the  $^{13}\text{C}$  CP relaxation measurements were conducted on static samples because of the difficulty of reliably spinning these soft samples.

## RESULTS AND DISCUSSION

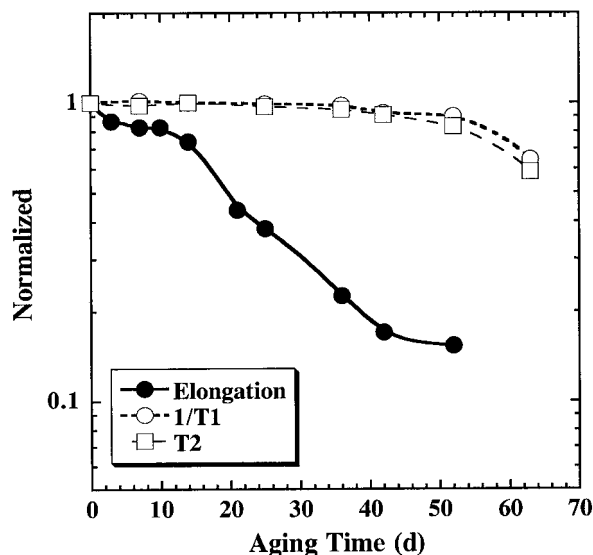
### $^{13}\text{C}$ Spectra and $^1\text{H}$ Relaxation

The  $^{13}\text{C}$  CP MAS spectra of an unaged and aged elastomer are shown in Figure 2. The low- and high-field regions consist primarily of the unsaturated and saturated carbons, respectively, in the polybutadiene chain segments. No significant differences in the positions and relative intensities of the resonances for the two samples can be seen. Additional resonances attributable to degradation products are not apparent. Thus, the chemical environments of a large fraction of the carbons of the sample have not been affected by thermal aging. The insensitivity of  $^{13}\text{C}$  spectra to aging has been previously reported by Alam et al.<sup>10</sup>

The linewidths of the  $^{13}\text{C}$  resonances of the aged elastomer increased relative to the unaged sample. The increase in linewidth is caused by a reduction in mobility of the chain segments. These results suggest that NMR relaxation times may be a sensitive probe of aging. Two common and easily measured relaxation times are the  $^1\text{H}$  spin-lattice,  $T_1$ , and  $^1\text{H}$  spin-spin,  $T_2$ , relaxation



**Figure 2**  $^{13}\text{C}$  CP MAS spectra of HTPB binder (a) unaged and (b) aged 52 days at  $95^\circ\text{C}$ .



**Figure 3** Normalized tensile elongation at break and  $^1\text{H}$  NMR  $1/T_1$  and  $T_2$  relaxation times for an HTPB sample aged at  $95\text{ }^\circ\text{C}$ .

times.<sup>3</sup> These relaxation times, normalized to a value of 1.0 for the unaged sample, are shown in Figure 3 as a function of aging time. The inverse of  $T_1$  is plotted so that all parameters show a decrease with increased aging time. For comparison, the tensile elongation at break of the elastomer is also shown. The tensile elongation of the binder elastomer is a sensitive probe of the mechanical state of the material and is expected to be closely related to the performance of a propellant binder.

After 40 days at  $95\text{ }^\circ\text{C}$ , the tensile elongation decreased to  $< 20\%$  of its initial value, whereas the  $^1\text{H}$  relaxation times  $T_1$  and  $T_2$  show almost no change. Thus, the  $^1\text{H}$  relaxation times are not a sensitive probe for monitoring the deterioration of the binder. Apparently, the high-frequency molecular motions measured by the  $^1\text{H}$  NMR relaxation times are too localized to be correlated with the mechanical properties of the material.

