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Solid-state C-13 and H-1 NMR imaging studies of the accelerated-sulfur cured high vinyl polybutadiene

Rana, Muhammad Akmal, Ph.D.

Case Western Reserve University, 1993
SOLID-STATE C-13 AND H-1 NMR IMAGING STUDIES
OF THE ACCELERATED-SULFUR CURED HIGH VINYL
POLYBUTADIENE

by

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Submitted in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

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January, 1993
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GRADUATE STUDIES

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SOLID-STATE C-13 AND H-1 NMR IMAGING STUDIES OF THE ACCELERATED-SULFUR CURED HIGH VINYL POLYBUTADIENE

Abstract

by

MUHAMMAD AKMAL RANA

Solid-state $^{13}\text{C}$ NMR and $^{1}\text{H}$ Imaging methods have been used to follow the progress of accelerated-sulfur vulcanization of unfilled high vinyl polybutadiene. Different NMR pulse sequences have been used to characterize the micro-network structures present in the bulk of the finally cured rubber samples. These studies were made as a function of formulation and processing variables. The time-resolved, integrated data have been used to interpret the development of the crosslinked rubber network. Mono-sulfidic as well as the residual accelerator fragments were differentiated from the polysulfidic crosslinks in a finally cured material.

Dynamic studies of these network structures were made using spin-spin relaxation ($T_{2e}$) measurements. The activation energies calculated based on $T_2$ were used to verify different carbons, directly attached to the sulfur atoms. A swelling method based on
Flory-Rehner's equation was also used to determine the crosslink densities and the number-average molecular weight between the nodal junctions in different formulations.

Different spatially resolved structural features have been detected in the swollen samples using NMR imaging method. The voids, no-voids and other impurities were differentiated on the basis of magnetic susceptibility differences. Cyclohexane was used as a swelling solvent to probe the morphological defects in these materials.

The $T_2$-weighted images were used to evaluate the crosslink densities in different samples. The quantitative estimations based on histogram was also employed to determine the average volume per crosslink region. The contrast based on H-1 spin-density or mobility was highlighted in $T_2$-weighted images. The variations were found to be closely related to variation in both concentration and mobility of the network.
DEDICATION

This work is dedicated to my parents for their patience, understanding and encouragement shown me during my graduate career.
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The author wishes to express his gratitude to Prof. Jack L. Koenig for his guidance, encouragement and motivation throughout the course of this research.

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CHAPTER I

DEVELOPMENT AND APPLICATIONS OF NUCLEAR MAGNETIC RESONANCE IMAGING IN LIQUIDS AND SOLIDS
BACKGROUND:

Until the discovery of X-rays by Roentgen in 1895 our ability to view the spatial organization of matter depended on the use of visible light with our eyes being used as the primary detector. X-ray vision gave us the capacity for the first time to see inside of biological and synthetic materials. In 1973 Lauterbur [1] reported the first reconstruction of a spin-density map using nuclear magnetic resonance (NMR). In the same year Mansfield and Grannell [2] independently demonstrated the Fourier relationship between the spin density and the NMR signal acquired in the presence of a magnetic field gradient. NMR has grown rapidly from its inception in 1946 into a sophisticated technique with many applications in both the medical and material sciences.

NMRI, like its predecessor, x-ray computed tomography (CT), which was introduced by Cromack [3] in 1963, is a computer based imaging modality that displays the body in thin tomographic slices. X-ray CT requires ionizing radiation, whereas NMRI is based on apparently safe interactions between radio waves and hydrogen nuclei in presence of a strong magnetic field. NMRI differs from the CT images in several respects, such as the relaxation effects on NMR image pixel
intensities and on the choice of pulse sequence parameters \([4,5]\). The NMRI signal is directly proportional to the magnetization.

Proton NMRI allows non-invasive examination of the spatial distribution of mobile nuclear species in biological structures, especially water, and provides the incentives to exploit this method in the detection of tumors, lesions and other tissue formations characterized by anomalous distribution of these species and by imageable differences in their relaxation parameters.

The physical mechanism is based on the resonant absorption of radio frequency power by nuclear spin precession in a magnetic field. The resonant frequency (Larmor frequency) is proportional to the magnetic field strength, where the proportionality constant is the gyromagnetic ratio.

With the continuous development in NMRI, it is now possible to do physiological studies of different systems. NMRI has acquired the capability of imaging different materials both at the macroscopic and microscopic level. This article will review the subject of NMRI from the perspective of its present and potential future applications in the study of organic
INTRODUCTION:

Conventional NMR spectroscopy is classically used to determine the different chemical structures in the sample, but it cannot be used to locate the position of the stimulated nuclei in the sample. NMR imaging is a method in which a stimulating signal is encoded so that an image can be reconstructed to show the spatial distribution of the nuclei.

Numerous examples now can be cited demonstrating the use of NMRI for studying the spatial distributions and the relaxation characteristics of mobile species in an appropriate material. A variety of techniques for directly imaging component nuclei in solid organic and inorganic materials has been explored.

The x-ray CT technique has a resolution which is limited by the beam collimation, whereas NMRI can in principle achieve a resolution considerably finer than 0.1 mm. In the case where resolved elements are smaller than 0.1 mm, this method of imaging may be termed as microscopic. The range of applications of NMRI at the microscopic level is enormous and, as yet, largely unexplored. While its resolution is
considerably coarser than optical and electron microscopy, magnetic resonance microscopy offers several major advantages such as, its potential for studying dynamical processes in living systems which gives special importance, and its sensitivity to the rotational and translational mobility of the molecules, which is the basis of some unique applications in material science and especially in polymer science.

Another advantage of NMRI over the CT technique is that one must scan in the plane of gantry, i.e., axial or semicoronal in the CT method, whereas in NMRI one is able to acquire the image directly in any plane that is axial, sagittal, coronal or oblique. The pixel intensity in CT reflects electron density while in NMRI it reflects the density of the mobile hydrogen nuclei modified by the chemical environment (the relaxation times). This NMR imaging method increases the versatility of NMR to include a determination of spatially resolved structures [6-9].

The images produced by this technique are determined by optimizing various parameters. Extrinsic parameters are operator-controlled parameters such as field strength, acquisition technique (projection reconstruction and Fourier transform), acquisition signal (spin echo and free induction decay), matrix
choice (spatial resolution), slice thickness, gap between slices, field of view, orientation of imaging plane, radio frequency pulses, pulse sequence timings and the shape of radio frequency pulse, whereas the intrinsic parameters are proton spin density, spin-lattice relaxation time ($T_1$), spin-spin relaxation time ($T_2$), chemical shift and flow velocity. Thus signal intensity is a complex interplay of these various parameters. A good quality image can be acquired if these parameters are well controlled and optimized.

The application of NMRI to network polymer structures is a relatively new technique [10-20]. Elastomers are particularly suitable for study by imaging because of the narrow linewidth due to their extensive re-orientational motion above the glass transition temperature. In order to study the molecular mobility of the polymer chain the NMRI technique provides a sensitive probe of the molecular state of the nuclear environment through short range magnetic dipolar interactions [21]. In particular the spin-spin relaxation times ($T_2$) are sensitive to low frequency motions in the network. So the heterogeneity of the rubber matrix can be directly estimated by $T_2$ measurements and can be related to macroscopic
mechanical properties. In the case of elastomers the quality of the image is highly dependent on chain segmental mobility ($T_2$) and echo time ($T_E$).

When material systems contain protons with different chemical shifts the NMR image often exhibits, such chemical shift artifacts as shadows, which complicates the image interpretation and evaluation. Currently, several techniques have been used to solve the chemical shift problem in the images. One of techniques used is to construct an image with a pre-selected chemical shift of the sample either locally or globally. Another common technique is to suppress the chemical shift artifacts mechanically using an increased gradient field strength so that the broadening due to the chemical shift falls within the pixel resolution.

**BASIS OF NMR IMAGING:**

Atomic nuclei exhibit the property of spin and so possess a magnetic moment aligned along the axis of the spin. This spin is quantized and characterized by a spin quantum number $I$. The nuclei primarily used in NMR are those with $I = 1/2$. When this nuclear spin is placed in a magnetic field, it will attempt to line up
with the field. Figure 1 shows the precession of a spin in a magnetic field and how it behaves when irradiated with shaped radio frequency (rf) pulses. The nuclear moments take one of the two states: parallel (low energy) or anti-parallel (high energy) to the magnetic field.

The distribution of high and low energy nuclei is random and is calculated using Boltzmann's equation,

\[ \frac{N_d}{N_u} = \exp \left( \frac{hf}{KT} \right) \]
\[ = 1 + \frac{hf}{KT} \]

Where \( N_d \) represents the number of nuclei in the lower energy state, \( f \) is the frequency of radiation and \( N_u \) indicates the spin population in high energy state. If \( hf \ll KT \), where \( K \) is Boltzmann's constant and \( T \) is temperature, then

\[ N_{\text{eff}} = N_d - N_u = N_u \frac{hf}{(2KT)} \]

The net magnetization is described as \( M_o = \mu N_{\text{eff}} \).

Where \( \mu \) is magnetic moment and \( N_{\text{eff}} \) is the number of effective nuclei. In all imaging techniques the general objective is to measure the NMR parameters (spin density and spin relaxations) as a function of their spatial co-ordinates. In figure 2 the projection of a series of simple homogeneous geometric spin
distributions in a horizontal magnetic gradient field is described. The projection changes with the shape of the object.

**NMR IMAGING METHOD:**

In the conventional NMR method the sample is placed in a homogeneous magnetic field $H_0$, so that all the chemically equivalent spins experience the same field and hence precess at the same Larmor frequency $\omega_0$ given by the following expression:

$$\omega_0 = \gamma H_0$$

where $\gamma$ is the gyromagnetic ratio. In contrast to NMR spectroscopy, NMRI involves placing a sample in a non-uniform magnetic field [22]. The homogeneous magnetic field is modified with a system of gradient magnetic coils to generate linear gradients on the order of few gauss/cm. This non-uniform field encodes different regions of the sample linearly with different NMR frequencies. Because the magnetic field is varied in a known manner at specific positions within the sample the frequency of the NMR signal indicates the spatial position of the resonating nuclei.

$$\Delta \omega_z = \omega_z - \omega_0 = \gamma G_z Z$$
Where, $G_z$ is magnetic field gradient in z-direction. When a linear magnetic field gradient is applied across the static field, the precession frequency of the spin becomes dependent on the position $z$, as given by the following,

$$\omega(z) = \gamma (H_0 + G_z z)$$

This frequency provides a one-dimensional projection of the distribution of spins along the gradient axis. This is expanded to two-dimensions by applying a gradient orthogonal to the first. The second gradient causes the spins to dephase faster depending on the gradient intensity. When the second gradient is incremented from negative to a positive value, the collection of echoes from each increment is then Fourier transformed to produce a two dimensional image. This process is known as phase encoding.

A three-dimensional image can be obtained by using a third gradient in the final orthogonal direction in conjunction with a shaped rf pulse which permits slice selection. The gradient produces a frequency dependence of the spins along the third direction. The shape of the radio frequency (rf) pulse (Gaussian or Sinc) determines its excitation bandwidth. The slice position $z$, is related to the gradient strength $G_z$ and the offset frequency ($01$) of the pulse by the following
equation:

\[ Z = \frac{01}{\gamma G_z} \]

The slice thickness \( \Delta Z \) is determined by the bandwidth of the selective pulse, \( \omega \), and the gradient strength as given in following equation:

\[ \Delta Z = \frac{\omega}{\gamma G_z} \]

FIELD GRADIENTS:

The controlled use of magnetic field gradients is explained by Lauterber [1] according to whom the strength of the main magnetic field is a linear function of the co-ordinates of the position. If \( B \) (the magnetic field) acts in the \( z \) direction and varies linearly in the \( x \) direction, then

\[ B_z = B_0 + x G_x \]

\[ \omega_1 = \gamma B_z = \gamma B_0 + \gamma x G_x \]

where \( \omega = 2 \pi f \)

The magnetic fields are generated by means of quadrupole coils that are designed to introduce a linear gradient along the static magnetic field and in the perpendicular direction. A stepped gradient can be produced by adjusting the current. The direction of this gradient field depends on the direction of the
current flowing in the wire, and the magnitude of the gradient field is inversely proportional to the distance from the coil. The three gradient coils x, y and z fit co-axially in the bore of the magnets. Figure 3 illustrates the use of a field gradient to produce an NMR spectrum representing a projection of spin density onto the x-axis.

VOLUME SELECTION TECHNIQUE:

The volume selection procedure in NMRI is the division of three elements \( n_x, n_y \) and \( n_z \), also called voxels into the three cartesian axis. Each of these elements is sampled by a separate experiment and this sampled volume can be moved electronically throughout the sample. Because the two coils are perpendicular, the planes selected are also perpendicular and the planes intersect in the line that is sampled. Once the plane has been selected by the z-gradient, the x and y gradients are employed to determine the location within the selected xy plane of the spin density and relaxation parameters.
IMAGE RECONSTRUCTION TECHNIQUES:

The same type of principle is used in x-ray computerized tomography. Two types of image reconstruction methods are used,

i) Fourier Imaging (FI)
ii) Filtered Back Projection (FBP)

FI requires the sequential application of orthogonal gradients. In contrast, the FBP involves the simultaneous application of gradients. Figure 4 explains the projection-reconstruction method in which a linear magnetic field is applied to the sample so that the resonance frequencies of the nuclear spin take on a spatial dependence. The resulting NMR spectrum represents a projection of nuclear spin densities perpendicular to the direction of the applied gradients. The figure also shows the experimentally obtained projections taken at $0^\circ$, $45^\circ$, $90^\circ$, $135^\circ$ and $180^\circ$.

A two dimensional image is a plot of intensity versus the spatial distance and in this a number of different projection or views of the sample distributed evenly around a circle or a semi-circle fashion are collected and combined to form 2-D images.
SELECTIVE EXCITATION TECHNIQUE:

In NMRI, selective excitation requires a radio frequency pulse that rotates the magnetization of only selected voxels within the slice of the object from along the z-axis to the y-axis. A gradient coil that permits the sample to be separated into a series of slices or planes is activated. Each slice has the characteristic resonant frequency, except for the central plane which varies slightly from the resonant frequency of the static magnetic field because of the superimposed gradient field.

A tailored radio frequency pulse (sinc function) is applied, so only protons in the thin slice perpendicular to the applied gradient will resonate with the frequency corresponding to

$$\omega = \gamma ( B_0 + G_x z )$$

The mean frequency of the pulse determines the position of the slice, and the range of frequencies in the pulse determines the thickness of the slice. Immediately after excitation, the y-gradient is switched off and a read-out gradient is applied in the x-direction while the free induction signal is collected. The schematic diagram is shown in figure 5.
ADVANCED IMAGING TECHNIQUES:

a) HARDWARE ORIENTATED SPECIAL FACILITIES:

Different coil geometries for cylindrical shapes are given in figure 6, where a) indicates the solenoidal coil producing the $B_1$ field parallel to the cylinder axis, b) describes the orientation of the same coil in a conventional electromagnet, c) is a saddle type coil producing a $B_1$ field perpendicular to the cylinder axis, d) is the orientation of the saddle type coil and e) is the preferred configuration of the four coil spherical system.

As NMR imagers have no moving parts, synchronization of operation to body movement is easy in principle. A signal from a transducer monitoring the patient is used to initiate excitation of the sample and data acquisition of the projection of the data set.

b) RECONSTRUCTION METHODS AND TECHNIQUES:

Most images are presented after a magnitude reconstruction, in which the gray scale is proportional to $(x^2 + y^2)$, where $x$ and $y$ are the real and imaginary component of the voxel signals after completion of the
Fourier transform. This section examines phase mapping, and its potential clinical applications. In order to enhance the contrast effects, a self-diffusion method is also used. The approach used is directly analogous to the method used by Hounsfield for X-ray CT scanners. A detailed explanation is given in the following section.

**FACTORS AFFECTING THE NMR SIGNAL:**

The factors which generally affect the NMR signal are explained as follow,

**CHEMICAL SHIFT:**

The electrons surrounding the nucleus slightly shield the applied magnetic field, so that the nucleus sees a lower field and hence its Larmor frequency is reduced. This effect is known as the chemical shift and is measured in parts per million (ppm).

**RELAXATION PROCESSES:**

Different spin-lattice relaxation times (T₁) and spin-spin relaxation times (T₂) in the voxels of a heterogeneous sample can be exploited to develop contrast in the NMR images. Once the nuclei are
excited, the $M$ eventually revert to $M_0$ in the equilibrium state. This reversion occurs by two distinct relaxation processes, each characterized by its own time constant. Longitudinal relaxation ($T_1$), also known as the spin-lattice relaxation, normally detects local molecular dynamics (in MHz range).

Transverse relaxation ($T_2$), also known as the spin-spin relaxation, is sensitive to the molecular chain motions in the KHz range. These two decay time constants can be incorporated into the equation of the motion of magnetization:

$$\frac{dM_x}{dt} = (M_yB_z - M_zB_y) - M_x/T_2$$

$$\frac{dM_y}{dt} = (M_zB_x - M_xB_z) - M_y/T_2$$

$$\frac{dM_z}{dt} = (M_yB_x - M_xB_y) - (M_z - M_0)/T_1$$

$T_1$ is longer than $T_2$ because only $T_2$ is affected by frequency components in the local magnetic field for which $\omega = 0$. $T_1$ is more frequency dependent than $T_2$ because of $T_2$'s sensitivity towards low frequency as shown in figure 7-a. Figure 7-b indicates changes in the $T_1$ and $T_2$ relaxation components with the change in the distance from the molecular surface.
THE SPIN-ECHO (SE) SEQUENCE:

The spin echo technique is the most common pulse sequence applied in NMRI. Since the intensity of the radio photons of NMR is approximately 11 orders of magnitude weaker than the x-ray photons of CT, each NMR pulse sequence must be repeated to increase the signal to noise ratio. A $90^\circ$ pulse flips the existing longitudinal magnetization (which is traditionally oriented along the z-axis) into the transverse xy plane. Whenever transverse magnetization is present it rotates at Larmor frequency and generates an NMR signal. The electrical signal is induced by the recovery of $M$ and is called a spin echo or Hahn echo [23]. The main use of spin-echo sequence is to measure $T_2$.

$90^\circ - \tau - 180^\circ - \tau - \text{echo}$

Figures 8-a and 8-b indicate the pulse sequences for spin-echo and slice profile imaging, respectively. In case of figure 9-a the formation of a spin echo is reviewed in the rotating frame, whereas 9-b shows the behavior of spins during a Carr-Purcell-Meiboom and Gill (CPMG) pulse sequence.
THE INVERSION RECOVERY (IR) SEQUENCE:

The 180° pulse inverts the initial magnetization \( M_0 \) to \(-M_0\), and \( M \) will then return to \( M_0 \) exponentially with a time constant \( T_1 \). \( M \) will remain aligned along the \( z \)-axis unless disturbed, and hence will not induce any signal in the receiver coil. A 90° following the 180° turns the magnetization \( (M_z) \) into \( xy \) plane. This causes an induction signal directly proportional to \( M_z \). For an accurate measurement of \( T_1 \), the experiment is repeated using a range of different \( T_1 \) recovery times, and the measured signal amplitudes are fitted to the best exponential curve.

MULTI-ECHO METHOD:

Spin-echo can also be used as a series of echoes. A non-selective 180° radio frequency pulse is applied at a time \( \tau \) after the acquisition. A second echo is produced at a time \( 2\tau \) after the second 180° pulse and is equal to \( 2T_2 \). This cycle is repeated until the desired number of echoes is acquired. The intensity of echoes decreases gradually because of the \( T_2 \) decay. A \( T_2 \) image can be calculated from the multi-echo scan without substantially increasing the scan time. The multi-echo spin CPMG pulse sequence is described in figure 10, using \( n \) repetitions of the refocusing hard
pulses.

**CONTRAST IN IMAGES:**

Contrast in NMRI depends on both (a) Material-specific, that includes spin density, spin-lattice relaxation and spin-spin relaxations; (b) Operator-specific, which includes pulse sequences, pulse delay, repetition time and are in conjunction with the intrinsic material parameters, which dictates the appearance of the final image.

Application of paramagnetic compounds such as Gadolinium diethylene pentacetic acid (Gd-DTPA) [24] is very helpful in generating contrast in NMR images. The effect of the contrasting agent is to reduce the relaxation time constants. Different types of contrast agents are used, e.g., molecular O₂, bulk susceptibility agents (Fe₃O₄) etc.
IMAGING OTHER THAN PROTONS:

In addition to protons, several other important nuclei have been used to generate images, including $^{13}\text{C}$, $^{19}\text{F}$, $^{23}\text{Na}$, $^{31}\text{P}$, $^{15}\text{O}$ and $^{39}\text{K}$. The problem with using nuclei other than the protons for imaging applications is that these nuclei have a much lower inherent NMR sensitivity. For example 0.4% of $^{31}\text{P}$ is present as compared to $^{1}\text{H}$ so the overall sensitivity is reduced by factor of $3 \times 10^4$. The problem faced in acquiring images of nuclei other than the protons are low sensitivity, long $T_1$ and low natural abundance. Table I depicts the nuclear sensitivities and the properties of various elements of biological interest. It also describes their spin, gyromagnetic ratios, natural abundance and their relative NMR sensitivities.
INTRODUCTION:

Another potential application of NMRI is in solid materials to detect the different inhomogeneities present in the bulk. The problem with imaging solid material is mainly due to the large NMR spectral linewidths (10-100 KHz) as compared to liquids (< 10 Hz). A number of techniques have been evolved to overcome the linewidth problems.

