

^1H -NMR Imaging Study of Molecular Mobility in Carbon Black-Filled, TBBS-Sulfur-Vulcanized *cis*-Polyisoprene

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ABSTRACT: The distributions of the T_2 relaxation times in carbon black filled, TBBS-Sulfur vulcanized *cis*-polyisoprene were studied using ^1H NMRI spin-echo experiments. It has been reported that more than two T_2 relaxation times are observed in carbon black-filled rubbers, reflecting the existence of the hard regions adjacent to the crosslinks or filler particle and soft regions distant from such rigid components. Our current concern is how the amount and distribution of the T_2 times are affected by the filler incorporation in the rubber compounds. A decrease in the T_2 relaxation times with an increase in carbon black content is observed. The average T_2 time, $\langle T_2 \rangle$, drops from 11.38 ms with no carbon black to 10.05 ms with 15 phr carbon black. The $\langle T_2 \rangle$ further decreases when the black loading level is increased from 15 to 30 phr and 30 to 50 phr, but the magnitude of the changes in the $\langle T_2 \rangle$ s are not as large as in the initial loading (0 to 15 phr). The observations of the $\langle T_2 \rangle$ s suggest inhomogeneities are induced in the network structure by the black incorporation. The distribution of the T_2 relaxation times becomes narrower as the black loading level increases. There are at least four factors governing the intensity of the images in the swollen, filled rubber vulcanizates as well as the NMR parameters (T_1 , T_2 , T_R , and T_E): (1) ^1H spin density, (2) inhomogeneity of the network structure, (3) degree of swelling in the sampling solvent, and (4) displacement effect of the carbon black. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 1385–1390, 1998

Key words: *cis*-polyisoprene; carbon black; nuclear magnetic resonance imaging; spin-spin relaxation time

INTRODUCTION

The applications in medicine of nuclear magnetic resonance imaging (NMRI) have grown tremendously for the purposes of clinical diagnosis. Accordingly, nonmedical applications of NMRI are also progressing,^{1–3} although at a slower rate. For a polymer sample to be examined in NMRI with suitable spatial resolution, the sample needs to

have rapid molecular motion so that the dipolar interactions and chemical-shift anisotropy are minimized, yielding narrow resonance lines. Thus, there are several inherent limitations in the application of NMRI to solid polymers below the glass transition. However, elastomers can be successfully imaged with conventional NMRI techniques due to the extensive reorientational motions in the molecules. Swelling the elastomeric sample in an appropriate deuterated solvent increases the molecular mobility and typically gives acceptable resolution in ^1H -NMRI.^{4–7}

One of the advantages of using NMRI over the other imaging techniques is the capability of mapping several material parameters including relax-

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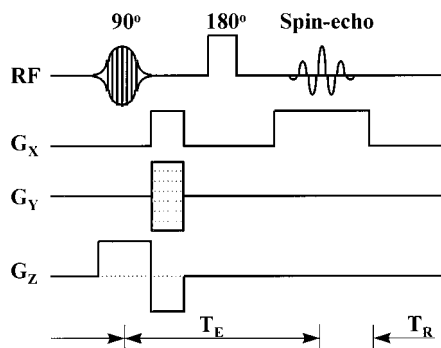


Figure 1 Diagram of the spin-echo NMR imaging program.

ation times and diffusion processes as well as the spin density of the observed nuclei. The spin-spin relaxation time, T_2 , is one of the most important parameters observable in the NMRI experiment, as it is sensitive to low-frequency motions that occur on the molecular level in the polymeric materials.⁸

In the present study, the distributions of the T_2 relaxation times in carbon black-filled, *N-t*-butyl-2-benzothiazole sulfenamide (TBBS)-sulfur-vulcanized *cis*-polyisoprene were studied using ^1H -NMRI spin-echo experiments. It has been reported, from the ^1H -pulsed NMR studies, that more than two T_2 relaxation times are observed in carbon black-filled rubbers, reflecting the existence of the hard regions adjacent to the crosslinks or filler particle and soft regions distant from such rigid components.⁹⁻¹³ However, it has also been shown that T_2 relaxation times are not seriously affected by carbon black loading.¹⁴⁻¹⁶ Our current concern is how the amount and distribution of the T_2 times are affected by the filler incorporation in the rubber compounds.