### $^{13}\text{C}$ CP Recovery Times

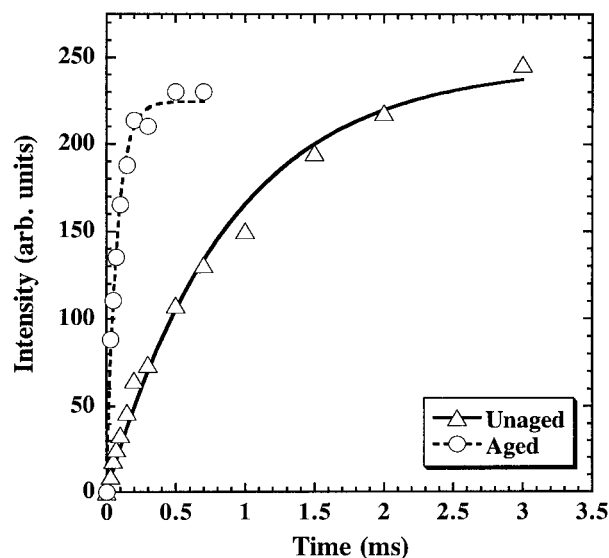
Parker et al.<sup>4</sup> and Marcinko et al.<sup>5, 6</sup> recognized that the  $^{13}\text{C}$  CP recovery time,  $T_{\text{cp}}$ , is sensitive to the low-frequency long-range cooperative motions of a polymer. These motions are expected to be more closely related to the mechanical properties of a material. These authors demonstrated a correlation between  $T_{\text{cp}}$  and the modulus of the sample for a variety of polymeric materials. A simpli-

fied expression for the relationship between  $T_{\text{cp}}$  and the correlation time for molecular motion,  $\tau_c$ , is given by

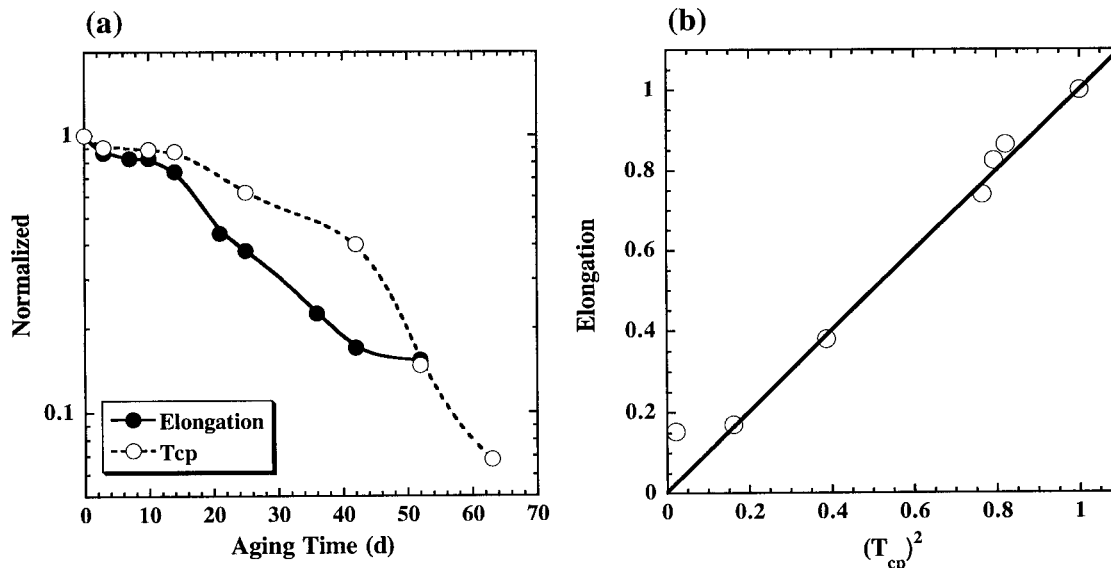
$$\frac{1}{T_{\text{CP}}} \propto M_2^{\text{CP}} [\tau_c \exp(-\Delta\omega^2 \tau_c^2 / 4)]$$

where  $M_2^{\text{CP}}$  is the second moment of the C—H dipolar-coupling interaction (proportional to  $1/r^6$ ) and  $\Delta\omega$  is the mismatch of the Hartman–Hahn condition.<sup>11, 12</sup>