Because of the much broader line resonance in solids, it is rather difficult to acquire an image with a 3-30 μs T1 relaxation time. In liquids the line narrowing is through rapid random isotropic motions, which are not averaged to zero in solids. Another contributing factor in solids is the chemical shift anisotropy.

To achieve the same resolution in solid-state or liquids requires a gradient strength of 1500 mT/m as compared to 0.15 mT/m in liquids. This gradient strength is achievable but a number of problems are associated with it. These include size of the sample over which a uniform gradient of this strength can be generated, difficulty in switching large field
gradients in a very short time and thus a large gradient field spreads the signal consequently increases the bandwidths and decreases the signal to noise (S/N) ratio.

**LINE-BROADENING MECHANISMS:**

Line broadening in solid materials occurs due to strong interactions involving mainly the dipole dipole interactions, chemical shift anisotropy (CSA) and quadrupole interactions. The ranges of these line broadenings are,

- Dipole-dipole interactions. \( (10 - 100 \text{ KHz}) \)
- Chemical shift anisotropy. \( (10 - 100 \text{ ppm}) \)

The quadrupole applies to nuclear spins with \( I > 1/2 \) and spin coupling factors can be neglected similarly because they are too weak to observe in solids.

**a) DIPOLAR INTERACTIONS:**

Dipolar interactions occurs through the space coupling of one magnetic spin with the local field of its neighbors. The intrinsic magnetic moment associated with each nuclear spin dipole exerts a great influence on its neighbors via the magnetic field
produced by this dipole on the dipole moments of remote spins. The interaction depends on the magnitude and orientation of the magnetic moments. Polymers with a glass transition temperature well above room temperature have thermal motions with a magnitude greater than the dipolar linewidths, so that only the isotropic average needs to be considered. The term \((1-3\cos^2\theta)\) in this case is averaged to zero, thus rendering the dipolar broadening in liquid to zero.

In case of solids where the inter-nuclear vectors have fixed orientations, the lineshape is dominated by dipolar interactions. The effective dipolar Hamiltonian would be non-zero in this case, resulting line broadening. Figure 11 shows the graphical representation of a dipolar coupled spin pair. The \(z\)-axis is defined to be parallel to the static field \(B_0\), and \(\theta_{ij}\) and \(\phi_{ij}\) are the polar and azimuthal angles of the internal vectors, respectively.

b) CHEMICAL SHIFT INTERACTIONS:

The magnetic field observed at a nuclear site is generally the static magnetic field \((B_0)\). In condensed matter the nuclei are surrounded by atomic or molecular electron clouds which interact with the nuclear spin angular momentum. These interactions are
characteristic of the local electronic environment, resulting in a shift in the resonance frequency away from the Larmor conditions.

In liquids, rapid isotropic molecular reorientation takes place and it averages to its scalar invariant, resulting in only the isotropic part of the chemical shift interaction being observed. In solids an induced shielding effect can be observed due to the rotational anisotropy in molecular orbitals. This phenomenon is known as the chemical shift. The magnitude of the rotational anisotropy is greater in solids as compared to liquids.
SOLID-STATE IMAGING METHOD:

The solid state imaging method falls into one of two categories. Attempts has been made to overcome the inherent broadlining by using a large magnetic field gradient and attempt to perform some form of line narrowing, thereby reducing the need for such large field gradients have also been made. One of the major problems is to reduce the dipolar couplings, and relatively few methods deal with the chemical shift anisotropy. The following are the different techniques used to acquire the NMR image of a solid material.

a) CONSTANT TIMING IMAGINGS.

i) Phase encoding method [25].

This method is used for removing all line-broadening mechanisms by sampling the free induction decay at a fixed time during a spin evolution period. It is not a true line-broadening process, but it masks the the line-broadening effect in the spectrum.

ii) Solid echo method [26-34].
An improved version of the Emid and Creyghton method was made using solid echoes phenomenon. This dipolar-decoupling sequence leads to an improvement in resolution by increasing the time available for spatially encoding the signal. The solid echo sequence is given by $90^\circ_x - \tau - \beta_\phi$, where $90^\circ_x$ represents a 90° pulse rotating about $x$ direction in the rotating frame, $\tau$ is the delay and $\beta_\phi$ is the pulse rotation of angle $\beta$ about $\phi$ axis.

The solid echo has been used by Saoilenko et al. [32] to image a PMMA disk achieving a resolution of 100 $\mu$m.

b) CONVOLUTION BACK PROJECTION METHOD:

Suits and White [35] developed a method similar to Lauterbur’s to obtain a two dimensional image of ($^{23}$Na) ion motions in solid ionic conductors. The graphical representation of a back projection image experiment is given in figure 12.

This method is used to image the single crystal sample of solid $\beta$-alumina dipped in molten KNO$_3$, where one-to-one substitution of sodium ions by potassium ions was obtained. The technique enables us to estimate the inter-diffusion co-efficient of Na$^+$ and K$^+$.
ions in β-alumina. The application of this technique is limited to cases where the NMR linewidth is already small.

Another application of this method is to detect the impact defects in NaCl crystals [36] by making use of the breakdown of its cubic crystal symmetry at the area of impact.

c) **MULTIPLE PULSE METHODS.**

A very efficient dipolar decoupling method can be made in which the spins in the solid would act as in liquids, undergoing rapid thermal motions [37,38]. WAHUHA[38] was the first multiple pulse sequence introduced in 1968 to reduce the effect of the static dipolar Hamiltonian. It consists of repeated cycles (τ–90°_x–τ–90°_y–τ–90°_y–τ–90°_x–τ) with signal sampling at the end of each cycle [39,40].

i) **MREV–8 cycle for Imaging.**

Eight 90° degree pulses with phase toggling states have been used in this method. A linear (chemical shift and gradient off-set) and bi-linear (dipolar) operators are switched through the states [2,41,42]. The MREV–8 pulse sequence has also been used in the
context of solid-state imaging using a surface coil [43] to provide position-dependent line narrowing. This multiple pulse sequence is very successful in reducing the effect of the dipolar Hamiltonian, often narrowing dipolar lines by a factor of 100. The pulse sequence is described in figure 13-a, in which a multiple pulse sequence of eight 90° pulses is shown, and in figure 13-b the pulse sequence is given in a standard pulse diagram. The NMR signal is phase encoded during $t_1$, and frequency encoded during $t_2$. Data are only sampled during $t_2$, resulting in a two-dimensional data set which can be Fourier transformed to give an image.

Miller and Garroway suggested a 32-pulse cycle to average all zeroth order Hamiltonians, except the gradient Hamiltonian, to zero. This method involves the oscillating gradient, with a period equal to the cycle time [44-49]. In the case of the second averaging method one serious problem encountered in multiple pulse line narrowing experiments is the off resonance dependency of the linewidth [50-54].
d) **MAGIC ANGLE SAMPLE SPINNING (MAS):**

If the sample is spun about an axis inclined to the polarizing field, the dipolar and other interactions could be suppressed in such a way that the spatial part becomes time dependent with zero average value. Andrew and Lowe [55,56] showed for the first time how these interactions were suppressed by spinning at an angle of 54.74° at a frequency greater than the linewidth to zero average.

Another important reason for using magic angle spinning is its effect on the chemical shift Hamiltonian. The first attempt was made by Corey [57] to use this angle in solid-state imaging. Magic angle spinning in a dipoles coupled spins whose internuclear vectors are inclined at an angle $\Theta_{ij}$ to $B_0$ spun with frequency $\omega$ about an angle $\alpha$ with respect to $B_0$ as shown in figure 14.

MAS has been applied with considerable success to imaging the elastomers in which the dipolar linewidth is already motionally narrowed. It has an advantage over multiple pulse methods in that anisotropic chemical shifts are also removed.
e) **COMBINED MULTIPLE-PULSE AND MAS:**

Combined rotation and multiple-pulse spectroscopy (CRAMPS) was also proposed by Haeberlon and Waugh [37] but was not practically demonstrated until 1977. The advantage of combining MAS with the multiple-pulse sequence is that the larger dipolar interaction can often be removed by a multiple-pulse line narrowing sequence, where magic angle spinning speeds would not suffice [58-61].

f) **ROTATING-FRAME MAGIC ANGLE:**

i) Lee-Goldburg Method:

A further technique to reduce the homonuclear dipolar interaction, which also involves the concept of a magic angle spinning, is rotating frame magic angle line narrowing. This technique was originally developed by Lee and Goldburg [62] as shown in figure 15.

ii) Field modulating selective spin imaging:

Wind and Yannoni [63,64] presented a method for imaging solids by modulating the Bo field in such a way that a magic angle condition is established in a rotating frame. This magic angle line narrowing
condition is established for a particular frequency offset, and for specific values of the radio frequency amplitude and modulation frequency. Signal is thus preferably collected from the part of the sample resonating in the region $\Delta \omega$,

$$\Delta \omega = \omega_0 - \omega$$

g) **IMAGING OF DILUTE SPINS BY POLARIZATION TRANSFER:**

The solid state imaging techniques developed so far have concentrated primarily on the imaging of abundant species such as $^1\text{H}$ and on the removal of homonuclear dipolar coupling terms in the Hamiltonian.

The low intensity broadlines resulting from such an interaction can be enhanced using double resonance cross polarization from $I$-spin (equilibrium magnetization) to $S$-spin (where $I=^1\text{H}$ and $S=^{13}\text{C}$) during preparation, and by decoupling the $I$ spins during evolution and detection.

Enhancement of dilute spin magnetization by cross-polarization has been used to obtain simple profiles of $^{13}\text{C}$ spin density and also chemically resolved $^{13}\text{C}$ profiles [65-68]. Figure 16 shows the basic cross polarization sequence and it is most effective if the conditions provided by Hartman-Hahn
are met. Despite the polarization enhancement of $^{13}$C magnetization, these techniques are still quite insensitive and require extensive signal averaging. Another problem is the generation of two simultaneous radio frequency fields in the sample. This problem can now partially be solved by using the double tuned probe.

A dynamic nuclear polarization (DNP) technique can also be used to transfer polarization from an abundant nucleus to another one [69]. The same technique was reviewed by Abragam and Goldman [70]. By using the DNP and cross polarization with high power heteronuclear dipolar decoupling during evolution and acquisition Maciel and Davis [69] were able to generate $^{13}$C images with a spatial distribution of paramagnetic impurities.

h) **MULTIPLE QUANTUM COHERENCE IMAGING:**

In pulse Fourier Transform methods only a single quantum coherence can be observed directly. However, higher order quantum coherence exists in coupled spin systems but can only be observed indirectly by their effect on observable single quantum coherences (SQC). The general scheme for observing multiple quantum coherence (MQC) is to prepare the desired coherence by a series of a suitable radio frequency pulses, and to
allow the MQC to evolve for a variable time $t_1$, which converts the MQC back into an observable SQC for detection during $t_2$.

Many methods available for the transformation of SQC to MQC and vice versa have been reviewed [71-73]. The potential use of high order of MQC for enhancing the resolution of solid-state images has been demonstrated by Garroway [74] and co-workers.

Figure 17 shows the pulse sequence used to obtain multiple quantum profiles. Another method of imaging solid objects has been successfully employed by Cotrell [75], which has several advantages over the multi-pulse line narrowing. This includes a simple method which requires a single rf pulse and shape. The radio frequency pulse synchronized to zero field gradient, so the strength of the rf pulse exceed the linewidth of the sample. In order to improve the signal to noise ratio, the bandwidth of the receiver can be reduced to match the range of the frequencies imposed on the sample by the field gradient. Another significant advantage of this technique is that the data acquisition is continuous.
APPLICATIONS:

Nuclear magnetic resonance imaging of liquid and solid materials is a technique of non-destructive testing (NDT), for which the range of experimental methods available to material and bio-scientists is currently experiencing rapid growth. Initially, NMR imaging was regarded more as a supplementary technique than a competitive one. With the rapid development of different pulse sequences and newer imaging software, it is now said to rival CT tomography as a clinical tool in medicine. The other diagnostic techniques in medicine are X-ray CT, ultrasonic imaging, electrocardiography (ECG) and positron emission.

The spatial mapping and contrast capabilities of NMR imaging have created a natural incentives for exploiting this technique in studying several classes of materials. Literature reports have accumulated in recent years citing the successful application of NMR imaging to a variety of studies involving medical and physical sciences. Morphological studies typically rely on the signal distributions of NMR images acquired from the protic solvents and the direct proton imaging technique using deuterated solvents.
MEDICINE :-

The high gyromagnetic ratio and the natural abundance of the proton makes it the dominant nucleus to study by the NMR Imaging method. Water experiences an inter- and intera-molecular interactions from the neighboring protons, causing fluctuation, as it diffuses in rotational and translational motions. The rotation correlation time $\tau_c$ for bound water ($10^{-8}$ s) is different from that of free water ($10^{-12}$ s). In bound water the $\tau_c$ leads to reduce both $T_1$ and $T_2$ unless the correlation time for dipolar function is of the order of Larmor period ($10^{-9}$ s).

Solid biomaterials, including bones, teeth, skin (collagens) and arteries (elastin), were also imaged to diagnose the abnormalities in these samples. NMR imaging has also been used to determine the Young's modulus of the carotid arteries of the human heart. The elasticity of the carotid artery derives largely from the structural proteins. Using stroboscopically sampled micro-NMR imaging, a variation in the arterial cross section for the entire heart cycle was also mapped. The dimensional changes were correlated with the absolute blood pressure to determine Young's modulus. These results were in excellent agreement with the value measured for the transverse modulus of
an excised artery.

**DIFFUSION** :-

Besides enabling detection of the size and locations of different flaws in the bulk of the sample, NMRI methods can also be used to do diffusion studies in order to determine the diffusion path lengths of solvent molecules. The basis for this technique lies in the fact that molecular diffusion leads to the attenuation of the signal intensity in spin-echo images [76]. A multicomponent diffusion of a mixture of acetone and methanol into bis(phenol-A polycarbonate) was also demonstrated [77]. The study of cyclic sorption–desorption of PMMA rods was made using methanol [78]. The rates of absorption, desorption and diffusion in bulk polymer systems were observed to provide an important basis for predicting their engineering tolerance and mechanical properties.

The other important diffusion related applications include water in nylon 6-6 [11], methanol into PMMA [79] and toluene in polystyrene [80]. Imaging can also be used to study the ingress of solvents into vulcanized rubber, which shows a case II type diffusion [81,82]. Flow velocity, diffusion kinetics in wood [83,84], and uptake of penetrants in polymer rods were
also monitored using the NMR imaging method. Case II diffusion arises from the competition between the osmotic pressure caused by driving the solvent involved, and the internal stresses arising from the swelling producing a sensitive force.

**COMPOSITES :**

In composite materials the different voids and other inhomogeneties were detected to improve the processibility and serviceability. Water has both a short term plasticizing effect and the potential for causing long term degradation in these materials. The diffusion of water and other organic solvents was studied [11,19].

**ELASTOMERS :**

Because of their inherent narrow linewidths, elastomers have been the subject of most of the early NMR images of solid materials [10-20]. Both filled and non-filled elastomers were studied in detail to detect the different spatial inhomogenieties and morphological discrepancies in the bulk. $T_2$ decay is an important parameter for determining the quality of an image. Because of the space existing between chains in elastomers, the segments are relatively free to
reorient, leading to the relaxation behavior characteristic of the solution phase.

Topological network characterization in cross-linked polymers is another important area of study amenable to NMR imaging. Different network studies have been made as a function of cure time, formulating and processing variables and cure temperatures. The presence of morphological defects along with other spatial inhomogeneties was detected in the bulk of the cured sample. Fillers in the elastomers and other impurities can be differentiated on the basis of magnetic susceptibility differences [85].

Different crosslink domains were also detected using an indirect imaging method. In this method appropriate solvent was used, which acts as a physical probe. The high intensity signal corresponds to low crosslinking domains and vice versa. The morphological defects are usually detected using this approach.

Materials including both filled and unfilled cured elastomers were studied by this method [86]. Some examples include polybutadiene [8-10, 87] swollen in organic solvents, natural rubber [88], isobutyl rubber [89] and others. to detect the presence of different
flaws and other spatial inhomogeneities.

Aging (oxidative, thermal, chemical or mechanical) is another important area in the vulcanized rubber material which influences the mechanical properties of the polymeric materials. NMR imaging is used to detect different aging processes in the elastomers.

The NMR images of elastomers (PVA and Nylon 6-6) were also acquired at higher temperature by Jezzard [90] and co-workers. The high temperature partly reduced the dipolar and chemical shift anisotropies due to the increase in thermal motions.

**QUANTITATIVE METHOD** :-

A successful attempt has been made to perform a quantitative analysis of TMTD cured cis-polybutadiene [9]. The analysis was made based on a pixel by pixel interpretation of crosslink densities. A model approach has also been used to correlate the network density measured by the swelling method and the values calculated using histograms of the T1 weighted images. Investigations of a similar nature have been reported in application to the model network polyethylene oxide and polydimethylsiloxane samples [91].
The calculation of relaxation parameters such as spin-lattice relaxations ($T_1$) and spin-spin relaxations ($T_2$) of NMR images was also made by Liu [92] and co-workers. A method was developed to compute a pure spin density image from the weighted $T_1$ and $T_2$ images.

$T_1$ normally increases with the field strength, whereas $T_2$ essentially remains constant. The $T_2$ weighted image is the one in which the contrast in the image is dependent upon the characteristic $T_2$ values. The relaxation parameters are used to understand the chain dynamics, which are directly related to the crosslink density.

$T_2$ contrast provides a high degree of sensitivity to slow motions; its multi-exponential relaxation makes it complex in analysis. As an alternative, the $T_1p$ relaxation technique was developed, which is dependent on the low frequency spectrum of molecular motions, but is generally single exponential in character.

**FOAMS** :-

Another application in foam industries is presence of different flaws and air bubbles is very important to determine the quality of these products. NMR imaging was also used to detect these defects [93], using water
as a physical probe for these defects.

POLYMER BLENDS :-

The compatibility of polymer blends can also be studied using the NMR Imaging method. The study of the composition of tire composites and elastomer blends was made by Sarkar [85] et. al. Multi-slice and a three-dimensional technique have also been applied to verify the compatibility of different monomers in styrene-butadiene rubber (SBR) materials. The difference in intensity is also characterized on the basis of magnetic susceptibility differences, whereas the presence and dispersion of fillers (carbon black) was also detected in elastomeric systems, which overall influence the macroscopic mechanical properties.

The ability of NMRI to permit non-destructive two- and three-dimensional investigation of different commercially important materials suggests the potential use of this technique for quality control.

ADHESIVE SYSTEMS :-

The use of NMRI techniques for non-destructive evaluation (NDE) of adhesives and adhesive joints was reported by Nieminen [20,94-96] and co-workers.
Relaxation parameters \( [92] \) (\( T_1 \) and \( T_2 \)) are very helpful in investigating the curing process in different systems. The interface study was one of the important areas explored using NMR imaging study for epoxy adhesive joints \([95]\) to monitor the cure pattern.

Another important contribution has been made \([97]\) in studying aluminum-epoxy interfaces. Both anodized and untreated aluminum were used to monitor the cure pattern. The anodized aluminum surface inhibits the curing of epoxy. The imaging results showed that the sample was simply-connected cure in the anodized surface, which indicates a lack of curing agents. A clear phase separation could be seen in the sample. In the case of the untreated aluminum the accelerated cure of epoxy resulted in a random type of curing; in other words the enrichment of curing agents throughout the sample.

**CERAMICS** :-

The utility of NMRI is not only in determining flaws and porosity, but in predicting the binder strength in green and partially sintered ceramic bodies \([98,99]\). In spite of all this information which can be accumulated using NMR images, it is still in an embryonic stage of development. The pore size and its
distribution in ceramic materials is very critical.

The detection of these flaws, non-uniformity in pores and binder distribution in ceramic compacts leads to an understanding of the integrity of the finally designed product. Different approaches have been used to solve this type of problem, one of which is to image a suitable (filler) fluid into the pores, while the other includes the direct imaging of the organic binder. The fate of binder can also be determined after the pyrolysis (de-polymerization, oxidation etc.) of these materials.