Spin-echo imaging is the most common pulse sequence in NMRI today. Figure 1 illustrates a diagram of the single spin-echo pulse program. The amplitude of the spin-echo, which determines the pixel intensity, is given by

$$I \sim N(\text{H})[1 - \exp(-T_R/T_1)]\exp(-T_E/T_2) \quad (1)$$

where $N(\text{H})$ is the ^1H spin density; T_1 , the spin-lattice relaxation time; T_R , the pulse repetition delay time; and T_E , the echo time. If the T_R is long compared to the longest T_1 of the pixel, the $\exp(-T_R/T_1)$ goes to zero and the signal intensity becomes independent of T_1 and is modulated by the T_2 relaxation process:

$$I \sim N(\text{H})\exp(-T_E/T_2) \quad (2)$$

Assuming that the sample is homogeneous, eq. (2) can be expressed as

$$I = k \exp(-T_E/T_2) \quad (3)$$

where k is a constant related to the $N(\text{H})$ of the homogeneous sample and the scaling factor for the signal gain in the instrument. Two experiments with different T_E lead to the values of k and T_2 .

The T_2 relaxation times are obtained from a single experiment by using a multiecho imaging technique, where the series of echoes are collected after the 90° rf pulse. In the multiecho method, the T_2 is given as

$$T_2 = T_E/\ln(I_1/I_2) \quad (4)$$

I_1 and I_2 represent the intensities of the resulting first and second echo signals, respectively.

In both single and multi-spin-echo experiments, the signal intensity decreases with increase in the T_E . To acquire an adequate S/N ratio in the image, the T_E in the single spin-echo mode and the nT_E in the multiecho mode should be short enough compared to the shortest T_2 in the sample. Under these circumstances, it is quite difficult to achieve $nT_E < T_2$ in the multiecho experiment for the solid polymer which has short T_2 times compared to liquid samples even in the swollen state.

In this study, two spin-echo experiments using the echo times of T_{E1} and T_{E2} are employed for the determination of the T_2 relaxation times, in which the T_{E2} was set to less than $2T_{E1}$ in order to minimize the loss in the imaging sensitivity.

EXPERIMENTAL

The rubber used in this study is Natsyn 2200, high-*cis*-1,4-polyisoprene. Four formulations were prepared which contain different amounts of HAF-HS (N347) carbon black (0, 15, 30, and 50 phr) and fixed contents of rubber (100 phr), elemental sulfur (2.38 phr), TBBS (0.75 phr), zinc oxide (5.00 phr), and stearic acid (3.00 phr). Four batches were cured in a hydraulic press with a pressure of 2000 psi at 140°C for the times corresponding to t_{90} (90% of rheometer torque increase) according to an ODR-2000, Monsanto oscillating disk rheometer. Those sam-

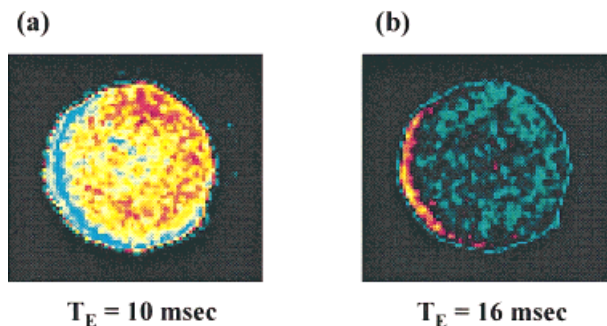


Figure 2 Spin-echo images of *cis*-polyisoprene cured without carbon black: (a) $T_E = 10$ ms; (b) $T_E = 16$ ms.

ples were mixed and cured at the research facilities of the Rubber and Process Chemical Division of the Flexsis America.