The total  $^{13}\text{C}$  signal intensities versus CP contact time for unaged HTPB and for HTPB aged at  $95\text{ }^\circ\text{C}$  for 52 days are shown in Figure 4. Note how the rise time increases much more quickly for the aged sample, indicating that this measurement is sensitive to thermal aging. For long contact times, the signal intensity begins to decrease with a time constant,  $T_{1\rho\text{H}}$ .<sup>12</sup> The  $T_{1\rho\text{H}}$  is much longer than 10 ms for the unaged HTPB sample, and couldn't be accurately measured given our instrumental limitations on high-power pulse lengths. For this reason, a complete fit of the intensity versus CP time using both  $T_{\text{cp}}$  and  $T_{1\rho\text{H}}$  time constants could not be accomplished. Instead, a single exponential  $T_{\text{cp}}$  was used to fit the initial portion of the recovery curve up to and including the time providing the maximum spectral intensity. The normalized values of  $T_{\text{cp}}$  for the aged HTPB samples are compared with normalized tensile elongation measurements in Figure 5a. Whereas the  $T_1$  and  $T_2$



**Figure 4** Total  $^{13}\text{C}$  signal intensity versus CP contact time for HTPB binder unaged and aged 52 days at  $95\text{ }^\circ\text{C}$ .



**Figure 5** (a) Normalized tensile elongation at break and  $^{13}\text{C}$  CP time constant,  $T_{\text{cp}}$ , of HTPB binder aged at 95 °C. (b) Correlation plot of normalized elongation versus normalized  $(T_{\text{cp}})^2$ .

relaxation times of the  $^1\text{H}$  nucleus were relatively independent of aging time,  $T_{\text{cp}}$  is responsive to age-induced changes in the binder.

Equation 1 predicts that a number of factors could contribute to a reduction in  $T_{\text{cp}}$  for aged samples. The second moment of the C—H dipolar-coupling interaction depends on the magnitude and number of C—H internuclear vectors. Because the chemistry of the material undergoes relatively modest changes, we do not expect a substantial change in the second moment with aging. The Hartman–Hahn match is adjusted for each sample and any error introduced by a mismatch would be expected to vary randomly among the samples. We conclude that thermal aging causes a reduction in the molecular correlation time. This result is consistent with a reduction in the tensile elongation at break of HTPB with aging time.<sup>1</sup>

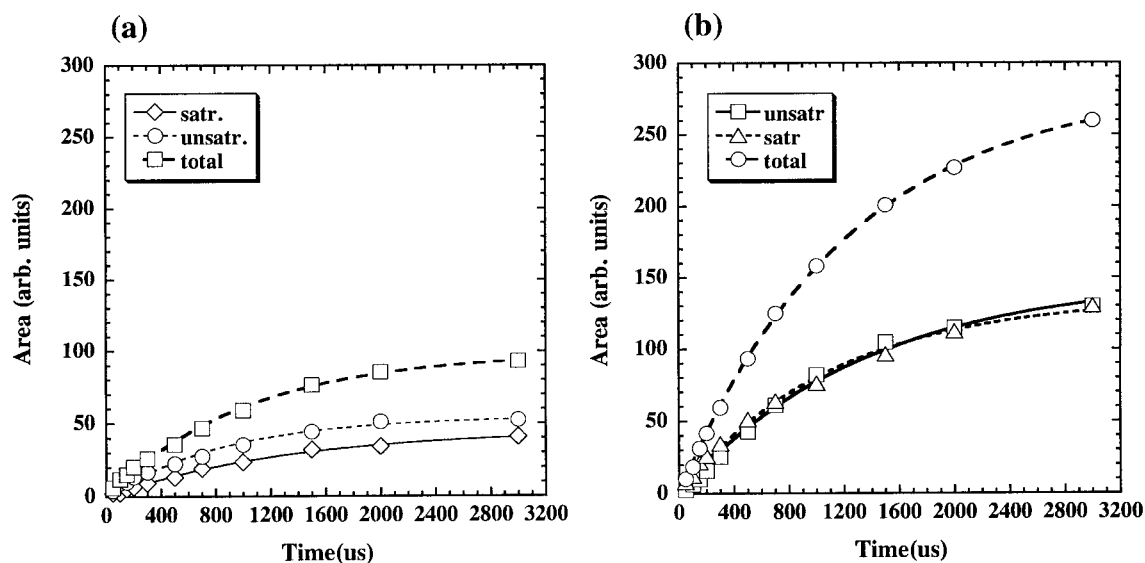
Parker et al.<sup>4</sup> used Maxwell's model for viscoelastic materials to derive a relationship between Young's modulus and  $T_{\text{cp}}$ . They showed that the modulus was related to a complex quantity involving  $(T_{\text{cp}})^2$  and the measurement frequency of Young's modulus. They found a reasonable correlation for a wide range of polymeric materials. For a measurement frequency of 1 Hz, Marcinko et al.<sup>5</sup> simplified the expression to show that Young's modulus and  $(T_{\text{cp}})^2$  are inversely related. Because the tensile elongation at break