OTHER APPLICATIONS :-

When the gradient strength is not strong enough to suppress the chemical shift effect, it is possible to apply a numerical deconvolution technique to remove the chemical shift artifacts. The deconvolution technique was developed [20] by combining the Fourier self-deconvolution and the Wiener filtering methods. This technique was applied to get the image of a crosslinking agent during the curing process [7]. The image with chemical shift was interpreted, which demonstrated how the spatial information was distributed in more than one signal. The dispersion of polyurethane coatings and the effect of water on this
dispersion were also studied. The increase in crosslinks significantly improved the resistance to water. The different voids, flaws, glue line with thickness of less than 100μm, and other spatial variations were detected in the epoxy adhesive systems. The curing of epoxies as a function of temperature and time was monitored using NMR imaging.

Another important development of conventional NMR imaging techniques to acquire an image of solid object has been explored by Cory [100] and co-workers. In this method, a multi-pulse line-narrowing sequence is introduced which averaged homonuclear dipolar couplings. The biggest advantage of this method is that it can be easily implemented on most existing micro-imaging instruments. At present the only restriction applied is on the size of the object. It is hoped that a similar type of experiment will allow a wider range of potential users to explore the possibility of solid state NMR imaging.

The NMR imaging technique can also be applied in the area of the paper industry (to determine the moisture in the paper), the food industry, the oil exploring field, botanical studies, agricultural and pharmaceutical applications. The disintegration of tablets in water and different pH solution was studied
by this method.

The application of NMRI to plant systems is quite recent. Water distribution in the plants gives useful information about the morphology of the system. The susceptibility effects provide useful contrasts to study different phenomena in plants. The applications related to the food industry based on the distribution of oil, water and other species during drying, ripening and cooking [101].

The introduction of small molecules as markers in porous materials provides a useful means to investigate the morphology of pores and the presence of different voids in polymer composites. Among mineral rocks studied by this method is a variety of sandstones important to the petrochemical industries. It provides information about the distribution of oil and water in the multiple fluid phases contained in the pores [102,103].
SUMMARY:

The range of different applications that have been cited in this article constitutes only the major area of different possible applications in NMRI that have been successfully employed. The technique has been described, indicating the general categories of gradient pulse sequences useful for imaging both liquids and solid materials.

NMRI offers a variety of means for overcoming different problems encountered as a result of the line broadening mechanism. The extent of application generally depends on the nature of the material. In the case of solids, the line narrowing technique, e.g., the multiple-pulse sequence, magic angle spinning, combined multiple-pulse and magic angle spinning (CRAMPS) and magic angle spinning in the rotating frame have been used. The multiple quantum coherence imaging method already has been successfully used to reduce the line broadening in solids.

These line narrowing techniques simultaneously reduce the homonuclear dipolar broadening and chemical shift anisotropy broadening found in the current state of solid-state imaging. For larger objects a surface coil
which can be progressively moved across the sample is also used. In rigid materials, besides using the different line narrowing techniques, elevated temperature studies have also been made to acquire the images.

The major inherent limitation of NMR imaging is its sensitivity towards the nuclei other than the $^1$H and its inability to resolve its resonant signal under present conditions. $^{13}$C NMR imaging will be one of the vital additions to this method both in biomaterials and in other polymers to understand the nature of different chemical reactions and their distribution in the bulk. Another advantage is the presence of wide range chemical shifts in $^{13}$C and the absence of the homonuclear dipolar line broadening effect.

In the case of elastomeric materials both direct and indirect imaging methods were used to investigate the different voids, flaws and other spatial inhomogeneties. The magnetic susceptibility differences have also been exploited to differentiate between the void and non-void defects.

NMRI ranges from the whole human body to the microscopic level. NMR microscopy resolves the spatial domains of polymer blends to characterize the
interfacial species. The compatibility of physical blends was also determined on the basis of magnetic susceptibility differences. It generally provides the basis of the morphological analysis of composites and other materials.

The applications of NMR imaging include the range and flexibility for different types of samples. It is to be expected in future years that many new possibilities will be explored to develop this non-invasive method.
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Table I. The nuclear sensitivities and properties of various elements of biological interest. (Adapted from P. Mansfield et al., "NMR Imaging in Biomedicine", Academic Press, New York, 1982.)

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Spin</th>
<th>$\gamma$ (kHz/O)</th>
<th>Abundance (%)</th>
<th>Relative NMR sensitivity (const. field)</th>
<th>Relative NMR sensitivity (const. frequency)</th>
<th>Typical human physiological conc. of the element</th>
<th>Relative imaging sensitivity (const. frequency)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>1/2</td>
<td>4.2573</td>
<td>99.98</td>
<td>1</td>
<td>$6.4 \times 10^{-5}$</td>
<td>100 $M^*$</td>
<td>1</td>
</tr>
<tr>
<td>$^2$H</td>
<td>1</td>
<td>0.6537</td>
<td>0.02</td>
<td>$2.4 \times 10^{-6}$</td>
<td>$6.4 \times 10^{-5}$</td>
<td>100 $M$</td>
<td>$6 \times 10^{-5}$</td>
</tr>
<tr>
<td>$^12$C</td>
<td>1/2</td>
<td>1.0705</td>
<td>1.11</td>
<td>$2.5 \times 10^{-4}$</td>
<td>$2.8 \times 10^{-3}$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$^14$N</td>
<td>1</td>
<td>0.3075</td>
<td>99.64</td>
<td>$1.9 \times 10^{-3}$</td>
<td>$1.9 \times 10^{-1}$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>$^16$O</td>
<td>5/2</td>
<td>0.5771</td>
<td>0.04</td>
<td>$1.9 \times 10^{-5}$</td>
<td>$5.9 \times 10^{-4}$</td>
<td>50 $M$</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>$^19$F</td>
<td>1/2</td>
<td>4.0052</td>
<td>100</td>
<td>$8.5 \times 10^{-1}$</td>
<td>$9.4 \times 10^{-1}$</td>
<td>$4 \mu M$</td>
<td>$4 \times 10^{-8}$</td>
</tr>
<tr>
<td>$^23$Na</td>
<td>3/2</td>
<td>1.1263</td>
<td>100</td>
<td>$1.3 \times 10^{-1}$</td>
<td>1.3</td>
<td>$80 mM$</td>
<td>$1 \times 10^{-3}$</td>
</tr>
<tr>
<td>$^31$P</td>
<td>1/2</td>
<td>1.7237</td>
<td>100</td>
<td>$8.3 \times 10^{-2}$</td>
<td>$4.0 \times 10^{-1}$</td>
<td>$75 mM$</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>$^35$K</td>
<td>3/2</td>
<td>0.1987</td>
<td>93.08</td>
<td>$1 \times 10^{-3}$</td>
<td>$2.2 \times 10^{-1}$</td>
<td>$40 mM$</td>
<td>$9 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Table II. Summary of the salient points of each of the main imaging methods discussed in the text. (Adapted from P. Mansfield et al., "NMR Imaging in Biomedicine", Academic Press, New York, 1982.)

<table>
<thead>
<tr>
<th>Method</th>
<th>Dipolar line narrowing</th>
<th>CSA removal</th>
<th>rf power</th>
<th>phase stability</th>
<th>gradient strength/mT cm⁻¹</th>
<th>gradient switching times</th>
<th>receiver bandwidth</th>
<th>sample spinning</th>
<th>oscillating gradients</th>
<th>minimum T²</th>
<th>number of rf pulses/scan</th>
<th>Imaging time for 512x512 image</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin-echo</td>
<td>no</td>
<td>no</td>
<td>~100 W</td>
<td>not critical</td>
<td>~0.1</td>
<td>~200 µs</td>
<td>~2 ms</td>
<td>no</td>
<td>~2 ms</td>
<td>2</td>
<td>64xTi</td>
<td></td>
</tr>
<tr>
<td>Constant time</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) FID</td>
<td>no</td>
<td>no</td>
<td>~200 W</td>
<td>not critical</td>
<td>~1</td>
<td>~500 µs</td>
<td>~100 kHz</td>
<td>no</td>
<td>~50 µs</td>
<td>1</td>
<td>64xTi</td>
<td></td>
</tr>
<tr>
<td>(ii) Solid echo</td>
<td>yes</td>
<td>no</td>
<td>~200 W</td>
<td>not critical</td>
<td>~1</td>
<td>~500 µs</td>
<td>~100 kHz</td>
<td>no</td>
<td>~15 µs</td>
<td>2</td>
<td>64xTi</td>
<td></td>
</tr>
<tr>
<td>(a) Phase encoded</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) STRAFI</td>
<td>yes</td>
<td>no</td>
<td>~200 W</td>
<td>not critical</td>
<td>~25</td>
<td>n/a</td>
<td>~100 kHz</td>
<td>no</td>
<td>~20 µs</td>
<td>~2.32</td>
<td>64x(Ti+64x)</td>
<td></td>
</tr>
<tr>
<td>Convolution back projection</td>
<td></td>
<td></td>
<td>~200 W</td>
<td>not critical</td>
<td>~1</td>
<td>~500 µs</td>
<td>~100 kHz</td>
<td>no</td>
<td>~1 ms</td>
<td>1</td>
<td>64xTi</td>
<td></td>
</tr>
<tr>
<td>Multiple pulse</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) constant gradient</td>
<td>yes</td>
<td>no</td>
<td>~1 kW</td>
<td>very important</td>
<td>~0.1</td>
<td>~500 µs</td>
<td>~1 MHz</td>
<td>no</td>
<td>&gt;10 µs</td>
<td>~1000</td>
<td>64xTi</td>
<td></td>
</tr>
<tr>
<td>(ii) reversed gradient</td>
<td>yes</td>
<td>yes</td>
<td>~1 kW</td>
<td>very important</td>
<td>~0.1</td>
<td>~100 µs</td>
<td>~1 MHz</td>
<td>no</td>
<td>yes</td>
<td>&gt;10 µs</td>
<td>~1000</td>
<td>64xTi</td>
</tr>
<tr>
<td>Magic angle</td>
<td></td>
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<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>(i) sample spinning</td>
<td>yes</td>
<td>yes</td>
<td>~500 W</td>
<td>not critical</td>
<td>~0.5</td>
<td>~200 µs</td>
<td>~100 kHz</td>
<td>yes</td>
<td>~200 µs</td>
<td>1.2</td>
<td>64xTi</td>
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<tr>
<td>(ii) rotating frame</td>
<td>yes</td>
<td>yes</td>
<td>~500 W</td>
<td>important</td>
<td>~0.5</td>
<td>~500 µs</td>
<td>~100 kHz</td>
<td>no</td>
<td>~20 µs</td>
<td>1</td>
<td>64xTi</td>
<td></td>
</tr>
<tr>
<td>CRAMPS</td>
<td>yes</td>
<td>yes</td>
<td>~1 kW</td>
<td>very important</td>
<td>~0.1</td>
<td>~200 µs</td>
<td>~1 MHz</td>
<td>yes</td>
<td>~10 µs</td>
<td>~500</td>
<td>64xTi</td>
<td></td>
</tr>
<tr>
<td>Dilute spins</td>
<td>yes</td>
<td>yes</td>
<td>~200 W</td>
<td>important</td>
<td>~0.5</td>
<td>~500 µs</td>
<td>~100 kHz</td>
<td>no</td>
<td>~50 µs</td>
<td>~5</td>
<td>64xTi</td>
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<tr>
<td>Multiple quantum</td>
<td>no</td>
<td>no</td>
<td>~1 kW</td>
<td>very important</td>
<td>~0.5</td>
<td>~500 µs</td>
<td>~100 kHz</td>
<td>no</td>
<td>~100 µs</td>
<td>~150</td>
<td>64xTi</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. (a) Precession of a spin in a magnetic field, (b) precession of the spin magnetization in a spherical spiral during irradiation, (c) the motion of (b) in the rotating frame and (d) the motion of $\mathbf{M}$ in the rotating frame when the main field is in error by $\Delta B_0$. 
Figure 2. Projection of a series of sample homogeneous geometric spin distributions in a uniform horizontal magnetic gradient.
Figure 3. Illustration of the use of field gradient to produce an NMR spectrum representing a projection of spin density onto the x-axis.
Figure 4. The projection reconstruction method in which a linear magnetic field gradient is applied to the sample so that the resonance frequencies of the nuclear spins take on a spatial dependence. The figure shows an experimentally obtained projection taken at 0°, 45°, 90°, 135° and 180° from a test phantom. (Adapted from Jack L. Koenig, "Spectroscopy of Polymers", ACS, Washington, 1992.)
Excitation of nuclei in selected region

Figure 5. The selective excitation scheme in the selected region, as described in the text.
Figure 6. The transmitter coil geometries for a cylindrical sample. (a) A solenoidal coil producing a $B_1$ field parallel to cylinder axis, (b) orientation of (a), (c) a saddle type coil producing a $B_1$ field perpendicular to the cylinder axis, (d) its orientation and (e) the preferred configuration for a four coil spherical system.
Figure 7. (a) Effect of increasing measurement frequency on the spectral density for a model proton and (b) effect of frequencies on T1 and T2 rates when compared with distance from the molecular surface.
Figure 8. (a) The pulse sequence for the spin-echo method and (b) the slice profile imaging sequence. (Adapted from Jack L. Koenig, "Spectroscopy of Polymers", ACS, Washington, 1992.)
Figure 9. (a) Describes the formation of spin echo viewed in the rotating frame and (b) represents the behavior of spins during a CPMG sequence.
Figure 10. The multi-echo CPMG pulse sequence using \( n \) repetitions of the refocusing hard pulses.
Figure 11. Graphical representation of a dipolar coupled spin pair, where the z-axis is parallel to the static field \( B_0 \), and \( \theta_{ij} \) and \( \phi_{ij} \) are the polar and azimuthal angles of the internuclear vector.
Figure 12. Graphical representation of a back projection imaging experiment. Projections are obtained for incremented values of $\phi$ between $0^\circ$ and $180^\circ$. The gradient projection angle is determined by the relative gradient values in the x and y directions.
Figure 13. (a) The MREV-8 multiple-pulse sequence consisting of eight 90° pulses with phases x, y, -x or -y. (b) Multiple pulse sequence used to obtain the images.
Figure 14. The schematic diagram of magic angle spinning showing a dipolar coupled spins whose internuclear vector is inclined at an angle $\theta_{ij}$ to $B_0$ and are spun with a frequency $\omega_r$ about an angle inclined at $\alpha$ with respect to $B_0$. 
Figure 15. Effective Zeeman field ($B_{\text{eff}}$) in the rotating frame seen by the spin off-resonance by ($\omega_0 - \omega$) to a transmitter pulse of field $B_1$, as used in Lee-Goldburg experiment.
Figure 16. The basic cross polarization pulse sequence. (Adapted from Jezzard et al., Prog. NMR spec., 23, 1, 1991).
Figure 17. The pulse sequence used to obtain multiple-quantum profiles. Period I indicates the preparation period using multi-pulse cycle; II represents the linear combination of MQC's for an incremented time $t_1$, III indicates the refocusing effect of period I and $z$-component magnetization of a sample during IV.
CHAPTER II

SOLID STATE C-13 NMR STUDIES OF SULFUR ACCELERATED VULCANIZED HIGH VINYL POLYBUTADIENE.
INTRODUCTION :-

High resolution solid state $^{13}$C FT-NMR is a well established technique [1-3] to determine the microstructures in polymer systems. The previously published papers of this series [4-13] have established the utility of this method for the study of crosslinked elastomers. The solid state $^{13}$C FT-NMR spectroscopic method has potential to identify and quantify the molecular network species in rubber vulcanizates as a function of formulating and processing variables. In this work the characterization of the microstructures of high vinyl polybutadiene rubber (BR) and the changes associated with curing have been investigated as a function of accelerator to sulfur ratios and the curing time.

The processing characteristics and the mechanical properties of high vinyl BR are strongly influenced by the presence of different microstructures and their distribution. During vulcanization, the formation of a three dimensional network takes place by the development of polysulfidic and monosulfidic crosslinks. The monosulfidic crosslinks have better chemical stability and reversion character than the
polysulfidic linkages. The rubber network is more resistant to deformation for higher levels of crosslinking. Hence modulus and hardness increase monotonically with the crosslink density.

In the oscillating disc rheometer (ORD), the torque required to oscillate the rotor is monitored as a function of cure time (Figure 1). Rheogram studies show that all the samples reported here are cured to the equilibrium level, which is the point where the rate of vulcanization becomes equal to the rate of reversion. Changes in the type and level of accelerator affect the cure rate, viscosity and scorch time. Viscosity and scorch time can be determined from the early portion of the curve, while the effect on cure rate and the relative modulus can be determined from the crosslinking and plateau region of ORD curve respectively.

The development of accelerator [14-19] not only focussed on a fast cure rate but also a subsequent increase in the induction period of the vulcanization process. The accelerator N-ter-butyl benzothiazole sulfenamide (TBBS) used in this study belongs to a class which exhibits high cure rates and longer induction periods, consequently prevents pre-vulcanization. The tert-butyl group in this case
induces steric screening which prolongs the induction period.

The three systems studied were conventional, semi-efficient and highly efficient, formulated with accelerator to sulfur ratios of 0.19, 1.0, and 4.54, respectively (Table 1). The influence on the mechanical behaviour of a rubber vulcanizate is affected by the selection and the balance among the sulfurlating species and auxiliary agents (ZnO, stearic acid and etc.,) of its cure formulations.

The mechanistic and kinetic aspects of vulcanization reactions leading to the formation of different active sulfurlating complexes and ultimate crosslinked species have been studied by various groups [20-23]. It is the intent of the present work to expand the information base which has accumulated to date. The basis of this work relies on previous network composition studies of sulfur cured [10] and TMTD [12] cured high cis 1,4 polybutadiene.
EXPERIMENTAL :-

The high-vinyl polybutadiene used in this work is commercially available under the trade name of NIPOL BR-1245. The samples were mixed in a Brabender with the accelerator (TBBS) and other ingredients (activators, stabilizers, etc.) according to ASTM standards. The formulated samples were cured using a template in a temperature-controlled hydraulic press under a pressure of 2000 psi at 150 °C for various lengths of time. Thin sheets of approximately 1.5 mm thickness were made and small discs were cut and stacked in the NMR spinner made up of zirconium oxide.

The solid state $^{13}$C FT-NMR spectroscopy was performed at 75.5 MHz on a Bruker 300-MSL spectrometer. Magic angle spinning was employed to obtain all spectra. All the samples were spun between 3.5 to 4.0 KHz at a temperature of 300 °K. The spectral width was 20,000 and 8K data points were collected for each spectrum. The delay time used to acquire the different spectra was 5.0 s, which is approximately five times greater than the longest $T_1c$ so that the longitudinal magnetization of all carbons reached equilibrium before the start of the next scan. Each GHPD (gated high
power decoupling) spectrum is the sum of 15000 transients.

A curve fitting program was used to measure the peak intensities and the total area under the curve. All the spectra were individually baseline corrected and scaled so that the integrated areas are normalized to a standard value. Cross polarization (CP) pulse sequence was also used because of its high sensitivity towards rigid structures. The CP-MAS experiment was performed with an acquisition time of 205 ms and contact time of 1 ms. The CP-MAS spectra used were the sum of 10,000 transients.

The crosslink densities of the three samples were determined at ambient temperature by the using equilibrium swelling method, [24,25] using cyclohexane as a swelling solvent. The number average molecular weight between the physical crosslinks $M_n(\text{phys})$ was determined by using the Flory–Rehner equation [24].

The Distortionless Enhancement by Polarization Transfer (DEPT) pulse sequence [26] was also employed to determine the number of proton attached to each carbon. The sample was spun at 3.7 KHz at a temperature of 60 °C. Each DEPT sub-spectrum is the sum of 4000 transients. These spectra were obtained by
using 7.0 $\mu$s, 90° carbon pulse and 10.3 $\mu$s 90° proton pulse. The repetition time used in this experiment was 5 seconds.
CHEMICAL SHIFT CALCULATIONS

For chemical shift calculations, one starts with a model compound to identify the different resonances. The shielding rules are empirical in origin but have proven to provide a good starting point for the assignments of different microstructures. Chemical shifts of different structures, expected from the sulfuration at the α and β positions, were calculated using this approach. These structures were derived from the basic cis, trans and vinyl units and their possible association with the sulfur and accelerator fragments [7,22]. The additivity constants used were the averages of the constants given in Sadtler guide to $^{13}\text{C}$ NMR spectra [27] and the constants derived in our laboratory based on sulfur derivatives of the 2-methyl-2-pentene [7,22] given in Table II. The values derived from sulfurated products of 2-methyl-2-pentene were selected to apply to 1,4 diene structures. These compounds are the closest structural analogues to BR sulfuratated at α-olefinic sites for which accurately known $^{13}\text{C}$ chemical shift information is available.
The detailed chemical shift calculation for different possible structures (shown in figure 2) are described in table III. The observed chemical shifts for cis olefinic and aliphatic carbons appeared at 128.1, 28.0 and 25.1 ppm, while for the trans at 130.5 and 32.6 ppm (Fig. 4). The vinyl units which are approximately 70% of the total polymer sample, appear at 115.0 and 143.0 ppm for =CH₂ and =CH⁻ carbons respectively and for the aliphatic carbons at 41.4, 39.3 and 34.6 ppm.