Samples were Soxhlet-extracted for 24 h in a cyclohexane to remove all nonnetwork components. The samples were then cut using a circular punch to fit into a 14-mm sample vial and stored in the cyclohexane at a temperature of approximately 5°C in a refrigerator. Before the start of each imaging experiment, the samples were dried in a vacuum for 24 h to completely remove the protonated solvent (cyclohexane). The sample pieces were then transferred to the vial and re-swollen in deuterated chloroform (CDCl_3) for 36 h to an equilibrium swelling.

^1H -NMR imaging was performed on a Bruker MSL 300 spectrometer at a resonance frequency of 300.14 MHz. The mini-imaging probe was used, in which the 14-mm sample vial was set for the examination. The images are 128×128 pixels with a spatial resolution of $78 \mu\text{m}$ per pixel. A spin-echo method^{17,18} was used to acquire the images. The 90° pulse was Gaussian and lasted for $2000 \mu\text{s}$. The 180° broad-band pulse was $90 \mu\text{s}$

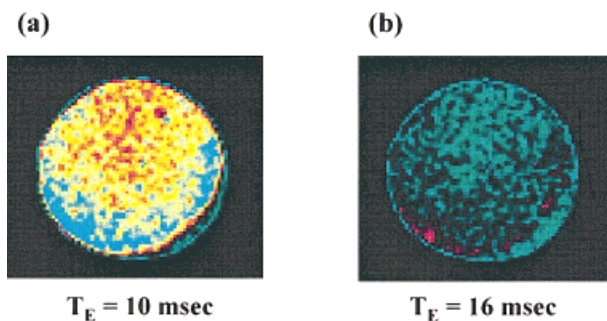


Figure 3 Spin-echo images of *cis*-polyisoprene cured with 15 phr of carbon black: (a) $T_E = 10$ ms; (b) $T_E = 16$ ms.

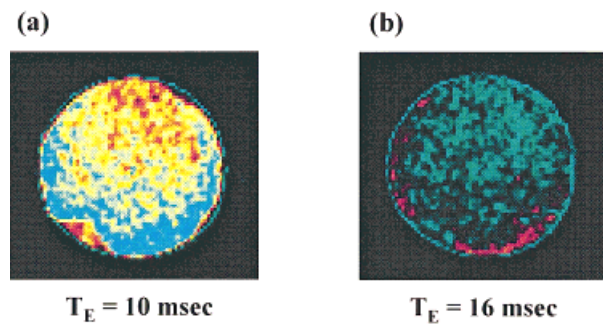


Figure 4 Spin-echo images of *cis*-polyisoprene cured with 30 phr of carbon black: (a) $T_E = 10$ ms; (b) $T_E = 16$ ms.

in length. The slice thickness was approximately 1 mm. A four-cycle phase routine was employed and 32 scans for each of the 128 points were accumulated with a recycle delay (T_R) of 2 s. For each sample, two experiments were performed where the echo times (T_E) were set to 10 and 16 ms. All images were transferred to an SGI/UNIX station using an Ethernet network and the data was processed by using Tripos IMAGE software.

The histograms of the pixel intensities were scaled to a common level determined by the unfilled sample (CB0) with a T_E of 10 ms. The average pixel intensities inside the largest square region of the rubber image were calculated automatically by the software package. The average intensity (I) of the pixels from the swollen rubber region is expressed as

$$\langle I \rangle = \langle k \rangle \exp(-T_E / \langle T_2 \rangle) \quad (5)$$

where $\langle k \rangle$ is a constant related to the average ^1H spin density ($\langle N(\text{H}) \rangle$) and $\langle T_2 \rangle$ is the average T_2 relaxation time in the rubber region. By solving