was a sensitive measure of aging in these binder materials, we wanted to determine if a similar relationship could be established between elongation and  $(T_{\text{cp}})^2$ . Such a correlation would prove useful even though it is phenomenological and cannot be derived from a simple mechanical model.

The results in Figure 5b show that indeed a similar relationship holds between the tensile elongation at break and  $(T_{\text{cp}})^2$ . The solid line represents a perfect inverse correlation between the two quantities. The data points follow an inverse relationship within experimental error with the exception of the sample aged for 52 days — well beyond the useful life of the material. A least squares fit of the data yields the dashed line, with a correlation coefficient ( $r^2$ ) of 0.98. We estimate that the elongation and  $(T_{\text{cp}})^2$  determinations have similar experimental errors ( $\pm 10\%$ ). Thus, the ability to monitor the condition of the polymer by  $^{13}\text{C}$   $T_{\text{cp}}$  relaxation times should be comparable to that of elongation measurements.

### Ramped-Amplitude CP

The rapid molecular reorientation of the HTPB elastomer reduces the efficiency of the CP process.<sup>11, 12</sup> Tuning the probe and adjusting the rf power levels to an exact Hartmann–Hahn match becomes more critical for good CP efficiency.



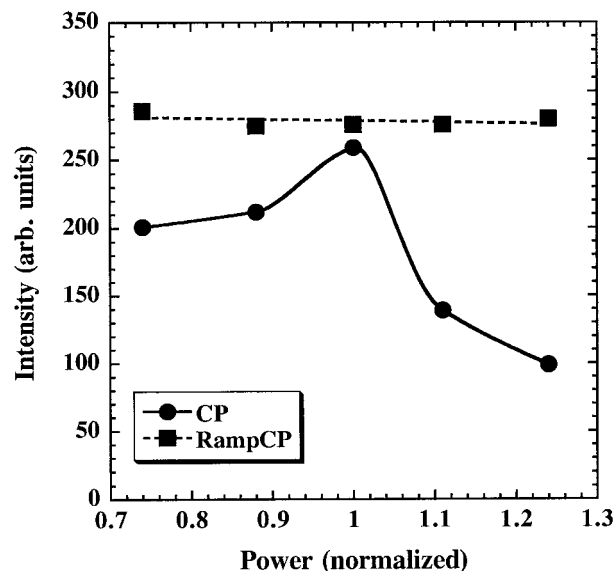
**Figure 6** Unsaturated (unsatr), saturated (satur) and total  $^{13}\text{C}$  signal intensities for (a) mismatched single-amplitude CP and (b) mismatched ramped-amplitude CP experiments.

Smith and co-workers<sup>7, 13, 14</sup> have developed several ramped-amplitude and variable-amplitude CP experiments to address this problem. They found that the modified CP experiments provide much better CP efficiencies than the single-amplitude CP experiments when the Hartmann–Hahn match is not optimized.