In figure 2, structures I, II and III exemplify the variety of cyclic intramolecular crosslink species, which have been observed in model olefin studies. The methylenes of structure (S1S) not adjacent to the double bonds were assumed to have a uniform base shift of 29.1 ppm by analogy with the model compound 1,9 decadiene [27]. The base chemical shift listed in this work for the methylene of cyclic structures are close to those reported in the literature [28]. In reviewing the calculated chemical shifts summarized in tables II and III, it is evident that considerable overlap and redundancy is expected to occur among the resonances of methylene carbons situated at β and γ position to sulfur.
RESULTS :

In this section part (a) describes the results associated with the study of vulcanizates cured at different accelerator to sulfur ratios at 300 °K, while part (b) deals with the effect of changes in the network microstructures as a function of cure time. The solution $^{13}$C NMR spectrum was acquired for pure TBBS using CDCl$_3$ as a solvent and is shown in figure 3.

Part a:--

CURED AS A FUNCTION OF ACCELERATOR/SULFUR RATIOS.

The $^{13}$C (GHPD) NMR spectra of high-vinyl BR acquired with different accelerator to sulfur ratios are shown in figure 4. The spectra were integrated, and the total area of each spectrum was divided by its corresponding sample weight to calculate the weight percent.

The equilibrium swelling method [24] was used to determine the crosslinking densities of the three samples (Table IV). The number average and weight average molecular weight of original high vinyl polybutadiene is 136,000 and 146,000 g/mole and it was
determined by using GPC method. The poly-dispersity for this sample was calculated to be 1.07, while the number average molecular weight between the physical cross-links \( M_{n_{\text{phys}}} \) was calculated by using the Flory-Rehner [24] equation as given below,

\[
\frac{1}{M_n \text{ phys}} = \nu = \frac{-[\ln(1-\nu_r) + \nu_r + \chi \nu_r^2]}{\rho_r \nu_0 (\nu_r^{1/3} - \nu_r/2)} \tag{1}
\]

Where, \( \nu \) is network chain density, \( \rho \) is uncrosslinked rubber density, \( \nu_r \) is volume fraction of rubber in swollen vulcanizates, \( \nu_0 \) is molar volume of the solvent and \( \chi \) is Huggin’s solvent-polymer interaction constant. The value of \( \chi \) for each sample was calculated by using Kraus [25] approach which is a linear function of \( \nu_r \) as shown below,

\[
\chi = 0.37 + 0.52 \nu_r \tag{2}
\]

The volume fraction of the rubber in the swollen vulcanizates is \( \nu_r \) and it can be calculated by using the following relationship.

\[
\nu_r = \left[ \left( \frac{\rho_r}{\rho_s} \right) \left( \frac{W_s - W_u}{W_u} \right) + 1 \right]^{-1} \tag{3}
\]

Whereas \( W_s \), represents the weight of the swollen rubber; \( W_u \), weight of the unswollen rubber and \( \rho_s \) as
solvent density. The densities of the rubber material used were 0.830, 0.886 and 0.896 g/cc for conv., sev. and ev. samples respectively. The molar volume of the cyclohexane used was 108 cc/mole while the density calculated was 0.774 g/cc. The three samples have $M_n(\text{phys})$ of 6700, 5050 and 4500 g/mole respectively. The average number of monomer units between cross-links and/or entanglements sites are 124, 93 and 84 for conv., sev. and ev. samples respectively.

These values were corrected using Kraus’ approach [25], the $M_n(\text{phys})$ for conv., sev. and ev. are 5500, 4400 and 4000 respectively. The average number of monomers per nodal junction decrease as the vulcanization progressed and these values are 102, 82 and 74 for the three formulations (Table IV).

The peak assignments made in this work are similar to ones reported in the literature [10,12,29–31] and are described in detail in table V. The aliphatic region (60–10 ppm) contains the resonances of the aliphatic methine and methylene carbons located at $\alpha$, $\beta$ or $\gamma$ position relative to the sulfur in C–S bonded structures as shown in figure 4.
Structures C1C, C1T and V1V (Fig. 2) are due to the intermolecular cross-linking and result from the substitutive sulfuration by an accelerated sulfur. Structure S1S is the saturated portion while the structure C11C represents the vicinal substituted methylene carbon adjacent to cis monomer units. The presence of vicinal and cyclic structures are less likely for accelerated compounds comparing to elemental sulfur vulcanization. Structures I, II and III exemplify the variety of cyclic intramolecular crosslink species which have been observed in the model compound studies. The basic chemical shift for cis, trans and vinyl carbons is in close agreement with Clough's [10] and Smith's [12] work as given in Table V.

In table V, resonances are reported for overlapping aliphatic region (24-44 ppm) which reflect the various mixed-configuration monomer sequences of polybutadiene. The olefinic region reveals the central cis and trans carbons (127-133 ppm) which occur in the different compositional triads. The solution $^{13}$C NMR technique [32-38] for the original rubber was also employed to resolve the different overlapped resonances in aliphatic and olefinic region.
It is reasonable to suggest that the resonance at 14.8 ppm is due to the methyl end groups (Fig. 4), which result from chain scission during the vulcanization, while the resonance at 23.3 ppm may be due to the hydrogenation of the pendent double bond of the vinyl unit. These resonances were entirely absent in the original rubber sample. The hydrogenation of the vinyl group could occur via transfer of hydride ions created by α methylenic substitution of the accelerator on neighbouring 1,4 monomer units. The intensity of this resonance increases with the increase in accelerator-to-sulfur ratio as shown in figure 4. Figure 5 represents the aliphatic region of cured and uncured CP-MAS spectra. In case of the uncured spectrum the presence of peak at 54.8 ppm is due to accelerator fragment.

Quantitative results were obtained from the GHPD spectrum of the original high vinyl BR samples. These are approximately 71.0% vinyl-1,2 units, 10.0% trans 1,4 units and 19.0% cis-1,4 units in the original rubber material. The detailed comparison of the quantitative results for the three formulations along with original rubber are demonstrated in table VI.
The results obtained from accelerated sulfur vulcanizates were compared with a vulcanizate cured with elemental sulfur. In figure 6 the aliphatic region was compared for the samples cured at 2 phr and 10 phr of elemental sulfur at 150 °C. In case of the spectrum of the sample with 2 phr of sulfur all the basic resonances were well resolved, while for the sample at 10 phr, the linewidth broadened and resulted in poor resolution. The band broadening results from the increase in overall rigidity with cure for the 10 phr sample.

Part (b):-

CURE TIME STUDIES

The development of new resonances in the vulcanizates cured at 2, 5, 10, 60 and 120 minutes are depicted in highly magnified spectra as shown in figure 7. The resonances present due to the accelerator residues start disappearing as the curing progressed and are completely absent at full cure. A resonance present at 30.4 ppm in samples cured for 2 and 5 minutes may be due to quaternary carbons of an accelerator fragment as shown in figure 3. The resonances appearing at 14.8 and 23.3 ppm, due to methyl end groups and saturation,
show an increase with the cure time.

Figure 7 depicts new peaks at 54.8, 36.3, 33.3, 30.1, 23.3 and 14.8 ppm in the aliphatic region of the samples\[19\] cured at different length of times. Of even greater interest than the resonances of carbons in the accelerator fragments themselves are the resonances of carbon in the rubber backbone to which the fragments are attached, since these resonances imply more specifically the nature of reactions which either precede or compete with the crosslink reactions.

Cis to trans isomerization is one of the events accompanying vulcanization evident even at low spectral magnification. The increase in line-width is due to two factors; (1) new resonances due to modified microstructures, and (2) the rubber becomes increasingly rigid with curing.

The DEPT sub-spectra were also depicted in figure 8 for the resonances in the aliphatic region. The different multiplicities (CH\(_3\), CH\(_2\) and CH) along with the normal spectrum (conventionally cured sample) were used to verify the different ambiguities present in the overlapped region. The DEPT results verify the peak assignments made in this work (Table V).
DISCUSSION :

The FT-NMR spectra obtained for the accelerated sulfur vulcanization system of high vinyl BR provides a wealth of valuable information for elucidating the presence of different microstructures. The kinetics of the three formulations used differ from each other but the final levels of cure are similar. The actual process of vulcanization starts after the consumption of accelerator (Figure 7). The hydrolysis of the sulfenamide in the presence of ZnO and stearic acid, results in the formation of BTH in the early stages of pre-scorch period. The TBBS reacts with water (inherent in rubber) yielding the cure accelerating MBT and BTH components. The behaviour of these intermediates are consistent with the theory of Coran [39], which proposes that the reaction of rubber with benzothiazole polysulfides is accompanied by the elimination of the MBT group. The MBT and other fragments have been successfully separated and studied by HPLC technique [40].

The vulcanization system used in high vinyl BR system favors the pathway in which the MBT is totally consumed during the first few minutes of curing. This can be verified by observing the trend of the corresponding peaks present at 54.8 and 185.02 ppm which are due to
accelerator fragments (figure 7). In the presence of rubber, TBBS, sulfur, ZnO and stearic acid, the Zn\(^{++}\) probably acts as a complexer of \(-S_X\) of the pendent \(-S_X\) groups to initiate the crosslinking.

The formation of the accelerator complex with the help of zinc stearate occurs initially followed by the formation of an active sulfurating species. The active sulfurating species may be radical or ionic in nature. This active sulfurating species then reacts with the rubber material to form a rubber bound intermediate or with persulfurated accelerator molecules forming Acc-\(S_2\)-Acc molecules.

The spectroscopic, HPLC [39] and DSC [41-44] results favor the argument that rubber bound intermediates are present in the early stages of the reaction. The next step is the formation of the polysulfidic crosslinks as observed by the resonances at 33.3 and 43.9 ppm. The process continues until all the available sulfur is consumed. Polysulfidic crosslinking reaches a maximum along with the MBT at the scorch midpoint. From conventional to an efficient system, the number of sulfur atoms progressively decreases and the average length of the crosslinks become shortened.
The complexity of the network increases with the increase in the amount of elemental sulfur and result in different cyclic and dangling structures (Figure 6). In the case of the sample cured at 2 phr of sulfur the resonance at 45.4 ppm may be due to the presence of cyclic structures (II). The sulfur cured vulcanizate may also undergo thermal oxidation at the surface of the BR sample.

Due to the presence of overlapped peaks in the aliphatic region it is not easy to determine the absolute areas of the different peaks with accuracy. The resonances present at 36.3 ppm may be due to monosulfidic cross-linking, while the resonances at 33.3 and 43.9 ppm are due to either disulfidic or polysulfidic linkages. The complex resonance pattern between 127-134 ppm is due to the sequence dependent splitting of the two olefinic carbons in central cis and trans units present in different combinations of homo and hetero-symmetric triads (ccc, ttt and ccv,ttc) and non-symmetric isolated triads (tct, vcv, etc).

The appearance of cis to trans isomerization is consistent with the view that cis to trans isomerization results from reaction sequences which require initial attack of active sulfurating agent on the rubber molecules. The decrease in overall percent
area (Table VI) of cis and trans isomers is probably due to shift in the resonance due to the presence of different crosslinks. The notable exceptions in table V are the absence of resonances present for methyl end group at 14.8 and methylene at 23.3 ppm for sulfur vulcanizations.

In figure 7, a slight decrease in intensity of the methyl group peak at 23.3 ppm for 120 minutes cure is observed when compared to 60 minutes, which may be due to overcure or reversion phenomenon. The other resonance at 23.3 ppm shows the same trend and is probably due to the methylene group resulting from saturation. The resonance responsible for the polysulfidic crosslink (33.3 ppm) decreases with cure time. On the other hand the peak responsible for monosulfidic crosslink (36.3 ppm) goes through a maximum for a fully cured sample and decreases for 120 minutes cure.

In CP-MAS spectra of uncured (formulated) and cured material, the resonance identified at 54.8 is due to accelerator fragment (Figure 5). The resonances due to TBBS start disappearing as the curing progressed. The resonance at 54.8 ppm is due to the presence of quaternary carbon of the accelerator fragments and is well resolved in the spectrum shown in figure 7.
In figure 9 the percent of total carbon corresponding to cis and trans are plotted as a function of accelerator in the three different formulations. The reaction indicates that the cis to trans isomerization increases with the amount of accelerator. Figure 10 represents the amount of mono and di/polysulfidic as a function of accelerator. The area corresponding polysulfidic crosslinks increased for conventional formulation and then decreases for sev. and ev. formulation. This indicates that with the increase in accelerator to sulfur ratios there is a lowering in the sulfur rank. In case of monosulfidic crosslinks it increases monotonically from lower to the higher accelerator level. Table VI shows the percent area of carbons associated with different chemical structures as a function of cure time.

The postulated hydrogenation of these units is supported by a noticeable decline in the area of aliphatic vinyl carbons. Reaction at the carbon 4 of a vinyl unit is not strongly favored due to the non-allylic nature of the methylene group, whereas the reaction at -CH= of the vinyl unit may be one of the sites for crosslinking. Since the system under observation comprises 70% of vinyl groups, therefore the configurational sequences of these structures are
very important in determining the sites, susceptible to attack of accelerator fragments.
CONCLUSIONS :-

In summary the solid state $^{13}$C NMR technique has proven to be a significant method for the detection of crosslinks and other structural modification which occur during the course of vulcanization reactions. The kinetics of the vulcanization reaction is relatively fast so a full account of the process is almost impossible. The use of sulfur and accelerator along with the other auxiliary agents generate a considerable amount of main chain structural modification.

It is evident from this study that in addition to the vulcanization reaction, cis to trans isomerization is the pre-dominant reaction, as was found previously in case of pure sulfur and TMTD vulcanized polybutadiene. Cis to trans isomerization reaches steady state during the early part of the reaction. A variety of stable sulfur-bonded accelerator fragments were found in the system, which reinforces the earlier proposed polar-radical mechanism. In accelerated sulfur vulcanization, the monosulfidic linkages are dominant over polysulfidic crosslinks. The chain scission and chain saturation increase with the progress in vulcanization. DEPT results verify the peak assignments made in this work.
The basic vulcanization chemistry depends on accelerator to sulfur ratios. $^{13}$C NMR measurements for an accelerated vulcanized high vinyl BR gives no evidence of cyclic and vicinal crosslink structures in the final cured material. The small change in the olefinic vinyl carbons before and after the cure verified that these pendent units do not form crosslinks, however the carbons identified as aliphatic vinyl are susceptible to react with an accelerator. The samples cured with pure elemental sulfur have more complex structures than the accelerated-sulfur network.

ACKNOWLEDGMENT:

The authors are indebted to A. B. Sullivan of Monsanto Corp., Akron, Ohio, for providing the samples and the technical assistance.
REFERENCES :


### Table I.

**HIGH VINYL POLYBUTADIENE FORMULATIONS**

(parts per hundred of rubber sample)

<table>
<thead>
<tr>
<th></th>
<th>(Conv.)</th>
<th>(Sev.)</th>
<th>(Ev.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB (high vinyl)</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>ZnO</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Elemental Sulfur</td>
<td>4.1</td>
<td>2.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Santocure NS</td>
<td>0.8</td>
<td>2.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

(TBBS)

**Curing Temperature:** 150°C

![](image)

**N-t-Butyl-2-Benzothiazolesulfenamide**

(TBBS)

PB = High vinyl Polybutadiene, ZnO = zinc oxide,
### Table II.

**SULFUR ADDITIVITY CONSTANTS FOR ALIPHATIC STRUCTURES**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>23.7</td>
<td>22.6</td>
<td>16.7</td>
<td>14.8</td>
<td>8.7</td>
</tr>
<tr>
<td>( \beta )</td>
<td>6.1</td>
<td>6.4</td>
<td>7.2</td>
<td>7.6</td>
<td>12.0</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>-2.2</td>
<td>-2.2</td>
<td>-2.3</td>
<td>-2.3</td>
<td>-1.6</td>
</tr>
</tbody>
</table>

Error = \( \pm 1.0 \) ppm
Table III.

CALCULATED CHEMICAL SHIFTS (ppm)

<table>
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<tr>
<th>STRS. CARBON</th>
<th>BASIC</th>
<th>R-SS-X</th>
<th>R-SS-R</th>
<th>R-S-X</th>
<th>R-S-R</th>
<th>R-S-H</th>
</tr>
</thead>
<tbody>
<tr>
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<td>51.7</td>
<td>50.6</td>
<td>44.7</td>
<td>42.8</td>
<td>36.7</td>
</tr>
<tr>
<td></td>
<td>28.0</td>
<td>34.1</td>
<td>34.4</td>
<td>35.2</td>
<td>35.6</td>
<td>40.0</td>
</tr>
<tr>
<td>ClT Cl</td>
<td>32.4</td>
<td>56.1</td>
<td>55.0</td>
<td>49.1</td>
<td>47.2</td>
<td>41.1</td>
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<tr>
<td></td>
<td>32.4</td>
<td>38.5</td>
<td>38.8</td>
<td>39.6</td>
<td>40.0</td>
<td>44.4</td>
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<tr>
<td>V1V Cl</td>
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<td>58.1</td>
<td>57.0</td>
<td>51.1</td>
<td>49.2</td>
<td>43.1</td>
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<tr>
<td></td>
<td>43.7</td>
<td>49.8</td>
<td>52.3</td>
<td>50.9</td>
<td>51.3</td>
<td>55.7</td>
</tr>
<tr>
<td>S1S Cl</td>
<td>29.1</td>
<td>59.7</td>
<td>51.7</td>
<td>45.8</td>
<td>43.9</td>
<td>37.8</td>
</tr>
<tr>
<td></td>
<td>29.1</td>
<td>35.2</td>
<td>35.5</td>
<td>36.3</td>
<td>36.7</td>
<td>41.1</td>
</tr>
<tr>
<td>C11C Cl</td>
<td>27.6</td>
<td>51.3</td>
<td>50.2</td>
<td>44.3</td>
<td>42.4</td>
<td>36.3</td>
</tr>
<tr>
<td>I Cl</td>
<td>39.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>53.9</td>
<td>-</td>
</tr>
<tr>
<td>II Cl</td>
<td>31.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>46.5</td>
<td>40.4</td>
</tr>
<tr>
<td>III Cl(cis)</td>
<td>29.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>46.4</td>
<td>-</td>
</tr>
<tr>
<td>C2</td>
<td>27.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>45.8</td>
<td>-</td>
</tr>
<tr>
<td>C3</td>
<td>26.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>42.0</td>
<td>-</td>
</tr>
<tr>
<td>C4</td>
<td>27.8</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>36.8</td>
<td>-</td>
</tr>
<tr>
<td>C5</td>
<td>29.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>29.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Error = ± 1 ppm

-R = cis, trans or vinyl units.
-X = ![Chemical Structure]
Table IV.

**EQUILIBRIUM SWELLING MEASUREMENTS DATA**

<table>
<thead>
<tr>
<th></th>
<th>CONV.</th>
<th>SEV.</th>
<th>EV.</th>
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<tbody>
<tr>
<td>$V_r$</td>
<td>0.17</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td>$v(10^{-5})$</td>
<td>7.46</td>
<td>9.91</td>
<td>10.9</td>
</tr>
<tr>
<td>$M_n(\text{phys})$ ($10^4$)</td>
<td>0.67</td>
<td>0.50</td>
<td>0.45</td>
</tr>
<tr>
<td>Ave. monomer units/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nodal junction</td>
<td>124</td>
<td>93</td>
<td>84</td>
</tr>
</tbody>
</table>

*Corrected values using Kraus' method*

<table>
<thead>
<tr>
<th></th>
<th>CONV.</th>
<th>SEV.</th>
<th>EV.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_n(\text{phys})$ ($10^4$)</td>
<td>0.55</td>
<td>0.44</td>
<td>0.40</td>
</tr>
<tr>
<td>Ave. monomer units/</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nodal junction</td>
<td>102</td>
<td>82</td>
<td>74</td>
</tr>
</tbody>
</table>
### TABLE V.