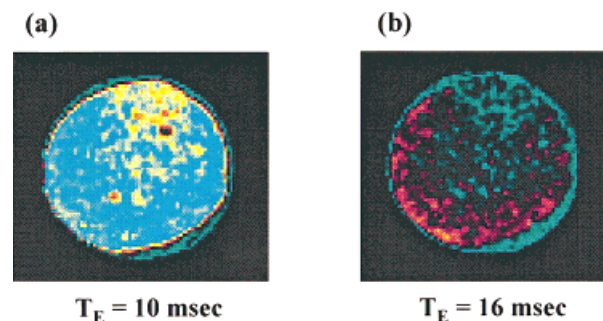


Figure 5 Spin-echo images of *cis*-polyisoprene cured with 50 phr of carbon black: (a) $T_E = 10$ ms; (b) $T_E = 16$ ms.

Table I Average Intensity of the Pixels Inside the Rubber Region

Sample	Average Intensity ($\times 10^5$)	
	$T_E = 10$ ms	$T_E = 16$ ms
CB 0	9.31	5.49
CB 15	9.24	5.09
CB 30	9.70	5.16
CB 50	10.79	5.73

the two equations with two sets of the data of the $\langle I \rangle$'s and T_e 's, the $\langle k \rangle$ and $\langle T_2 \rangle$ for the individual formulation are obtained. The T_2 relaxation times for each pixel are then calculated by eq. (6):

$$T_2 = T_E / (\ln \langle k \rangle - \ln I_p) \quad (6)$$

where I_p is the intensity of the individual pixel. The T_2 profile of the each formulation (number of pixel versus T_2) is obtained by applying eq. (6) to the intensity histogram (number of pixel versus signal intensity) directly obtained from the images.

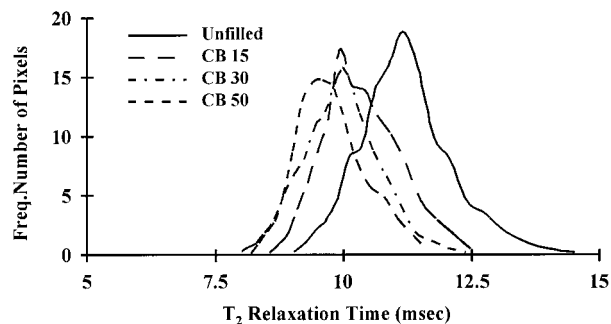
Equilibrium-swelling measurements were performed to determine the swelling ratio of the four vulcanizates in a good solvent. Sample pieces with known weights were soaked in benzene for 3 days in the dark. After the sample reached equilibrium, the weight of the swollen sample was recorded. The swelling ratio, Q , was determined by the following equation:

$$Q = (\rho_r / \rho_s) \times (\text{wt of solvent in network}) / (\text{wt of network}) \quad (7)$$

where ρ_r is the density of the rubber ($=0.91 \text{ g/cm}^3$) and ρ_s is the density of the solvent ($=0.879 \text{ g/cm}^3$).

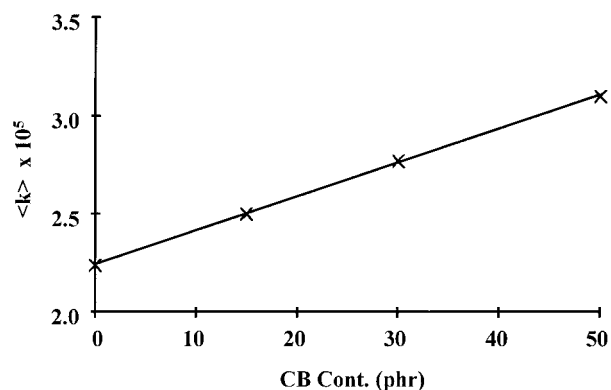
Table II Constant, $\langle k \rangle$, and Average T_2 Relaxation Time, $\langle T_2 \rangle$