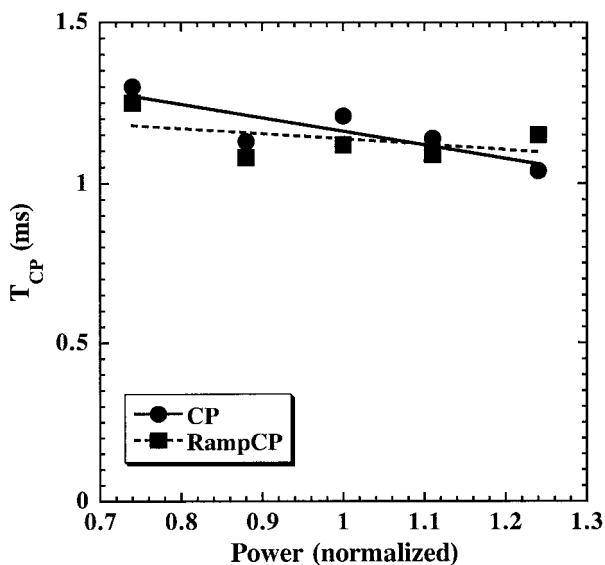
A ramped-CP experiment (Figure 1b),<sup>7</sup> was investigated to determine if the effect of a mismatch of the Hartmann–Hahn condition could be minimized for the HTPB elastomer. Unsaturated, saturated, and total  $^{13}\text{C}$  signal intensities for mismatched single-amplitude CP and mismatched ramped-amplitude CP experiments are shown in Figure 6. The  $^{13}\text{C}$  power level is 1.24 times the Hartmann–Hahn match in Figure 6(a), whereas the  $^{13}\text{C}$  power level varies  $\pm 20\%$  from the 1.24 power ratio level in Figure 6(b). The signal intensities for the single-amplitude CP experiment are substantially less than the corresponding signal intensities for the ramped-amplitude CP experiment.

The performance of the single-amplitude and ramped-amplitude CP experiments versus power-level offset levels are compared in Figure 7. The total magnetization intensities are shown over a normalized power-level range from 0.74 to 1.24. The  $\pm 20\%$  ramping function of the ramped-amplitude CP experiment provides a flat spectrum intensity with  $< 5\%$  deviation over the entire power range. The spectrum intensity of the sin-

gle-amplitude CP experiment is nearly as large as the intensity of the ramped-amplitude CP experiment when the Hartmann–Hahn match is optimized. However, the intensity of the single-amplitude CP signal decreases by 28 and 65% at the extremes of the low and high power levels, respectively.



**Figure 7** Total  $^{13}\text{C}$  signal intensity for the single-amplitude and ramped-amplitude CP experiments versus normalized power. A power level of 1 corresponds to the optimized Hartmann–Hahn match for the single-amplitude CP experiment.



**Figure 8** CP time constant,  $T_{cp}$ , for the single-amplitude and ramped-amplitude CP experiments versus normalized power.

The CP time constants,  $T_{cp}$ , for both CP experiments as a function of power levels are shown in Figure 8. Note that the average  $T_{cp}$  value does not differ greatly for the two methods. The average  $T_{cp}$  value calculated for the ramped-CP experiments is 1.14 ms versus 1.16 ms for the standard, fixed-amplitude CP experiments. The standard deviation of the  $T_{cp}$  values for the ramped-CP experiments are  $\sim 30\%$  less than those for the fixed-amplitude CP experiments; however, this improvement may not be experimentally significant. The power-level offset apparently reduces the signal intensity by a constant factor independent of the CP time. Thus, the primary advantage of the ramped experiment is better signal-to-noise that is independent of Hartmann–Hahn mismatches. Loss of signal intensity from improper setting of the power levels or from changes in probe tuning during the experiment due to rf heating will be minimized by the ramped-amplitude CP experiment.

## CONCLUSIONS

The aging of an HTPB/IPDI elastomer has been investigated by correlating NMR relaxation times with tensile elongation at break measurements. Several approaches to develop a correlation between the mechanical properties of the binder and

NMR relaxation parameters were investigated. The  $^1\text{H}$   $T_1$  and  $T_2$  relaxation times were relatively insensitive to aging of the elastomer. A strong correlation was found between elongation and  $^{13}\text{C}$  NMR CP time,  $T_{cp}$ . Evidently, the  $^1\text{H}$  relaxation times are dominated by high-frequency local motions that are not strongly coupled with the mechanical properties.  $T_{cp}$  is dependent on low-frequency cooperative motions that are more strongly coupled to mechanical properties, such as elongation. For this mobile material, the CP efficiency is critically dependent on the proper setting of instrumental power levels. Using a ramped-amplitude CP experiment, however, the effects of power-level mismatches are minimized.

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