**COMPARISON OF PEAK ASSIGNMENTS FOR TBBS/SULFUR DEPT, TMTD AND PURE SULFUR (ppm)**

<table>
<thead>
<tr>
<th>ASSIGNMENTS</th>
<th>PRESENT</th>
<th>DEPT</th>
<th>TMTD¹</th>
<th>S²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WORK</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl (-CH₃)</td>
<td>14.8</td>
<td>14.6(CH₃)</td>
<td>14.3</td>
<td>-</td>
</tr>
<tr>
<td>Methylene(-CH₂⁻)</td>
<td>23.3</td>
<td>23.2(CH₂)</td>
<td>22.9</td>
<td>-</td>
</tr>
<tr>
<td>Cis (CV)</td>
<td>25.1</td>
<td>25.0(CH₂)</td>
<td>25.1</td>
<td>25.1</td>
</tr>
<tr>
<td>Cis CCC (-CH₂⁻)</td>
<td>28.0</td>
<td>27.9(CH₂)</td>
<td>27.6</td>
<td>27.6</td>
</tr>
<tr>
<td>TBBS-C(CH₃)</td>
<td>30.4</td>
<td>30.0(CH₂)</td>
<td>30.5</td>
<td>-</td>
</tr>
<tr>
<td>Trans (TV)</td>
<td>32.6</td>
<td>32.5(CH₂)</td>
<td>32.9</td>
<td>32.9</td>
</tr>
<tr>
<td>Cis(Di/poly S)</td>
<td>33.3</td>
<td>33.1(CH₂)</td>
<td>33.9</td>
<td>33.9</td>
</tr>
<tr>
<td>Vinyl (-CH₂⁻)</td>
<td>34.6</td>
<td>34.3(CH₂)</td>
<td>34.4</td>
<td>34.4</td>
</tr>
<tr>
<td>Mono S &lt; to trans</td>
<td>36.3</td>
<td>36.2(CH₂)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vinyl (-CH⁻)</td>
<td>39.3</td>
<td>39.2(CH⁻)</td>
<td>39.3</td>
<td>39.8</td>
</tr>
<tr>
<td>Vinyl (&gt;CH⁻)</td>
<td>41.4</td>
<td>41.2(CH⁻)</td>
<td>40.9</td>
<td>40.9</td>
</tr>
<tr>
<td>(Di/Poly S)</td>
<td>43.9</td>
<td>43.8(CH⁻)</td>
<td>43.7</td>
<td>43.8</td>
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<tr>
<td>Fragments (TBBS)</td>
<td>54.8</td>
<td>-</td>
<td>53.9</td>
<td>-</td>
</tr>
<tr>
<td>Vinyl(=CH₂)</td>
<td>114.9</td>
<td>114.6(=CH₂)</td>
<td>114.5</td>
<td>-</td>
</tr>
<tr>
<td>Cis (=CH⁻)</td>
<td>128.1</td>
<td>128.0(=CH⁻)</td>
<td>127.9</td>
<td>-</td>
</tr>
<tr>
<td>Cis - VCV, CCV</td>
<td>129.8</td>
<td>129.7(=CH⁻)</td>
<td>129.5</td>
<td>129.6</td>
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<tr>
<td>Trans (-CH=)</td>
<td>130.5</td>
<td>130.5(-CH=)</td>
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<td>130.1</td>
</tr>
<tr>
<td>Vinyl (=CH⁻)</td>
<td>143.1</td>
<td>143.0(=CH⁻)</td>
<td>142.3</td>
<td>-</td>
</tr>
<tr>
<td><strong>Error = ± 1.0 ppm</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹ Ref. no. 12, ² Ref. no. 10
Table VI.

PERCENT OF TOTAL CARBON IN DIFFERENT CHEMICAL STRUCTURES AS A FUNCTION OF CURE TIMES

(Conventional Formulation)

<table>
<thead>
<tr>
<th>Regions</th>
<th>2.0</th>
<th>5.0</th>
<th>10.0</th>
<th>20.0</th>
<th>35.0</th>
<th>60.0</th>
<th>120.0</th>
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<tbody>
<tr>
<td>CIS</td>
<td>10.0</td>
<td>8.6</td>
<td>8.5</td>
<td>9.0</td>
<td>7.2</td>
<td>7.0</td>
<td>8.3</td>
</tr>
<tr>
<td>TRANS</td>
<td>14.5</td>
<td>14.0</td>
<td>14.2</td>
<td>13.0</td>
<td>15.9</td>
<td>16.0</td>
<td>15.4</td>
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<tr>
<td>VINYL</td>
<td>70.0</td>
<td>68.2</td>
<td>65.0</td>
<td>65.0</td>
<td>64.0</td>
<td>63.8</td>
<td>64.0</td>
</tr>
<tr>
<td>POLYSULFIDIC</td>
<td>1.2</td>
<td>2.0</td>
<td>4.0</td>
<td>4.0</td>
<td>2.8</td>
<td>2.6</td>
<td>2.5</td>
</tr>
<tr>
<td>MONOSULFIDIC</td>
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<td>7.6</td>
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<td>7.8</td>
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<tr>
<td>SATURATION</td>
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Error = ± 2.0 %
Figure 1: ODR (Oscillating Disc Rheometry) response of high vinyl polybutadiene cured at different accelerator to sulfur ratios.
Figure 2: Different network structures expected for TBBS/S vulcanization of high vinyl polybutadiene.
Figure 3: Solution C-13 NMR spectrum of accelerator N-t-butyl-2-benzothiazole sulfenamide (TBBS) in CDCl₃.
Figure 4: C-13 NMR spectra of the conventional (CONV.), semi-efficient (SEV.) and efficient (EV.) using GHPD pulse sequence (x=side bands).
Figure 5: Magnified CP-MAS spectra of vulcanizates corresponding aliphatic region of cured (SEV.) and uncured (formulated) samples.
Figure 6: CP-MAS spectra of sulfur cured (using 2 phr and 10 phr of sulfur) high vinyl polybutadiene representing aliphatic region.
Figure 7: Magnified aliphatic region of the conventional system cured at 2, 5, 10, 60 and 120 minutes using GHPD pulse sequence.
Figure 8: Distortionless enhancement polarization transfer (DEPT) subspectra showing different multiplicities along with the normal spectrum of conventionally cured high vinyl PB sample.
Figure 9: Percent of total carbon corresponds to cis (o) and trans (x) carbons calculated using GHPD technique representing cis to trans isomerization.
Figure 10: Percent of total carbons specified as, monosulfidic (O) and polysulfidic (x) cured at different accelerator to sulfur ratios.
CHAPTER III

NMR-IMAGING STUDY OF CROSS-LINK DISPERSION IN
TBBS–SULFUR VULCANIZED HIGH VINYL POLYBUTADIENE
INTRODUCTION:

High resolution solid state $^{13}$C NMR has been extensively used to investigate the different microstructures and their dynamics in a crosslinked network systems [1-3]. The conventional NMR techniques determine the average signal of the bulk but do not determine the spatial distribution of structures in the polymer networks. Nuclear magnetic resonance imaging (NMRI) expands the realm of NMR to provide the spatial information for these polymer systems [4-7].

NMRI can be used to study the chemical and motional distribution of structures in polymers [4-7]. The NMRI applications include, diffusion of liquids in solids [4], absorptions[6], distribution of solid particles in liquids [5] or mobile matrices and imperfections such as voids in manufactured articles [8-17]. The main advantage of NMRI over other imaging methods is its ability to map spatially a wide variety of parameters in a non-invasive way. The crosslinked elastomeric systems yield high spatial resolution in NMRI due to the narrow proton resonances arising from the high segmental mobility when swollen in an appropriate solvent. In this study unfilled vulcanized high vinyl
polybutadiene samples swollen in both protonic and non-protonic solvents were studied.

An image of a specimen is obtained by acquiring its NMR spectrum in the presence of a large magnetic field gradient. The resonance frequency is directly proportional to the field strength, and the gradient encodes the spatial location of each spin packet in the sample [17]. Thus a 2-D image is the plot of intensity versus spatial direction.

The spread of frequencies imposed by the gradients forming the image must be larger than the spectral linewidths. In the case of the solid state, linewidths of 10–100 KHz are typical, corresponding to $T_2$ relaxation times of 3–30 μs, a value that precludes NMR imaging of rigid solids using standard gradient strengths of about 1–2 G/cm. In order to obtain high resolution images, line narrowing techniques must be applied to these experiments. These techniques include multiple pulse rotating [14,15,18–22] frame, magic angle spinning [2], solid echo [14] and heteronuclear decoupling techniques [10], multiple quantum NMR to magnify the effect of the field gradients [21], combined multiple sequences, radio frequency field gradient and incrementing the field gradient during a fixed evolution time [19]. In addition more powerful
gradients [22,23] 20-200 G/cm can also be used.

One disadvantage of using a large gradient field is that although it increases the resolution it greatly reduces the sensitivity of the technique. The signal-to-noise ratio of an NMR spectrum is inversely proportional to square root of the band width of the receiver. The other observed drawback of this technique is the appearance of chemical shift artifacts such as shadows [5] which complicate interpretation of the image.

For the study of molecular mobility of the polymer chains the NMRI technique provides a sensitive probe of the molecular state of the nuclear environment through the short range magnetic dipolar interactions [24]. In particular the spin-spin relaxation times (T2) are sensitive to low frequency motions. The change in motional heterogeneity of the rubber matrix can be directly estimated by T2 measurements and can be related to macroscopic mechanical properties [25].

The variation in T1 and T2 derives from the extent of motion of the elastomer chain segments reflecting their position relative to a site of decreased mobility such as crosslinks, filler particles or to the site of increased mobility such as swollen areas. The quality
of an image is highly dependent on the chain segmental mobility, that is, on $T_2$ and $T_1$ (spin echo time)[17].

The present work concerns the investigation of inhomogeneties in vulcanized high vinyl polybutadiene samples. These samples were vulcanized at 150 °C by using different accelerator-to-sulfur ratios along with other auxiliary curing agents. The three samples are named as conventional (conv), semi-efficient (sev) and efficient (ev) according to their formulations (Table I). The results demonstrate the ability of proton NMR to spatially distinguish structural features of cured polybutadiene samples. Single and multi echo ($T_1$ resolved) imaging techniques were also used to investigate these inhomogeneties. The crosslink density changes as a function of accelerator-to-sulfur ratios were studied at a constant temperature. All the samples were extracted with cyclohexane in order to remove the non-network components. NMR images of the swollen material probe spatial variations in the proton signal intensity of the rubber samples directly.
IMAGING METHOD:

In conventional NMR spectroscopy the protons spin precess about the static magnetic field \( H_0 \), at the Larmor frequency, \( \omega_o \), as given in equation 1.

\[
\omega_o = \gamma H_0 \quad (1)
\]

Where \( \gamma \) is a gyromagnetic ratio.

When a linear magnetic field gradient \( G_X \) is applied across the static field, the precession frequency of the spins become dependent on the position \( X \), as given in equation 2.

\[
\omega(x) = \gamma (H_0 + G_X X) \quad (2)
\]

This frequency encoding provides a one dimensional projection of the distribution of spins along the gradient axis. This is expanded to two dimensions by applying a gradient orthogonal to the first. The second gradient causes the spins to dephase faster depending on the gradient intensity. When the second gradient is incremented from a negative value to a positive value, the collection of echoes from each increment is Fourier transformed in two dimensional image and this is known as phase encoding.
A third gradient in the final orthogonal direction in conjunction with a shaped rf pulse permits slice selection. The gradient produces a frequency dependence of the spins along the third direction. The shape of the rf pulse (Gaussian or sinc) determines its excitation bandwidth. The finite bandwidth excites only a certain region of spins in the presence of the gradient. Manipulation of the selective rf pulses and the third gradient controls the position and the thickness of the slice. The slice position, \( Z \), is related to the gradient strength \( G_z \) and the offset frequency \( O_1 \) of the pulse by equation 3.

\[
Z = O_1 / \gamma G_z
\]  

(3)

The slice thickness \( \Delta Z \) is determined by the bandwidth of the selective pulse, \( \omega \), the gradient strength as given in equation 4.

\[
\Delta Z = \omega / \gamma G_z
\]  

(4)

Stronger gradients result in smaller slice thicknesses and smaller positional changes for a constant bandwidth and offset frequency, respectively. Large bandwidths and offset produce larger changes in thickness and position. A typical spin-echo pulse sequence for generating a two-dimensional image is shown in figure 1. The first line is the rf timing and it shows a selective 90° pulse and a non-selective 180°
pulse and is based on the sequence by Carr and Purcell [26] and Meiboom and Gill [27].
EXPERIMENTAL:

The sample under investigation is a high vinyl polybutadiene a product of NIPPON ZEON CO. Ltd. having the commercial name of Nipol BR-1245. This sample has approximately 70% of vinyl 1,2 polybutadiene and the rest (30%) comprised of cis and trans 1,4 polybutadiene isomers. The samples were blended on a Brabender mixer and formulated to different accelerator to sulfur ratios along with the other auxiliary agents (e.g., zinc oxide, stearic acid and etc.). The three formulations described in table I are conventional (conv), semi-efficient (sev) and efficient (ev) with accelerator to sulfur ratios of 0.19, 1.0 and 4.54 respectively. The quantities of auxiliary agents used in these formulations were unchanged.

These samples were vulcanized in a cylinder (7 mm diameter) on a hydraulic press using a pressure of 2000 psi and a constant temperature of 150 °C. These samples were cured at the above conditions for the different lengths of times and then quenched immediately by immersing in a finely powdered bed of dry ice. The cured samples were later extracted with cyclohexane overnight in a soxhlet extractor in order to remove the dispersed and sol phase materials. All
these samples were later stored in cyclohexane at a temperature of approximately 40 °F in a refrigerator. This method helps in avoiding any type of undesirable degradation reaction. Before the start of each imaging experiment the cyclohexane was removed by vacuum at room temperature to a constant weight of the rubber sample. The samples were then transferred to imaging tubes of 25 mm diameter and re-swollen by using deuterated cyclohexane. All the samples were imaged at 300 °K on a Bruker MSL-300 spectrometer at a proton frequency of 300.13 MHz. The samples were contained in a glass tube and were positioned vertically in a micro-imaging probe. The imaging probe was equipped with a saddle type rf (radio frequency) coil of 25 mm diameter. The pulse sequences used in order to obtain images are standard CPMG spin echo which is selective 90°- non-selective 180° pulse cycle with a collection of sequential echoes as shown in figure 1.

Thirty two scans per phase encoding step were signal averaged in producing each image, using 90° increment (X, -Y, -X, Y) phase cycling. Each sample was reshimmed to maintain the quality of image. A spectral width of 62,500 Hz was used in acquisition. The three images were acquired using a repetition time (TR) of 5 s and echo time (TE) of 7 ms. The field of view (FOV)
for these images are 9 x 9 mm displayed as 256 x 256 pixels. The effective pixel resolution will be 39 μm/pixel. The read out gradient was set at 10.45 G/cm and the phase encode gradient varying between -8.96 \rightarrow +8.96 G/cm in an increments of 0.07 G/cm.

For multi echo the read out gradient strength was 8.40 G/cm while the phase encoding gradient was -35.84 \rightarrow +35.84 G/cm with 256 equal increments of 0.28 G/cm. The receiver gain in this case was also held constant for all the experiments for comparison purposes. The FOV was 7 x 7 mm displayed as 256 x 256 pixels with an effective pixel resolution of 39 μm/pixel.

The crosslinking densities were determined using equilibrium swelling method for conv., sev. and ev. systems. All these studies were made at ambient temperature. The number average and weight average molecular weights of the original rubber sample were determined using GPC technique and these are 13,6000 and 14,6000 g/mole respectively. The poly-dispersion calculated was 1.07 for this material. The number average wt. between the physical crosslinks $M_n^{(phys)}$ was derived by using Flory-Rehner [28] equation as given below,

$$
\frac{1}{M_n^{phys}} = \nu = \frac{-[ln(1-V_r) + V_r + \chi V_r^2]}{\rho_r V_0 (V_r^{1/3} - V_r/2)}
$$
Where,

\[ \chi = \text{Huggin's solvent-polymer interaction constant.} \]
\[ \rho = \text{Uncrosslinked rubber density.} \]
\[ \nu = \text{Network chain density in moles of chain/g of rubber.} \]
\[ V_r = \text{Volume fraction of rubber in swollen vulcanizates.} \]
\[ V_o = \text{Molar volume of swelling solvent.} \]

The value of \( \chi \) can be calculated by using Kraus [29] approach,

\[ \chi = 0.37 + 0.52V_r \quad (6) \]

Where \( V_r \) can be calculated by using the following equation,

\[ V_r = [(\rho_r/\rho_s)(W_s - W_u/W_u) + 1]^{-1} \quad (7) \]

Where,

\( W_s = \text{Weight of the swollen rubber.} \)
\( W_u = \text{weight of the un-swollen rubber.} \)
\( \rho_s = \text{solvent density.} \)
\( \rho_r = \text{rubber density.} \)

The densities of the rubber material used were 0.830, 0.886 and 0.896 g/cc for conv., sev. and ev. respectively. The density of the solvent used was
0.774 g/cc, while the molar volume of solvent was 108 cc/mole.

The three unfilled cured samples have $M_n^{(phys)}$ of 6700, 5050 and 4500 g/mole respectively. The average number of monomer units between crosslinks and entanglement sites are 124, 93 and 84 corresponding to conv., sev. and ev samples (Table II). These values were corrected by using Kraus' method. These $M_n^{(phys)}$ are 5500, 4400 and 4000 for conventional, semi-efficient and efficient systems. The average number of monomers calculated by using this approach correspond to 102, 82 and 74 for conv., sev. and ev systems. Experimentally it has already been proven that the kinetics of the diffusion of solvent molecules for the rubbery polymers is approximately Fickian, [30–33] for which the boundary condition is the condition of constant surface concentration.

The images shown in this article were displayed on the scale from blue to red. All signal intensities are scaled on a 0–255 relative scale, where 0 corresponds to least signal and 255 to the most intense. These numbers are then translated into a color where 0 is the blue while red corresponds to 255. The other colors represent intensities between these extremes.
RESULTS:

The signal intensity in a proton image depends on the proton concentration, $T_1$ and $T_2$ relaxation times. Pure proton density images are relatively difficult to acquire, since they require long repetition times and very short spin echo times. Therefore, most NMR images are concentration maps weighted by $T_1$ and $T_2$ relaxation times. The NMR imaging technique produces visual pictures of the spatial variation of selected NMR properties. These properties include the possibility of selectively mapping the distribution of the particular chemical species in the region of interest.

The images shown in figures 2a–2c are direct images of the protons of the rubber and acquired by swelling with deuterated cyclohexane. The variations in magnetic susceptibility show that structural inhomogeneities are present in all three samples.

Generally, the variation of the signal intensity in the displayed images are largely attributed to the $T_2$ weighting of the contributions of the different components of the structure. In figure 2a to 2c, the areas corresponding to the background color (dark blue) are a result of voids as indicated by the crack
prominent in figure 2a. The crosslinked aggregates in these images can be distinguished by looking at the areas of intermediate color (light blue or gray) and the yellow or red intensities corresponding to high gray levels arise from uncrosslinked regions.

The crack is identified by the large background signal and it appeared during the extraction of the samples with cyclohexane. Small defects, like voids, which exhibit no signal may be due to trapped air bubbles. Other defects exhibiting no signal may be either due to the areas of high crosslink density (low mobility) or due to the presence of the insoluble Zn complex present in the rubber matrix. From conventional to the efficient system, the high signal intensity area gradually decreases as a result of greater crosslink density.

Histograms displayed in figure 3 correspond to the images shown in figure 2-a to 2-c. The mean value decreased as the vulcanization progressed from con. to an ev. system. The histogram values were described in table III. The skewness and kurtosis of these histogram are tabulated, which explain how the dispersity decreases from conv. to an ev. system. The median shifted to the lower value for higher crosslink density. The skewedness calculated for these
histograms indicate that they move towards gaussian distribution as we progressed from conv. to an ev. system. The kurtosis calculated for the histograms displayed in figure 3 indicate that the conventionally cured sample has a leptokurtic curve (curve having a value greater than 3.0), whereas the efficiently cured sample has approximately a gaussian distribution. In the case of semi-efficiently cured sample the curve represents platykurtic behaviour (a curve having a kurtosis value less than 3.0). The fraction (area) corresponding to the gray level of 170 and 192 were also determined, which indicates that the area decreased with the increase in accelerator to sulfur ratios. The gray level 192 corresponds to a relatively high intensity signal and is related to the mobile fraction of the rubber material. The images plotted using the above gray level are shown in figure 4 and the areas are tabulated in table III.

The image contrast arises from the spin density and the spatial variation of spin relaxation times, since the T1 and T2 of the vulcanized rubber differ substantially from those of uncrosslinked rubber. These quantitative results are consistent with the previous studies of relative dependence of T1 and T2 values on crosslink density [34-39].
The $T_2$ weighted images are shown in figures 5-a, 5-b and 5-c for conv., sev. and ev. systems respectively. The $T_2$ weighted signal intensity of each pixel serves to characterize the degree of segmental motion of its contents. The decrease in total signal in $T_2$ images with the increase in accelerator to sulfur ratios demonstrates that the average length of chain segments between effective crosslink sites decreases, as well as the extent of their relative motions. The higher intensities observed near the voids are due to the less hindered motions of the free segments of the chain.

The maximum intensity displayed in the $T_2$ weighted samples corresponds to a $T_2$ of 150 ms (Figure 6). Table IV demonstrates the $T_2_{(ave)}$ values calculated from the weighted $T_2$ images using a repetition time of 5.0 ms and variable echo times.

DISCUSSION:

The spin density and the $T_2$ maps of NMR parameters provide a measure of molecular mobility in the cured elastomers. Figure 2-a to 2-c represent the direct imaging of polybutadiene using deuterated cyclohexane. The total signal intensity decreases as the curing
proceeds from conventional to an efficient system. The $M_n^{(p_y)}$ also decreases as we proceed from conventional to an efficient system, which indicates that the average length of chain segments between the effective crosslink sites decreases.