Sample	$\langle k \rangle (\times 10^5)$	$\langle T_2 \rangle$ (ms)
CB 0	2.24	11.38
CB 15	2.50	10.05
CB 30	2.77	9.53
CB 50	3.10	9.49

**Figure 6** Distribution of T_2 relaxation times for four *cis*-polyisoprene vulcanizates.

RESULTS

The $^1\text{H-NMR}$ spin-echo images of the swollen *cis*-polyisoprene cured with 0, 15, 30, and 50 phr carbon black are shown in Figures 2–5, respectively. (a) in Figures 2–5 represents the spin-echo image obtained with a T_E of 10 ms, while (b) represents the image recorded with a T_E of 16 ms. The red color corresponds to high intermediate, and the darker, to low values. The average intensities of the pixels inside the rubber region for the eight images are summarized in Table I. For each formulation, the average pixel intensity decreases with increase in the T_E from 10 to 16 ms. The constant, $\langle k \rangle$, and average T_2 relaxation time, $\langle T_2 \rangle$, for the four swollen rubber samples calculated from eq. (5) using the paired data (two $\langle I \rangle$'s and T_E 's) are presented in Table II. The $\langle T_2 \rangle$ of the swollen vulcanizates decreases with increase in the carbon black content. The $\langle k \rangle$ increases with the black loading level. The distribution profiles of the T_2 relaxation time for the four samples, obtained from eq. (6), are illustrated in Fig-

**Figure 7** The constant, $\langle k \rangle$, versus carbon black content for the four *cis*-polyisoprene vulcanizates.

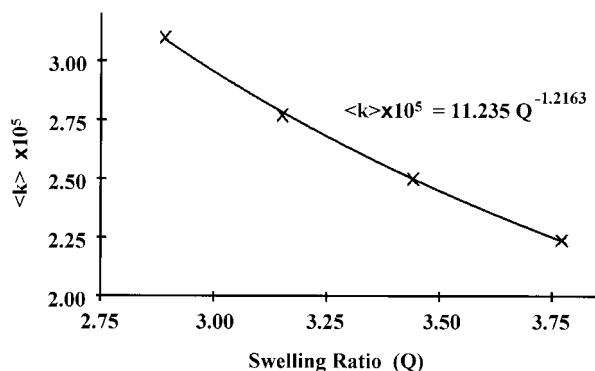


Figure 8 The constant, $\langle k \rangle$, versus swelling ratio for the four *cis*-polyisoprene vulcanizates.

ure 6. The curves shifted toward the smaller T_2 times as the black loading level increases and are slightly narrow due to the experiment limitation on T_2 .

DISCUSSION

The decrease in the T_2 relaxation times with the black content is due mainly to the restricted molecular mobility induced by adsorption of the rubber on the carbon black. The average T_2 time, $\langle T_2 \rangle$, decreases from 11.38 ms (CB0) to 10.05 ms with 15-phr carbon black. The $\langle T_2 \rangle$ further decreases when the black loading level is increased from 15 to 30 phr and from 30 to 50 phr, but the magnitude of the changes in the $\langle T_2 \rangle$'s are not as large as in the initial loading (0–15 phr). Typically, the degree of the filler-reinforcement effect is proportional to the filler content within the moderate loading level. The observations of the $\langle T_2 \rangle$'s here postulate that the inhomogeneity of the network structure induced by the black incorporation also contributes, to some extent, to the decreases in the $\langle T_2 \rangle$'s as well as the major contribution of the restricted molecular mobility.

Figure 7 illustrates the values of the constant, $\langle k \rangle$, as a function of carbon black content. Since the scaling factor for the signal gain has been fixed during the signal acquisition in the NMRI measurements, the $\langle k \rangle$ is mostly related to the spin density in the swollen rubber samples. The linear relationship between the $\langle k \rangle$ and black content postulates the growing of the spin density in the swollen rubber as the black loading level is increased. This trend can be simply interpreted as an effect of the degree of swelling for the individual samples, which is considered to linearly

decrease with increase in the black content. The relationship between the $\langle k \rangle$ and the swelling ratio for the four samples is illustrated in Figure 8. As expected, the $\langle k \rangle$ decreases with increase in the swelling ratio; however, the relationships between these two variables are not precisely linear. The deviation of the curve from the linear trend, especially at the region with lower swelling ratio, may suggest the slight contribution of the displacement effect of the black incorporation, that is, a few spaces in the network structure are displaced by the black particle, which results in the decrease in the spin density for the swollen rubber network in the filled vulcanizates.