The use of $T_2$ as a probe to investigate the network formation leads to some important quantitative estimations. In order to develop a relationship between $T_2$ and $\nu$, a simple model approach was used [41–43]. This model correlates the distribution of $T_2$ and crosslink density distribution along the chain. This model is quite helpful in interpreting the dynamic behaviour of these networks in terms of two distinct populations of chain segment correlation times ($\tau_c$). The $\tau_c$ can be resolved into two components, one in which $\tau_c$ is related with the motionally restrained region of the elastomer network next to physical or chemical crosslinks, while the other with the relatively unrestrained region of elastomer distant from the crosslinks.

On this basis the $\tau_c$ can be inversely related to $T_2$, where $T_2$ corresponds to the protons associated with chemical crosslinks and $T_2$ are the protons in the region relatively far from the crosslinks. Table IV describes the $T_2$, $T_2$, $T_2^{(w)}$, median and standard
deviation values for the even echo images as calculated from the histograms. Table V reports the different values corresponding to average $V_{xi}$, average repeat units (RUs)/network chain, average RUs/crosslink region, average volume per crosslink region and average $v_i$ (volumetric chain density per pixel) for even echoes. The values reported in tables III and V are used only of the even echoes, because the attenuating effects of $180^\circ$ pulse imperfections are largely compensated.

The model used in this study assumes that each $T_2$ component of the image histogram is a volume fraction weighted inverse of the short and long values of relaxation parameters.

$$\frac{1}{T_{2i}} = \frac{V_{xi}}{T_{2S}} + \frac{(1-V_{xi})}{T_{2L}} \quad (8)$$

where $V_{xi}$ is the volume fraction of the rubber material per pixel associated with the constrained or crosslinked areas, while $1-V_{xi}$ corresponds to the remaining uncrosslinked area. Another important assumption is that the $V_{xi}$ is proportional to the volumetric chain density per pixel ($v_i$). The sign of proportionality is represented by $\alpha$ which is half the mass of the polymer repeat units per crosslink region.
The above equation now can be modified as,

\[ \frac{1}{T_{2i}} = \left[ \alpha(T_{2S}^{-1} - T_{2L}^{-1}) \right] \nu_i + T_{2L}^{-1} \]  \hspace{1cm} (9)

If the \( \nu_i \), which are pixel quantities, are assumed to spatially average to the bulk crosslink densities measured by the equilibrium swelling method, the slope and the intercept of the above equation are obtainable as least square parameters of straight line fits to plot of \( (1/T_{2i})_{ave} \) vs \( \nu \) swelling. Therefore equation 8 can be modified as follows,

\[ \nu_i = \frac{(T_{2i}^{-1} - T_{2L}^{-1})}{\left[ \alpha(T_{2S}^{-1} - T_{2L}^{-1}) \right]} \]  \hspace{1cm} (10)

Further modification has been made for the interpretation of empirical data. Since the equilibrium swelling behaviour and the \( T_2 \) relaxations are vastly different from each other, therefore the \( T_2 (ave) \) might reflect each sample concentration of covalently bonded chemical crosslink structures, while the \( \nu \) reflects the contribution from both chemical crosslink and the permanent physical entanglement structures.
Figure 6 displays the histogram of the number of pixels with a particular $T_2$ versus $T_2$ for conv., sev. and an ev. systems. However it is reasonable to assume that $T_2^{(ave)}$ might preferentially reflect each sample's concentration of chemical crosslinks. On this basis the $\nu$ values were extrapolated to determine the chemical crosslinks using the proposed correction scheme both for Moore and Watson and Kraus [29] and replotted against $(1/T_2)$. The resulting correlation is linear (Fig. 7), indicating that indeed $T_2^{(ave)}$ is a linear function of the number of chemical crosslinks.

A modification can be made in equation (8) to calculate the $(1/T_2)^{ave}$.

$$\frac{1}{T_{2i}} = \frac{V_{xi}/V_r}{T_{2S}} + \frac{(1-V_{xi})/V_r}{T_{2L}} \quad (11)$$
The \((1/T_{11})_{AV}\) calculated from the above equation are 8.0, 5.0 and 3.0 ms for conv., sev. and ev. systems. The crosslink density distributions are very useful for providing a general qualitative picture of the crosslink events as the vulcanization proceeds from conventional to an efficient system. The number of polymer repeat units per number average network chain can also be calculated using swelling measurements. Polymer repeat units per crosslink are calculated using the above data which is twice the product of RUs/network chain and the \(V_x\). Similarly the effective volume occupied by the crosslink regions have also been calculated by using the following expression,

\[
\text{Vol/Xlink region}(\mu\text{m}^3) = \frac{2V_x}{\nu_r \nu_r N_A} x 10^{12} \tag{12}
\]

where \(N_A\) is the Avogadro's number. The number of RUs per crosslink region is predicted to increase with the increase in amount of accelerator. Similarly the increase in the volume per crosslink region with the accelerator to sulfur can be viewed. Figure 8 is a plot of area versus the different gray levels for conventional, semi-efficient and an efficient systems. These gray level can be directly translated into the chain mobility. The value corresponding to zero has a fraction due to the constrained region, whereas 255
corresponds to highly mobile fraction. The chain mobility decreases from conv. to an ev. system.
CONCLUSIONS:

$^1$H NMRI can spatially resolve different structural features in unfilled swollen samples of TBBS-Sulfur vulcanized high vinyl polybutadiene. The single echo method can be used to image the protons of polybutadiene directly using deuterated cyclohexane as a swelling agent. This method shows the presence of different structural inhomogeneties such as voids, fillers, crosslink aggregates and crosslinked regions in the bulk of the sample.

An attempt has been made to correlate the dependence of $T_2$, with crosslinks and/or entanglements as a function of accelerator to sulfur ratios. $T_2$-weighted images were used to evaluate the crosslink densities. A quantitative estimation of histograms corresponding to these images was also employed. The interpretation of data is based on the Rouse' model. We have assumed two different values of $T_2$'s, a short and long $T_2$. The $T_2$ depends primarily on the average number of monomer units between the crosslinks. The $T_2$ corresponds to molecules carrying no crosslinked units or isolated crosslinks on long chains. The contrast shown between the different regions is highlighted with spin-density $T_2$-weighted images, suggesting that the variation seen
in these images may be closely related to variations in both concentration and the mobility of the network segments.
ACKNOWLEDGEMENTS:

The authors would like to acknowledge Monsanto Corporation, Akron, Ohio, for providing the samples and their technical assistance.

REFERENCES:


22. MRI, Probes; Product Literature, Doty Scientific, Columbia, SC 29223.


### TABLE I.

**HIGH VINYL POLYBUTADIENE FORMULATIONS**

*(in parts per hundred of rubber)*

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*Curing Temperature: 150°C*

![N-t-Butyl-2-Benzothiazolesulfenamide](image)

**N-t-Butyl-2-Benzothiazolesulfenamide**

*(TBBS)*
**TABLE II.**

**EQUILIBRIUM SWELLING MEASUREMENT DATA**

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<tr>
<td>((V_r))</td>
<td>0.17</td>
<td>0.21</td>
<td>0.22</td>
</tr>
<tr>
<td><strong>(v) (Swelling)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>((10^5))</td>
<td>7.46</td>
<td>9.91</td>
<td>10.9</td>
</tr>
<tr>
<td><strong>Mn(_{\text{phys}})</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>((10^{-4}))</td>
<td>0.67</td>
<td>0.50</td>
<td>0.45</td>
</tr>
<tr>
<td><strong>Monomer units/ nodal junction</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>124</td>
<td>93</td>
<td>84</td>
</tr>
</tbody>
</table>

**KRAUS' CORRECTION**

<table>
<thead>
<tr>
<th></th>
<th>CONV.</th>
<th>SEV.</th>
<th>EV.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mn(_{\text{phys}})</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>((10^{-4}))</td>
<td>0.55</td>
<td>0.44</td>
<td>0.40</td>
</tr>
<tr>
<td><strong>Mn(_{\text{chem}})</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>((10^{-4}))</td>
<td>0.34</td>
<td>0.25</td>
<td>0.22</td>
</tr>
<tr>
<td><strong>Monomer units/ nodal junction</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>102</td>
<td>82</td>
<td>74</td>
</tr>
</tbody>
</table>
### TABLE III

#### TABULATION OF THE HISTOGRAMS SHOWN IN FIGURE 3

<table>
<thead>
<tr>
<th></th>
<th>CONVENTIONAL</th>
<th>SEMI-EFFICIENT</th>
<th>EFFICIENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median</td>
<td>178.0</td>
<td>153.0</td>
<td>71.0</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>53.0</td>
<td>36.3</td>
<td>20.7</td>
</tr>
<tr>
<td>Skewness</td>
<td>-1.1</td>
<td>-1.2</td>
<td>0.3</td>
</tr>
<tr>
<td>Kurtosis</td>
<td>4.4</td>
<td>2.2</td>
<td>2.8</td>
</tr>
<tr>
<td>Area cut at</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(gray level 170)</td>
<td>2430</td>
<td>797</td>
<td>375</td>
</tr>
<tr>
<td>(gray level 192)</td>
<td>1665</td>
<td>142</td>
<td>84</td>
</tr>
</tbody>
</table>

#### TABULATION OF THE HISTOGRAMS SHOWN IN FIGURE 6

<table>
<thead>
<tr>
<th></th>
<th>CONVENTIONAL</th>
<th>SEMI-EFFICIENT</th>
<th>EFFICIENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median</td>
<td>47.0</td>
<td>25.0</td>
<td>16.0</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>19.5</td>
<td>10.5</td>
<td>6.7</td>
</tr>
<tr>
<td>Skewness</td>
<td>3.8</td>
<td>2.9</td>
<td>1.7</td>
</tr>
<tr>
<td>Kurtosis</td>
<td>1.6</td>
<td>3.4</td>
<td>5.3</td>
</tr>
</tbody>
</table>
TABLE IV.

CHARACTERISTIC T2 VALUES CALCULATED USING MODEL STUDY FOR POLYBUTADIENE CURED AT DIFFERENT ACCELERATOR TO SULFUR RATIOS

<table>
<thead>
<tr>
<th></th>
<th>CONV.</th>
<th>SEV.</th>
<th>EV.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T2r (ms)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(even echo)</td>
<td>17.0</td>
<td>13.0</td>
<td>10.0</td>
</tr>
<tr>
<td>T2⑴ (ms)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(even echo)</td>
<td>92.0</td>
<td>94.0</td>
<td>91.0</td>
</tr>
<tr>
<td>T2ave (ms)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(even echo)</td>
<td>37.0</td>
<td>34.0</td>
<td>31.0</td>
</tr>
<tr>
<td>Median.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(even echo)</td>
<td>52.0</td>
<td>50.0</td>
<td>47.0</td>
</tr>
<tr>
<td>Standard Deviation.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(even echo)</td>
<td>19.0</td>
<td>10.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>

Error = ±10 %
### Table V

**Characteristic-Model Related Parameters Using T₂- Calculated Images for Different Accelerator/Sulfur Ratios.**

<table>
<thead>
<tr>
<th></th>
<th>CONV.</th>
<th>SEV.</th>
<th>EV.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ave. Vₓ₁ (10⁻⁴)</td>
<td>0.22</td>
<td>0.47</td>
<td>0.61</td>
</tr>
<tr>
<td>(even echo)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ave. Ru/network</td>
<td>205</td>
<td>162</td>
<td>148</td>
</tr>
<tr>
<td>chain.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ave. Ru/Xlink region.</td>
<td>89</td>
<td>152</td>
<td>181</td>
</tr>
<tr>
<td>(even echo)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ave. Vol/crosslink region.</td>
<td>6.75</td>
<td>8.34</td>
<td>9.61</td>
</tr>
<tr>
<td>(μm³ x 10⁻⁷)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(even echo)</td>
<td>1.24</td>
<td>3.68</td>
<td>6.11</td>
</tr>
<tr>
<td>Ave. vₛ (mol/G) (10⁴)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(even echo)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. The different imaging pulse sequences used in this paper. Single echo CPMG spin echo pulse sequence shown in figure (a) using selective 90° excitation/non selective 180° refocussing radio-frequency pulses, while figure (b) represents multi-echo CPMG pulse sequence, using n repetition of the refocussing hard pulses.
Figure 2-a. Single-echo images of high vinyl PB cylindrical sample cured with Acc/S ratio of 0.19 (conv.) at 150 °C. Field of view 9mm x 9mm, displayed as 256 x 256 pixels. The effective pixel resolution is 39.0 μm/pixel. The gray level used in this image is cut at 150.
Figure 2-b. Single-echo images of high vinyl PB sample cured with Acc./S ratio of 1.0 (sev.) at 150 °C. FOV - 9mm x 9mm displayed as 256 x 256 pixels. The effective pixel resolution is 39.0 μm/pixel. The gray level used in this image is cut at 150.
Figure 2-c. Single-echo images of high vinyl PB sample cured with Acc./S ratio of 4.54 (ev.) at 150 °C. FOV = 9mm x 9mm displayed as 256 x 256 pixels. The effective pixel resolution is 39.0 μm/pixel. The gray level used in this image is cut at 150.
Figure 3. Histograms of the number of pixels with value of gray level displayed in figures 2-a to 2-c for conv., sev. and ev. respectively.
Figure 4-a. Parameter imaging of a conventionally cured sample displayed as a gray level 170 and 192 on 0-255 scale.
Figure 4-b. Parameter imaging of a semi-efficiently cured sample displayed as a gray level 170 and 192 on 0-255 scale.
Figure 4-c. Parameter imaging of a efficiently cured sample displayed as a gray level 170 and 192 on 0-255 scale.
Figure 5-a. $T_2$ resolved multiecho image of swollen high vinyl polybutadiene cylindrical sample, cured with Acc./S ratio of 0.19 (conv.). FOV = 7 mm x 7 mm displaced as 256 x 256 pixels with the effective pixel resolution of 39.0 μm/pixel. The displayed image is calculated only from even echoes.
Figure 5-b. T₂ resolved multiecho image of swollen high vinyl polybutadiene cylindrical sample, cured with Acc./S ratio of 1.00 (sev). FOV = 7 mm x 7 mm displaced as 256 x 256 pixels with the effective pixel resolution of 39.0 μm/pixel. The displayed image is calculated only from even echos.
Figure 5-c. $T_2$ resolved multiecho image of swollen high vinyl polybutadiene cylindrical sample, cured with Acc./S ratio of 4.54 (ev). FOV = 7 mm x 7 mm displaced as 256 x 256 pixels with the effective pixel resolution of 39.0 μm/pixel. The displayed image is calculated only from even echos.
Figure 6. Histograms of the number of pixels with a particular $T_2$ versus $T_1$ value for the conv., sev. and ev. images displayed in figures 5-a to 5-c.
Figure 7. Plots of the $1/T_2^*$ versus $v_{(swelling)}$ for the even echoes of the $T_2$ resolved images.
Figure 8. Area of the contour maps plotted as a function of different gray levels for con. (O), sev. (X) and ev. (Δ) formulations.
CHAPTER IV

OBSERVATION OF SPATIAL INHOMOGENETIES IN TBBS–SULFUR
CURED HIGH VINYL POLYBUTADIENE USING NMR–IMAGING

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INTRODUCTION:

Flourishing in the field of medicine [1,2] nuclear magnetic resonance imaging (NMRI) is also recognized as an important tool in the area of materials research. The NMRI is extensively used to study the chemical and motional heterogeneities in the crosslinked elastomeric networks because of their greater segmental mobility and large extensibility when swollen in an appropriate solvent [3-5]. The image provides a picture of NMR signal intensity as a function of location (in one, two and three dimensions) in an object. The main advantage of this technique over the other imaging methods is its ability to map spatially a wide variety of structures, both static and dynamic parameters in a non-invasive way [6].

Until recently the only techniques available to study spatial microstructures required sectioning the sample and analyzing the resulting slice by using different methods such as scanning electron microscopy (SEM), infrared spectroscopy (IR) and electron spectroscopy (ESCA). In certain cases X-ray tomography has also been used to study the cured microstructures [7,8].
NMR imaging involves acquiring the NMR spectra in the presence of large magnetic field gradients in the x, y and z directions. One gradient is used in conjunction with a selective pulse to excite spins only in a slice of the sample, while the other two gradients spatially encode the spins so that the resonant frequency of the nuclear spins are correlated with spatial position. A two dimensional Fourier-transform is performed after collecting the data. Thus a 2-D image is a plot of intensity vs spatial direction. The images produced by this technique are determined by optimizing various parameters. Extrinsic parameters include operator controlled parameters such as field strength, radio frequency pulses and pulse sequence timings. Whereas the intrinsic parameters are the proton spin density \( \rho \), spin-lattice relaxation time \( (T_1) \), spin-spin relaxation time \( (T_2) \), chemical shift and flow velocity. Thus a signal intensity is a complex interplay of these various parameters. A good quality image can be acquired if these parameters are well controlled and optimized.

The spatial mapping and contrast capabilities of NMRI have created natural incentives for exploiting NMRI in the field of elastomers [9-24] and solid samples [25-27]. For the study of the molecular mobility of
the polymer chains, the NMRI technique provides a sensitive probe of the nuclear environment through the short range magnetic dipolar interactions [28]. The variety of characteristic motions can be interpreted in terms of relaxation parameters which include spin-lattice relaxations time (T₁), sensitive to group motions in the megahertz frequency regime. The motions inducing the spin-spin relaxation (T₂) are in the kilohertz range and are sensitive to chain mobility.

The detection of internal voids, defects and inhomogeneities constitutes an important class of applications for NMRI. This category of morphological investigation typically relies on the NMR signal acquired from a protic solvent imbibed in the sample.

The goal of this study has been to evolve a better understanding of structure/property relationships in an accelerated-sulfur vulcanized high vinyl polybutadiene rubber (BR). Both imbibed solvent (cyclohexane) and direct proton imaging (deuterated cyclohexane) approaches have been evaluated.
EXPERIMENTAL:–

The elastomeric sample under investigation is high vinyl BR a product of Nippon Zeon Co. Ltd., sold under a commercial name of NIPOL BR-1245. This system has approximately 70 % of the vinyl 1,2 units and the rest (30 %) comprises of 1,4 BR units. The samples were blended on a Brabender mixer and formulated to different accelerator to sulfur ratios along with the other auxiliary agents (e.g. zinc oxide and stearic acid). The formulated rubber samples consisted of 100 phr (parts per hundred of rubber) of Nipol BR-1245 rubber and the other components include 4.1, 2.0 and 1.1 phr of elemental sulfur and 0.8, 2.0 and 5.0 phr of n-ter-2- butyl benzothiazole sulfenamide (TBBS) for conventional (conv.), semi-efficient (sev.) and efficient (ev.) respectively. The accelerator (TBBS) contributes relatively longer induction period and a fast cure rate and is a product of Monsanto Corporation.

The formulated samples were cured at 150 °C forming a rubber sheet (1 mm thick) on a hydraulic press using a pressure of 2000 psi for different lengths of times. These rubber sheets were cured from 20 to 120 minutes in order to monitor the changes associated with the cure as a function of cure time. These cured samples
were immediately quenched by immersing in a powdered bed of dry ice. The samples were later extracted with cyclohexane overnight in a soxhlet extractor in order to remove the non-network materials. All these samples were stored in a refrigerator in cyclohexane to avoid degradation.

The equilibrium swelling method was used in order to measure the crosslink densities. All the studies were made at ambient temperature using cyclohexane as a swelling solvent. The number average (Mn) and weight average (Mw) molecular weight of unfilled original BR material was determined by using GPC method. The average Mn and Mw calculated for original BR were 13,6000 and 14,6000 g/mole respectively with the poly-dispersity value of approximately 1.07.

A Bruker MSL-300 NMR spectrometer equipped with a microimaging probe was used to acquire the images at a proton frequency of 300.13 MHz. All these images were taken at 300 °K. The cured samples were swollen both in n-cyclohexane and in deuterated cyclohexane in a 20 mm tube for 48 hours prior to the experiment. The resulting images were displayed as 256 x 256 pixels in size.
The pulse sequence used was a standard CPMG (Carr–Purcel, Meiboom–Gill) [29,30] spin-echo with a selective 90° pulse followed by a delay time \( \tau \) and then the non-selective 180° pulse is applied by another delay \( \tau \) then the signal is acquired. The pulse sequence diagram is shown in figure 1. The slice thickness was approximately 1 mm and was performed by using a magnetic field gradient in the z-direction during the selective 90° pulse. The images were acquired using an echo time of 7 ms and a repetition time of 5s. A spectral width of 62,500 Hz was used in acquisition.

Sixteen scans per phase encoding steps were signal averaged in producing each image, using 90° increment \((x, -y, -x, y)\) phase cycling. The read-out gradient set as 19.80 G/cm and the phase encode gradient varying between \(-16.25 \rightarrow +16.25\) G/cm in an equal 256 increments of 0.13 G/cm.

The T1 images were taken using the saturation recovery pulse sequence. The echo time (T2) used was 5.75 ms while the repetition time ranges 10 ms to 5 s. The read-out gradient was set at 19.80 G/cm while the phase encoding gradient was \(-16.25 \rightarrow +16.25\) G/cm with an equal 256 increments of 0.14 G/cm. Twelve scans per phase encoding steps were signal averaged in producing
each image.

The second set of samples were swollen in deuterated cyclohexane in order to image the rubber material directly. Sixteen scans per phase encoding step were signal averaged in producing each image. The echo time was 7 ms while the repetition time was 5 s. The read out gradient was set at 23.30 G/cm while the phase encode gradient varying between $-19.20 \rightarrow +19.20$ G/cm in 256 equal increments of 0.15 G/cm. The images are displayed on the arbitrary scale of 0-255, which corresponds from blue (low) to red (red) intensities. Where 0 correspond to lowest signal intensity and 255 to the highest signal intensity. The other colors represent intensities between these extremes.

RESULTS:

The signal intensity in proton imaging depends on the proton concentration, $T_1$, and $T_2$ relaxation times. The spin echo signal intensity increases if $T_2$ increases, $T_1$ decreases or $T_2$ is shortened. In case of a cured rubber which acts as a pseudosolid, the images were hampered by the problem of excessive linewidths and poor signal-to-noise ratio. The experimental criterion for generating a high resolution NMR image is that, it must be possible to encode spatial information in an
NMR signal in a time order of T₂, the relaxation time.

Swelling measurements have been used for the determination of crosslink density in elastomers [31-33]. The method is based on the fact that higher the crosslink density the less solvent imbibed in the system and lower the degree of swelling and vice versa. The results of equilibrium swelling measurements of differently cured high vinyl polybutadiene are shown in tables (I-III). These studies were made at ambient temperature using cyclohexane as a swelling solvent.

The number average molecular weight between the physical crosslinks (\(M_{\text{n,phys}}\)) was derived by using Flory-Rehner equation [31].

\[
\frac{1}{M_n \text{ phys}} = \nu = \frac{-[\ln(1-V_r) + V_r + \chi V_r^2]}{\rho_r V_0 (V_r^{1/3} - V_r/2)}
\]

The \(\chi\) value is solvent–polymer interaction parameters characteristic of the interaction between the solvent system and cured solid. The lower the \(\chi\) value the greater the solvent will swell the crosslinked polymer.

\[
V_r = \left[\left(\frac{\rho_r}{\rho_s}\right)(\frac{W_s - W_u}{W_u}) + 1\right]^{-1}
\]

\[
\chi = 0.37 + 0.52V_r
\]

Where \(\chi\) is evaluated for each sample as a linear
function of \( V_r \) as shown in the above equation. Tables (I-III) show the average number of monomer units between the crosslinks. These values were corrected by using Kraus' [32] approach.

**Solvent Imaging:**

The cured samples were swollen in cyclohexane and were imaged using the spin-echo pulse sequence at 300° K. The intensities of the mobile protons of the solvent probe the homogeneities and spatial distribution of the crosslinked network systems. The areas of low solvent concentration can be correlated with higher crosslink density similarly areas of high solvent concentration can be correlated with lower crosslink density. The imaging experiment is essentially a two dimensional swelling experiment.

The non-uniformity of the signal indicates that a system under investigation has an inhomogeneous crosslink distribution. The color scale used in the displayed images are from 0-255 corresponding from blue to red. The lighter (blue) area represents the lowest signal intensity while the red area indicates the high signal intensity. The intermediate level of solvent signal (i.e., between red to blue color) is indicative of intermediate level crosslinking.
The images acquired using the spin-echo pulse sequence are shown in figures 2, 3 and 4 swollen in cyclohexane. Figures 2-a to 2-e represent the conventional formulation and cured ranging from 20 minutes to 120 minutes respectively. The lower signal intensities shown at the boundaries of the these samples correspond to the highly cured area. The circular rings with the different signal intensities may be the result of thermal gradients leading to reduced mobility of the network structures. A similar kind of trend is found in other images with different formulations. In figures 2-d and 2-e which were cured at 60 and 120 minutes, respectively, thus show relatively high intensity signal area and one possible explanation is that the sample is undergoing reversion.

Figures 3-a to 3-e represent the semi-efficient formulation. The image 3-a represents a 20 minutes cured sample and intensity distribution shows regions of a low level of cure. The sample cured using 120 minutes (3-e) gives the overcure distributions of signal intensities. Similarly, figures 4-a to 4-e represent the efficient formulation. The inhomogeneous distribution of high intensity signal along with structural defects can be seen in all these images. The effective pixel resolution is 39 μm/pixel in these
images.

Direct Rubber Proton Imaging:

The relatively high chain mobility and consequent narrow proton linewidth of the swollen elastomer allow one to acquire the direct image of the rubber. Representative images of conventional formulation are shown in figure 5. These images were acquired using deuterated cyclohexane as the swelling agent. Inhomogeneities, like spatial defects, voids and the domains of high crosslink density, can be identified in the bulk of the samples. The inhomogeneities based on the magnetic susceptibility differences were also detected which probably arise from residual (unreacted) Zn complex etc.

Figure 5-a to 5-e represent the conventional formulation cured between 20 to 120 minutes. All these figures are displayed as gray level cut at 150, and the corresponding intermediate to high intensity signal. In the case of 5-a which is a 20 minutes cured sample the distribution of high signal intensity can be differentiated from the other images. The differences presumably are based on T2 differences which decrease with the increase in crosslinks. On the other hand the image shown in figure 5-e gives the high intensity
signal because of possible reversion or chain scission reactions. A similar kind of trend is observed in sev. and ev. formulations. The effective pixel resolution in these images is 32 μm/pixels.

**T₁ IMAGING:**

Representative spin-lattice relaxation (T₁) images are shown in figure 7 corresponding to the ev. formulation. These images are displayed as 256 x 256 pixels with an effective resolution of 32 μm/pixels. A T₁ weighted image was calculated using in-house software written [34] in FORTRAN 77.

For T₁ weighted images the contrast within the image is dependent on the polymeric material’s characteristic T₁ values. The best TR value depends upon the T₁ of the polymer being imaged. The slight increase in the high intensity signal with the crosslink densities are probably due to the contribution of short T₁ components.
DISCUSSION:

The spatial inhomogeneities present in these samples are the result of different factors, e.g., poor mixing of different ingredients, large thermal gradients, presence of small foreign particles as well as chemical shift and susceptibility artifacts. The presence of the magnetic susceptibility pattern (shadows) help in differentiating between voids and unmixed auxiliary agents (Figure 2-4).

Inhomogeneities of various sizes and shapes can be seen throughout the bulk of the sample. The portion of the images represented by an intermediate signal (yellow-green) have an intensity corresponding to an intermediate level of crosslinkings. Abrupt changes in magnetic susceptibility at defect interfaces can create shape and intensity artifacts in NMR images [35,36]. Another source of inhomogeneities may be due to the presence of interfaces between the diamagnetic rubber and unmixed paramagnetic materials.

Figure 4-d is an image of a sample cured 60 minutes which shows more areas corresponding to low intensity or the high cross-link density region. The 20 minutes cured sample having a conventional formulation is shown in figure 5-a and gives a greater high intensity
signals as compared to 35, 45 and 60 minutes cure. The exception is the 120 minutes cure resulting from reversion or overcure reactions. The high intensity region is due to the presence of mobile proton fractions in the sample.

The NMR image is generally characterized by three factors, (a) spatial resolution, (b) object-contrast level and (c) its signal-to-noise ratio (S/N). The decrease in the S/N after the maximum cure time may be due to the lowering of the sulfur level or decrease in crosslinks. Going through the maximum and then decreasing with additional cure time is not likely due to the loss of network structure by reversion. The reversion reaction normally occurs when the desulfurization reactions are faster then the crosslink reactions. The desulfurization can also follow other pathways in which the species decomposes into conjugated chains, cyclic sulfides, shorter sulfur-links and other main chain modifications.

A graphical representation of \( M_n(\text{phys}) \) calculated (using equilibrium swelling method) versus the cure time is given in figure 8. The decrease in \( M_n(\text{phys}) \) as a function of cure times is due to the decrease in number average molecular weight between the crosslinks. The study of accelerated-sulfur cured high vinyl BR
demonstrated the existence of correlation between swelling measured crosslink densities and the intensities associated with it [37].

A histogram of the number of pixels with a particular value of T2 versus T2 can be interpreted in terms of the distribution of crosslinks along the chain. Figure 6 shows the different histograms for conv. system. The peak maxima is shifted to the left in all these samples. Also shown is a narrowing of the distribution of the cross-link densities as we move from low to high cure times. In other words the probability of finding the molecules with lower mobility (crosslinked) become greater for an efficiently cured system.

The histogram intensity corresponding to a gray level 200 (red color) plotted as a function of cure times (figure 9). The intensity decreases gradually for 20 to 60 minutes cure but starts to increase for 120 minutes cure and is probably a result of reversion reactions. Similarly the histogram intensities cut at 170 on a gray scale (yellow color = intermediate crosslink level) are plotted against cure times and give the same trend as shown in figure 10.
Table IV shows the calculation of the histograms for conventionally cured samples displayed in Figure 6. The average, median and standard deviations are described in Table IV. The standard deviation is calculated for these histograms and it decreases from low to high crosslink density indicating a narrowing of the distributions. The skewness and kurtosis of these histograms have also been calculated. The proton NMRI T1 data was analyzed assuming the presence of only one component (a mono-exponential function). The samples were prepared using the cure time ranges from 20 to 120 minutes. All these images were taken in deuterated cyclohexane. In case of T1-weighted images of the efficient formulation (Figure 7) the high intensity signal increases from 20 minutes to 60 minutes cure and then decreases. The rationale behind this process is the desulfurization after a certain level of cure.

Similar trends were found in conventional and semi-efficient formulations. In sev. the intensity increases from 35 minutes to 60 minutes and decreases at 120 minutes. As the curing proceeds from conventional to an efficient system, there is an increase in the molecular rigidity which is reflected in a reduction of the T1 and T2 of the proton. Besides
enabling detection of the size and location of voids and structural defects in a rubber sample by visual observation of the images, NMRI methods can be made to yield numerical evaluation of void size and fraction of voids in a sample.

Table V shows the percent areas of the images cut at 220 (lightly crosslink regions) and 100 (high crosslink regions) as displayed in figures 2-4. The percent area corresponding voids are cut at 150 on the scale of 0 to 255. The resolution of the micro-imaging probe in this case is 0.07 mm. With the exception of few large morphological defects, the spin echo image appears uniform but mottled.

CONCLUSIONS:

$^1$H imaging reveals the different physical and spatial microstructures present in an unfilled accelerated-sulfur cured high vinyl polybutadiene. Advantages of this technique are its non-destructive nature and the abundance of detectable molecular parameters including molecular motions.
Voids and non-voids can be differentiated based on magnetic susceptibility differences. Morphological defects and the areas corresponding different crosslink densities are detected using solvent imaging method. Cyclohexane was used as a solvent to act as a physical probe. Swelling measurements method based on Flory-Rehner’s equation was also employed to determine the crosslink densities and number average molecular weight between the crosslinks as a function of cure times. Non-uniform signal intensities and T2 times within the swollen high vinyl polybutadiene network material indicate inhomogeneties on the order of tens of microns.

The images acquired in cyclohexane demonstrate a different cure pattern in these samples. The high crosslink regions are present adjacent to the mold, which indicates that it is thermal gradient driven. The sample cured for 120 minutes shows greater solvent intensities demonstrating reversion reaction and this reversion or overcure reactions also results in spatial inhomogeneties. The inhomogeneties may arise from poor mixing and, residual auxiliary agents. The percent areas corresponding to uncrosslinked, highly crosslinked and voids regions are calculated using contour imaging method.
$T_1$ weighted images were also calculated for the three formulations. These intensities are relatively less affected with the progress of vulcanization. The contrast between the different regions is due to proton density and $T_1$ weighted images, suggesting that the variation seen in the images may be closely related to the variation in both concentration and the mobility of the network systems.
ACKNOWLEDGEMENTS:

The authors wish to acknowledge the Monsanto Corp., Akron, Ohio, for their technical support of this research.

REFERENCES:


TABLE I.

EQUILIBRIUM SWELLING MEASUREMENT DATA FOR
CONVENTIONAL FORMULATION

<table>
<thead>
<tr>
<th>Cure Time (in Minutes)</th>
<th>20.00</th>
<th>35.00</th>
<th>45.00</th>
<th>60.00</th>
<th>120.00</th>
</tr>
</thead>
</table>

Vol. fraction rubber
Vr 0.238 0.239 0.239 0.238 0.267

\( v \) (Swelling)
\((10^{-4})\) 1.25 1.22 1.31 1.42 1.64

\( \text{Mn}_{\text{phys}} \)
\((10^4)\) 0.42 0.41 0.38 0.35 0.30

Ave. monomer units/
nodal junction
77.0 75.0 70.0 65.0 56.0

KRAUS' CORRECTION

\( \text{Mn}_{\text{phys}} \)
\((10^4)\) 0.40 0.38 0.36 0.33 0.29

\( \text{Mn}_{\text{chem}} \)
\((10^4)\) 0.21 0.20 0.19 0.17 0.15

Ave. monomer units/
nodal junction
73.0 71.0 66.0 62.0 54.0

Standard deviation: \( \pm 0.011 \)
<table>
<thead>
<tr>
<th>CURE TIME (IN MINUTES)</th>
<th>20.00</th>
<th>35.00</th>
<th>45.00</th>
<th>60.00</th>
<th>120.00</th>
</tr>
</thead>
</table>

Vol. fraction rubber

\[ V_r \]

\[ \nu (\text{Swelling}) \]

\[ (10^{-4}) \]

\[ 1.04 \]

\[ 1.11 \]

\[ 1.21 \]

\[ 1.33 \]

\[ 1.43 \]

\[ \text{Mn}_{(\text{phys})} \]

\[ (10^4) \]

\[ 0.48 \]

\[ 0.45 \]

\[ 0.43 \]

\[ 0.38 \]

\[ 0.35 \]

Ave. monomer units/

nodal junction

\[ 89.0 \]

\[ 83.0 \]

\[ 79.0 \]

\[ 70.0 \]

\[ 65.0 \]

**Kraus' Correction**

\[ \text{Mn}_{(\text{phys})} \]

\[ (10^4) \]

\[ 0.45 \]

\[ 0.42 \]

\[ 0.40 \]

\[ 0.36 \]

\[ 0.33 \]

\[ \text{Mn}_{(\text{chem})} \]

\[ (10^4) \]

\[ 0.24 \]

\[ 0.22 \]

\[ 0.21 \]

\[ 0.19 \]

\[ 0.17 \]

Ave. monomer units/

nodal junction

\[ 82.0 \]

\[ 78.0 \]

\[ 75.0 \]

\[ 66.0 \]

\[ 61.0 \]

Standard deviation: \( \pm 0.015 \)
TABLE III.
EQUILIBRIUM SWELLING MEASUREMENT DATA FOR EFFICIENT FORMULATION

<table>
<thead>
<tr>
<th>CURE TIME (IN MINUTES)</th>
<th>20.00</th>
<th>35.00</th>
<th>45.00</th>
<th>60.00</th>
<th>120.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vol. fraction rubber</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_r$</td>
<td>0.275</td>
<td>0.238</td>
<td>0.216</td>
<td>0.232</td>
<td>0.241</td>
</tr>
<tr>
<td>$v$ (Swelling)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(10^{-4})$</td>
<td>1.00</td>
<td>1.09</td>
<td>1.22</td>
<td>1.43</td>
<td>1.70</td>
</tr>
<tr>
<td>$M_n(\text{phys})$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$(10^4)$</td>
<td>0.50</td>
<td>0.46</td>
<td>0.41</td>
<td>0.35</td>
<td>0.29</td>
</tr>
<tr>
<td>Ave. monomer units/</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>nodal junction</td>
<td>92.0</td>
<td>84.0</td>
<td>76.0</td>
<td>65.0</td>
<td>54.0</td>
</tr>
</tbody>
</table>

KRAUS' CORRECTION

| $M_n(\text{phys})$     |       |       |       |       |        |
| $(10^4)$               | 0.46  | 0.42  | 0.38  | 0.33  | 0.28   |
| $M_n(\text{chem})$     |       |       |       |       |        |
| $(10^4)$               | 0.25  | 0.23  | 0.20  | 0.17  | 0.15   |
| Ave. monomer units/    |       |       |       |       |        |
| nodal junction         | 86.0  | 79.0  | 71.0  | 61.0  | 52.0   |

Standard deviation: $\pm 0.019$
### TABLE IV:

**TABULATION OF HISTOGRAMS SHOWN IN FIGURE 6 (CONV)**

<table>
<thead>
<tr>
<th>TIME (MIN.)</th>
<th>AVERAGE</th>
<th>MEDIAN</th>
<th>STANDARD DEVIATION</th>
<th>SKEWEDNESS</th>
<th>KURTOSIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.0</td>
<td>78.8</td>
<td>99.0</td>
<td>39.1</td>
<td>5.7</td>
<td>-3.1</td>
</tr>
<tr>
<td>35.0</td>
<td>75.5</td>
<td>94.1</td>
<td>36.6</td>
<td>5.2</td>
<td>-2.5</td>
</tr>
<tr>
<td>45.0</td>
<td>71.5</td>
<td>87.8</td>
<td>33.3</td>
<td>4.9</td>
<td>-1.8</td>
</tr>
<tr>
<td>60.0</td>
<td>63.0</td>
<td>80.0</td>
<td>31.6</td>
<td>3.8</td>
<td>-1.0</td>
</tr>
<tr>
<td>120.0</td>
<td>56.0</td>
<td>69.8</td>
<td>26.7</td>
<td>1.7</td>
<td>1.9</td>
</tr>
</tbody>
</table>

*Standard Deviation = ± 0.11*
### TABLE V:

**PERCENT AREA OF HIGH AND LOW INTENSITY SIGNAL OF THE IMAGES SHOWN IN FIGURE 2-4**

<table>
<thead>
<tr>
<th>CUT LEVEL</th>
<th>CURE TIME (MIN)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20</td>
</tr>
<tr>
<td>CONV.</td>
<td></td>
</tr>
<tr>
<td>Un-crosslinked.</td>
<td>85.5</td>
</tr>
<tr>
<td>Crosslinked.</td>
<td>10.5</td>
</tr>
<tr>
<td>Voids.</td>
<td>4.0</td>
</tr>
<tr>
<td>SEV.</td>
<td></td>
</tr>
<tr>
<td>Un-crosslinked.</td>
<td>96.1</td>
</tr>
<tr>
<td>Crosslinked.</td>
<td>2.8</td>
</tr>
<tr>
<td>Voids.</td>
<td>1.1</td>
</tr>
<tr>
<td>EV.</td>
<td></td>
</tr>
<tr>
<td>Un-crosslinked.</td>
<td>89.4</td>
</tr>
<tr>
<td>Crosslinked.</td>
<td>6.8</td>
</tr>
<tr>
<td>Voids.</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Error = ± 5.0%