The distribution of the T_2 relaxation times, seen in Figure 6, becomes narrower as the black loading level increases. Because of the lack of the pixel resolution in the images, no evidence is found for the existence of the two distinct T_2 relaxation times in carbon black-filled vulcanizates although it has previously been found in the ^1H -pulsed NMR studies.^{14–16} Rather, these imaging results suggest a distribution of T_2 relaxation times which narrows as the carbon black content increases.

CONCLUSIONS

The average amount and the distribution of the spin–spin relaxation time, T_2 , in the swollen *cis*-polyisoprene cured with a varying content of HAF–HS carbon black and fixed contents of curing agents have been successfully obtained by ^1H spin–echo NMR imaging. It is suggested that two spin–echo NMRI experiments employing different spin–echo times (T_{E1} and T_{E2} , $T_{E2} < 2T_{E1}$) are more suitable for the determination of the T_2 relaxation times in the sample which has short T_2 times than using the multiecho experiment. It is observed that the overall and average T_2 relaxation times of the swollen rubber vulcanizates decreases with increase in the carbon black loading level. It is shown that there are at least four factors governing the intensity of the images in the swollen, filled rubber vulcanizates as well as the NMR parameters (T_1 , T_2 , T_R , and T_E): (1) ^1H spin density, (2) inhomogeneity of the network structure, (3) degree of swelling in the sampling solvent, and (4) displacement effect of the carbon black.

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REFERENCES

1. J. L. Koenig, in *Spectroscopy of Polymers*, American Chemical Society, Washington, DC, 1992, Chap. 11.
2. R. A. Komoroski, *Anal. Chem.*, **65**, 1068 (1993).
3. B. Blumich and P. Blumler, *Macromol. Symp.*, **87**, 187 (1994).
4. S. R. Smith and J. L. Koenig, *Macromolecules*, **24**, 3496 (1991).
5. M. R. Krejsa and J. L. Koenig, *Rubber Chem. Technol.*, **64**, 635 (1991).
6. X. Zhao, Y. M. Shen, Y. R. Du, and C. H. Ye, *Appl. Magn. Reson.*, **5**, 39 (1993).
7. M. A. Rana and J. L. Koenig, *Macromolecules*, **27**, 3727 (1994).
8. C. Chang and R. A. Komoroski, *Macromolecules*, **22**, 600 (1989).
9. R. J. Roe, D. D. Davis, and T. K. Kwei, *Bull. Am. Phys. Sci. Ser. 2*, **15**, 308 (1970).
10. S. Kaufman, W. P. Slichter, and D. D. Davis, *J. Polym. Sci. A*, **2**, 9, 829 (1971).
11. J. O'Brien, E. Cashell, G. E. Wardell, and V. J. McBrierty, *Rubber Chem. Technol.*, **50**, 747 (1977).
12. T. Nishi, *Rubber Chem. Technol.*, **51**, 1075 (1978).
13. H. Serizawa, T. Nakamura, M. Ito, and K. Tanaka, *Polym. J.*, **15**, 201 (1983).
14. V. R. Hannold, F. McCattery, and B. A. Mrowca, *J. Appl. Phys.*, **25**, 1219 (1951).
15. W. P. Slichter, *Rubber Chem. Technol.*, **34**, 1574 (1961).
16. V. I. Kvlividze, S. G. Klimov, and N. N. Lezhnov, *Vysokomolekul. Soedin.*, **9**, 1924 (1967).