Values are cut for un-crosslinked at 220, crosslinked at 100 and voids at 150 on the scale of 0 – 255 of histograms.
Figure 1: Block diagram of the Carr-Purcell spin-echo pulse sequence. Slice selection is accomplished with the selective 90° pulse and the Gz gradient, while the Gx gradient are the frequency encoding and read gradients, and the Gy is phase encoding gradient.
Figure 2-a: Proton image of high vinyl polybutadiene 20 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 39 μm/pixel. (conventional formulation)
Figure 2-b: Proton image of high vinyl polybutadiene 35 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 x 9 mm displayed as 256 x 256 pixels. The effective pixel resolution is 39 \( \mu m \) per pixel. (conventional formulation)
Figure 2-c: Proton image of high vinyl polybutadiene 45 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 39 μm/pixel. (conventional formulation)
Figure 2-d: Proton image of high vinyl polybutadiene 60 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 39 μm/pixel. (conventional formulation)
Figure 2-e: Proton image of high vinyl polybutadiene 120 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 39 μm/pixel. (conventional formulation)
Figure 3-a: Proton image of high vinyl polybutadiene 20 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 39 μm/pixel. (semi-efficient formulation)
Figure 3-b: Proton image of high vinyl polybutadiene 35 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 x 9 mm displayed as 256 x 256 pixels. The effective pixel resolution is 39 μm/pixel. (semi-efficient formulation)
Figure 3-c: Proton image of high vinyl polybutadiene 45 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 39 μm/pixel. (semi-efficient formulation)
Figure 3-d: Proton image of high vinyl polybutadiene 60 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 39 μm/pixel. (semi-efficient formulation)
Figure 3-e: Proton image of high vinyl polybutadiene 120 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 x 9 mm displayed as 256 x 256 pixels. The effective pixel resolution is 39 μm/pixel. (semi-efficient formulation)
Figure 4-a: Proton image of high vinyl polybutadiene 20 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 x 9 mm displayed as 256 x 256 pixels. The effective pixel resolution is 39 μm/pixel. (efficient formulation)
Figure 4-b: Proton image of high vinyl polybutadiene 35 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 39 μm/pixel. (efficient formulation)
Figure 4-c: Proton image of high vinyl polybutadiene 45 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 39 μm/pixel. (efficient formulation)
Figure 4-d: Proton image of high vinyl polybutadiene 60 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 39 μm/pixel. (efficient formulation)
Figure 4–e: Proton image of high vinyl polybutadiene 120 minutes cured sample swollen in cyclohexane using spin-echo pulse sequence. FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 39 μm/pixel. (efficient formulation)
Figure 5-a: Proton image of high vinyl polybutadiene 20 minutes cured sample swollen in deuterated cyclohexane using spin-echo pulse sequence FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 32 μm/pixel. (conventional formulation)
Figure 5-b: Proton image of high vinyl polybutadiene 35 minutes cured sample swollen in deuterated cyclohexane using spin-echo pulse sequence FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 32 μm/pixel. (conventional formulation)
Figure 5-c: Proton image of high vinyl polybutadiene 45 minutes cured sample swollen in deuterated cyclohexane using spin-echo pulse sequence FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 32 μm/pixel. (conventional formulation)
Figure 5-d: Proton image of high vinyl polybutadiene 60 minutes cured sample swollen in deuterated cyclohexane using spin-echo pulse sequence FOV = 9 X 9 mm displayed as 256 X 256 pixels. The effective pixel resolution is 32 μm/pixel. (conventional formulation)
Figure 5-e: Proton image of high vinyl polybutadiene 120 minutes cured sample swollen in deuterated cyclohexane using spin-echo pulse sequence FOV = 9 x 9 mm displayed as 256 x 256 pixels. The effective pixel resolution is 32 μm/pixel. (conventional formulation)
Figure 6: Histogram of the number of pixels corresponding to particular intensity of the images shown in figure 5-a to 5-e having conventional formulation.
Figure 7-a: T1 weighted images of an efficient formulation cured at 20 minutes cure time using saturation-recovery pulse sequence.
Figure 7-b: $T_1$ weighted images of an efficient formulation cured at 35 minutes cure time using saturation-recovery pulse sequence.
Figure 7-c: T₁ weighted images of an efficient formulation cured at 45 minutes cure time using saturation-recovery pulse sequence.
Figure 7-d: T1 weighted images of an efficient formulation cured at 60 minutes cure time using saturation-recovery pulse sequence.
Figure 7-e: T1 weighted images of an efficient formulation cured at 120 minutes cure time using saturation-recovery pulse sequence.
Figure 8: Experimental Mn(phys) versus cure time at 150° using equilibrium swelling method and are represented as Conv. = O, Sev = X and Ev = △.
Figure 9: Plot of histogram intensity versus cure time for all three formulations. The gray level cut at 200 on the scale of 0-255. Where O = conv., X = sev. and = ev.
Figure 10: Plot of histogram intensity versus cure time for all three formulations. The gray level cut at 170 on the scale of 0-255. Where O = conv., X = sev. and Δ = ev.
CHAPTER V

DYNAMIC NMR STUDY OF ACCELERATED VULCANIZED HIGH VINYL POLYBUTADIENE
INTRODUCTION:

Solid state nuclear magnetic resonance (NMR) has long been employed in observing molecular motions and has also been extensively used to study the complex dynamic problems presented by network polymer chains [1,2]. A better understanding of the molecular motions of vulcanized polymers is required to correlate with the physical and mechanical properties. The application of solid state NMR to polymers has contributed to significant advances in understanding their structures at the molecular level [3-8]. Direct observations of carbon resonances are particularly useful to identify the presence of network microstructures.

With the advent of Fourier transform (FT), dipolar decoupling (DD), magic angle spinning (MAS) and cross polarization (CP) techniques, it is now possible to observe the specific resonance of different chemical structures in solid polymers. Dipole-dipole interactions with neighboring magnetic nuclei principally $^1$H, are significant in solid polymer samples. The motions of these neighboring nuclei give rise to fluctuating magnetic fields and are characterized by a broad range of frequencies. High power proton decoupling is necessary to reduce the
dipolar interactions, and magic angle spinning is required to remove chemical shift anisotropy.

Generally relaxation experiments measure $T_1$ (spin-lattice relaxations), and $T_2$ (spin-spin relaxations) which are dominated by the dipolar interactions. The other relaxations including scalar, chemical shift anisotropy, spin rotation and quadrupole are much less effective in solid polymers.

On the basis of different motions present in elastomers, these can be categorized into the following, 1) motions on the time scale of $10^{-3}$ or slower and corresponding to slow movement of large portion of the chains, 2) motions on the time scale of $10^{-9}$ or shorter corresponding to local motions of chain between the entanglement points.

The basic theory of NMR relaxation and molecular dynamics was derived assuming Brownian motions by Bloembergen, Purcell and Pound [9], also known as BPP theory. This theory was later modified by the Solomon [10] and Kubo and Tomita [11], an additional theory of spin-lattice relaxation times in the rotating frame was developed [12].
Dipole-dipole relaxation is the most commonly observed relaxation mechanism in polymeric solids because of its high efficiency. For a bonded proton with a carbon atom, the bond distance is only 1.09 Å, which makes dipole-dipole relaxation very efficient.

Variation of spin lattice relaxation rates, observed as a function of both temperature and field strength have been widely used to characterize local motions of polymer chains [13–21].

In the case of spin-spin relaxation the fundamental relationship was adapted from the Doddrell’s [22] work. The assumption made in this study is that the nuclei are relaxing purely by a dipolar mechanism as given in the following two cases, 1) isotropic orientation of the rigid body, 2) a rotating group attached to a body undergoing isotropic rotational reorientations. The expression is given as follow,

\[
\frac{1}{NT_t} = \frac{1}{20} \frac{\gamma m^2 \tau_c^2 h^2}{\tau_c - \omega_e} \left[ \frac{\tau_c}{1 + (\omega_e - \omega_e)^2 \tau_c^2} + 3\tau_c/1 + \omega_e^2 \tau_c^2 + \frac{6\tau_c}{1 + (\omega_e + \omega_e)^2 \tau_c^2} + 4\tau_c + \frac{6\tau_c}{1 + \omega_e^2 \tau_c^2} \right]
\]

\[
J(\omega) = \frac{\tau_c}{(1 + \omega^2 \tau_c^2)}
\]
where,

\( N \) = number of bonded protons

\( T_2 \) = spin-spin relaxation time

\( \tau_\theta \) = rotational correlation time

\( \gamma_H \) = gyromagnetic ratio for proton

\( \gamma_C \) = gyromagnetic ratio for carbon

\( h \) = Planck’s constant

\( r_{C-H} \) = distance between carbon and hydrogen atom

\( J_0 \) = spectral density function

\( \omega_C \) = resonant frequency of carbon

\( \omega_H \) = resonant frequency of proton.

Spin-spin relaxations in polymer systems range from about \( 10^{-5} \) s for the rigid lattice to a value greater than \( 10^{-3} \) s for the rubbery state. The temperature dependence of \( T_2 \) above \( T_g \) and its sensitivity to low frequency motions make it a powerful method to study polymeric motions. The \( T_2 \) relaxation time is very sensitive to slower relative translational motions of the polymer chains and provides information on intramolecular couplings such as chemical crosslinking and chain entanglements. A review of relaxation studies on both permanent and temporary networks was reported by Charlesby and co-workers [23–32].
The relaxation times for the various carbons can not be compared directly because different relaxation mechanisms have different inherent efficiencies. The rotational correlation times ($\tau_c$) are the most suitable parameters for comparison of different carbon atoms, as it is directly related to the rate of motions [22].

This work deals with the characterization of chain motions occurring in a high molecular weight crosslinked polymers as a function of temperature and of accelerator to sulfur ratios.

EXPERIMENTAL:—

A number of pulse sequences are available to measure relaxation times defining different relaxation processes occurring in NMR experiments. The experiments were carried out on a Bruker MSL-300 spectrometer at a carbon frequency of 75.47 MHz. All the experiments were performed using gated high power decoupling. Zirconium oxide rotors of 7 mm diameter with Kel-F caps were used to acquire the NMR spectra. The chemical shift was scaled using adamantane, and magic angle spinning was employed to all the samples to reduce the chemical shift anisotropy.
Carbon T2 is measured by using a Carr-Purcell [33] pulse sequence as shown in figure 1. In carbon T2 a $90^\circ - \tau - 180^\circ - \tau$, and then the signal is acquired. A $90^\circ$ pulse of 7.25 $\mu$s duration and a $180^\circ$ pulse of 14.5 $\mu$s was used in this experiment. 5000 scans were signal averaged for each spectrum. A delay time of 5 s was used while a variable delay list has been created starting from 10$\mu$s to 3 s to acquire the spectra.

Peak intensities, instead of peak areas, and were plotted as a function of variable delay times and curve fit to determine the T2. Theoretically, peak areas are more reliable, but the determination of peak areas in the case of overlapped peak result into the significant departure from actual values due to the line shape problem.

RESULTS:

Figure 2 depicts the aliphatic region of differently cured high vinyl polybutadiene acquired using the Gated High Power Decoupling (GHPD) pulse sequence. Peak assignments are based on chemical shift calculations of different model compounds which are the closest analogues to the polybutadiene. The resonance at 25.1 ppm is designated as the cis carbon which is adjacent
to a vinyl groups, whereas the peak at 28.0 ppm indicates the presence of cis-1,4 CH₂ BR units. The resonance at 30.4 ppm is probably due to an accelerator (TBBS) fragment. Trans CH₂ of 1,4 BR units appeared at 32.6 ppm, while the resonance at 33.3 ppm corresponds to carbon attached either with di- or polysulfidic crosslinking. The peak at 34.6 is assigned as methylene carbon from the vinyl units. The carbon attached to the monosulfidic crosslink is predicted approximately at 36.3 ppm. The area from 39.0 to 44.0 ppm is ascribed to CH₂ carbon corresponding to 1,2 BR units. All these peak assignments were taken from initial work [34] using solution and solid-state ¹³C NMR techniques.

For T₂ experiments the magnetization of high vinyl polybutadiene was plotted versus the τ values as shown in figure 3. This plot shows that the magnetization decays exponentially with the τ values. In figure 4 the ν values obtained from swelling measurements are plotted as a function of T₂ for a resonance appeared at 25.0 ppm. It reflects the general trend that with the increase in ν (swelling) the T₂ decreases monotonically. Figure 5 represents the plot of T₂ versus the accelerator to sulfur ratios for a resonance that appeared at 25.0 ppm at 300 and 350 °K. The
values of $T_2$ increase as the temperature was increased from 300 K to 350 K. Generally the introduction of each crosslink decreases the relaxation time by providing an additional contribution to the relaxation.

Table I describes the $T_2$ values associated with different aliphatic carbons of vulcanized high vinyl BR for different formulations at 300 K. $T_2$ decreases from conventional to an efficient formulations, indicating decrease in mobility due to increase in crosslink density.

The activation energies for the reorientation of the polymer chain have been calculated using the Arrhenius expression,

$$\tau_c = \tau_0 e^{-E_a/RT} \quad (3)$$

where $E_a$ is the activation energy for reorientation, $R$ is the molar gas constant and $T$ is the absolute temperature [8]. The natural logarithm of the correlation time has been plotted as a function of the inverse temperature. A linear relationship is found with a slope proportional to the activation energy of the motion. The activation energies for the aliphatic carbons, determined via curve fit of equation 3, are listed in table VI.
DISCUSSION:

It is of interest to determine how the relaxation processes are influenced by the vulcanization. The dependence of chain mobility on stereo-chemical configuration has been observed in vinyl polymers, both for entire chain and for the steric sequences in atactic chain.

In synthetic polymers, the nuclear dipole-dipole interactions are the primary sources of relaxation. The relaxation of each carbon is determined primarily by the fluctuation of the C-H vectors with respect to the external magnetic field. In liquids the dipolar interactions are averaged out by rapid motion, but in polymers a complete averaging of dipolar interactions requires not only high frequency motion but also the co-operative motions of large sections of the polymer molecules.

The unvulcanized polybutadiene have relatively higher mobility because of the high Tₘ value is much lower than room temperature. With the introduction of crosslinks in the system the mobility is reduced by a significant amount and consequently broadening of the linewidth occurs. With the onset of cure the molecular motions become slower and become more anisotropic.
It is expected that any constraint present such as chemical crosslinks and entanglements will have a major effect on these long-range motions and produce a dominant contribution to $T_2$ relaxation. The $T_2$ dependence on an average mass between crosslinks demonstrates that $T_2$ measurements provide valuable information about low frequency long-range conformational motion. The presence of vinyl units greatly affects the chain motions since they relax differently from the corresponding 1,4-BR units. With the increase in crosslinking steric interferences increases among the local chain segments. The steric hindrance arising from the pendent vinyl units in polybutadiene also contributes in increasing the co-operativity of the segmental motion.

In the case of $T_2$, which involves the decay of the transverse magnetization to zero by dephasing, it is brought about only by fluctuating local magnetic dipoles. The increase in temperature results in an increase in the rate of molecular motions, ultimately exceeding the linewidth and consequently the resonance begins to narrow.
T₂ₜ was determined at different temperatures and is described in tables II to V for all formulations. Generally, T₂ₜ values show an increase with the temperature in all the samples. Small differences in T₂ₜ values indicate that we are probably dealing with the slow motion regime of typical T₁ vs τc plot. For the conventional formulation, the resonance appearing at 43.8 ppm corresponds to a crosslinking site reflects less change in the T₂ values. The overall rigidity increases with the introduction of crosslinks.

Cis, trans and vinyl methylene show an increase in T₂ₜ with the temperature for all three formulations. The aliphatic region is more susceptible to changes during the vulcanization reaction, compared to the olefinic carbons.

The correlation times were calculated using equation 1 for different temperatures. Figure 4 is a plot of T₂ₜ vs the ν (swelling); it shows the decrease in T₂ₜ as the ν value increased. The ν values were measured from swelling method for different formulations using cyclohexane as the swelling solvent. This indicates that the T₂ₜ decreases as we proceed from low to higher accelerator to sulfur ratios or greater crosslink density (Figure 5).
The observation of the formation of crosslinks is equivalent to the measurement of the variation of the relaxation rate of carbon of the polybutadiene. In this system the presence of permanent crosslinks gives an enhancement of the anisotropic effect, which appears as a linear function of accelerator to sulfur ratios.

The correlation times are plotted versus the reciprocal of temperature to observe the trend at different temperatures. In the case of correlation times ($\tau_c$), the introduction of each crosslink modifies its distribution in the similar manner to that caused by the entanglements. If the $\tau_c >> T_2$ the system is expected to behave as a pseudo-solid material. Similarly the effect of entanglements are the same as that of crosslinks on $T_2$ when present in significant numbers. The shape and distribution of the correlation times describing polymer chain motion might also be expected to change as a function of entanglements or physical crosslinks.

Figures 6 - 8 are the graphical illustrations of $\ln \tau_c$ versus the reciprocal of temperature. The variable positive slopes reflect the behavior of these motions in the polymer chains. The greater positive slope reflects the high rigidity of that particular carbon. The correlation times are roughly $1.1 \times 10^{-8}$ sec for
slow motions and $8.5 \times 10^{-9}$ sec for fast motions. The difference between the correlation times of carbons for the crosslinked and un-crosslinked chains is an order of magnitude.

The activation energies reflect the degree of rigidity in a polymer chain. The higher the activation energy, the more rigid a system will be. The methylene carbons assigned to $\text{CVV}$ (25.0 ppm), $\text{TTV}$ (32.6 ppm) and $\text{VVV}$ (39.0 ppm) have an activation energy approximately 2 orders of magnitude lower than the carbons involved in crosslinks. The resonances present at 28.0 ppm ($\text{CCC}$), 41.0 ppm ($-\text{CH}< \text{ of } \text{VVV}$) and 43.8 ppm ($-\text{CH}_2- \text{ of } \text{VVV}$) have higher activation energies (more rigid) due to the $\alpha$ nature to the crosslinks. The relatively lower activation energies for $\alpha$ carbons in original rubber material showed a more flexible backbone.

CONCLUSION:

Solid state NMR spectroscopy has been a valuable method for the characterization of macromolecular dynamics. The application of the NMR coherent averaging method to probe the chain dynamics has led to a renewed emphasis on describing the dynamic process in terms of both rate and the angular amplitude of motions.
In the case of T_{2c}, when studied as a function of accelerator to sulfur ratios, shows a significant increase in their values. The T_{2c} study deals with the slower motions of the chain as reflected in the plot versus the τ_{c}'s. At high temperature the effect of increasing crosslink density is to monotonically decrease the T_{2c} relaxation times.

Activation energies calculated from values of τ_{c} determined by a T_{2} experiment show that the backbone \(-\text{CH}_2-\) group corresponding CVV, TVV and VVV is more mobile, whereas the carbons directly attached to crosslinks are more rigid. The correlation times (τ_{c}) were used to compare the different mobilities as a function of temperature. It is reasonable to suggest that the increased freedom in the polymer chain is due to the increase in the temperature. Correlation times and activation energies studies based on T_{2} is an important tool for differentiating carbons involved in crosslinks. At this time, without molecular simulation techniques these results cannot be used to define the nature of the motion.
ACKNOWLEDGEMENTS:—

The authors wish to acknowledge the Monsanto Chemical Company, Akron, Ohio, for their technical support of this research.

REFERENCES:—


**TABLE I:**

T<sub>c</sub> TIMES (ms) OF ACCELERATED-SULFUR CURED HIGH VINYL POLYBUTADIENE AT 300 K.

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<tr>
<th>PPM</th>
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<th>SEV.</th>
<th>EV.</th>
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</thead>
<tbody>
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<td>1.89</td>
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<td>1.07</td>
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Error = ± 0.03 ms
TABLE II:--

CARBON-13 T2 VALUES CALCULATED AT DIFFERENT TEMPERATURES (ORIGINAL RUBBER)

<table>
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<th>PEAK POSITION</th>
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<th>330 (ms)</th>
<th>340 (ms)</th>
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<td>3.01</td>
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<td>3.13</td>
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<td>2.16</td>
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TABLE III:–

CARBON–13 T₂ VALUES CALCULATED AT DIFFERENT TEMPERATURE (CONVENTIONAL)

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<td>2.69</td>
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TABLE IV:–

CARBON-13 T2 VALUES CALCULATED AT DIFFERENT TEMPERATURE (SEMI-EFFICIENT)

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<td>2.57</td>
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<td>2.96</td>
<td>3.00</td>
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<td>1.63</td>
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TABLE V:

CARBON-13 T$_2$ VALUES CALCULATED AT DIFFERENT TEMPERATURE (EFFICIENT)

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TABLE VI:–

**ACTIVATION ENERGIES CALCULATED FROM ARRHENIUS PLOTS**

**FOR DIFFERENT FORMULATIONS.**

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<th>PPM</th>
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<th>CONV.</th>
<th>SEV.</th>
<th>EV.</th>
<th>COMMENTS</th>
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<td></td>
<td>( \times 10^3 \text{ J/mole} )</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>25.0</td>
<td>11.25</td>
<td>10.73</td>
<td>14.09</td>
<td>11.54</td>
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<tr>
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<td>MOBILE</td>
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<td></td>
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<td>36.55</td>
<td>33.77</td>
<td>RIGID</td>
</tr>
<tr>
<td>(-CH&lt; )</td>
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Error = \pm 0.50 \times 10^3
Figure 1. The schematic pulse sequence for C-13 NMR Carr-Purcell T2 experiment.
Figure 2. Magnified GHPD C-13 NMR spectra of aliphatic regions of conventional, semi-efficient and an efficient formulations, where "*" indicates the residual accelerator resonance.
Figure 3. A typical plot of C-13 magnetization of high vinyl BR vs the \( \tau \) for a \( T_2 \) experiment at 25 ppm.
Figure 4. The C-13 T_2 values plotted against the ψ (swelling) for 25.0 ppm obtained from the swelling measurement method.
Figure 5. Plot of T2 vs accelerator to sulfur ratios for 25.0 ppm resonance at $0 = 300 \text{ K}$ and $X = 350 \text{ K}$. 
Figure 6. Plot of $\ln \tau_c$ vs the $1000/T$ for different resonances, a) 25.0 ppm and b) 28.0 ppm for original = O, conv. = X, sev. = Δ and ev. = systems.
Figure 7. Plot of $\ln \tau_c$ vs the $1000/T$ for different resonances, a) 32.6 ppm and b) 39.0 ppm for original = O, conv. = X, sev. = $\Delta$ and ev. = systems.
Figure 8. Plot of $\ln \tau$ vs the $1000/T$ for different resonances, a) 41.0 ppm and b) 43.8 ppm for original = O, conv. = X, sev. = Δ and ev. = systems.


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