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Magnetic resonance imaging of elastomers and ion exchange resins

Kogovsek, Laurie Maylish, Ph.D.

Case Western Reserve University, 1994

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MAGNETIC RESONANCE IMAGING OF
ELASTOMERS AND ION EXCHANGE RESINS

by

LAURIE MAYLISH KOGOVSEK

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

Thesis Advisor: Professor William M. Ritchey

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August 1994
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GRADUATE STUDIES

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date 07/21/94

*We also certify that written approval has been obtained for any proprietary material contained therein.
MAGNETIC RESONANCE IMAGING OF ELASTOMERS AND ION EXCHANGE RESINS

ABSTRACT

by

LAURIE MAYLISH KOGOVSEK

Magnetic resonance imaging is a noninvasive technique used to study the properties of materials. For this research, various imaging methods were utilized to examine the morphology of elastomers and ion exchange resins.

Several imaging techniques were employed to study the properties of elastomers. Both spin-echo and multi-slice sequences were used to acquire images of polyisoprene with 10% carbon black to determine the distribution of carbon black. Variable temperature imaging was employed to image samples with short spin-spin relaxation times: filled and/or cured samples of styrene-butadiene rubber. Also a variable temperature multi-slice technique was used to image a portion of a tire tread that contained fibers. With multi-slice imaging the size and shape of defects within the elastomers and tire tread were determined in three dimensions without cutting into the material.

Magnetic resonance imaging was not only utilized to locate defects within elastomeric material but also used in determining their identity. The quantification of signal loss artifacts in gradient-echo images, when compared to a spin-echo image, could provide insight to
the identity of the substance in the defect. A greater signal loss at their interface reflects a larger the susceptibility difference between two substances. Several models were designed with rectangular defects that created a carbon black/polyisoprene and an air/polyisoprene interface. In some models, a greater signal loss was seen at the air/polyisoprene interface than at the carbon black/polyisoprene interface. Also the signal loss in the gradient-echo images increased with increasing echo time. A model consisting of agar gel and four circular defects was also imaged. Two of the defects contained air while the other two contained carbon black. This model design better resembled the round voids seen in the elastomer and tire tread samples. The two defects that contained air exhibited a smaller signal loss than the defects containing wet clumps of carbon black.

Also spin-echo imaging was used to examine the morphology of ion exchange resins. A multiple bead mount was developed to investigate the consistency of a sample of styrene divinyl benzene beads. Also several different types of styrene divinyl benzene beads, both cationic and anionic, were exposed to extremely acidic and basic environments after being swelled in deionized water. Images of the resins suggested that the average signal area of the beads changed. These changes were dependent on the solution and resin type. Signal loss due to a reduction in spin-spin relaxation below the echo time of the imaging sequence was ruled out by Carl-Purcell-Meiboom-Gill relaxation experiments.
DEDICATION

To my husband, Frank, and my parents Carol and Jack
and Jenny and Frank, Sr.
These special people helped me achieve my goals.
ACKNOWLEDGMENTS

There are many people who helped me earn this degree. First I would like to thank my husband Frank who for instance would accompany me to Case at three in the morning to start a run and who did all the household chores in the final months of writing. Without his help I would still be in grad school. This thesis was also made possible because of support of my extended family - especially my parents, Jack and Carol, who taught me how to set and achieve my goals, and to Frank’s parents, Frank, Sr. and Jenny, who always lend a helping hand in times of need which were many.

I would need to thank the many people at Case who made graduate life a little easier. Thanks to Dr. William Ritchey, my thesis advisor, for never letting me give up on my work; Dr. Garnett McMillan for his insights to science, thermodynamics, differential equations as well as life; and Dr. Adrian Valeriu for answering all my questions about the theory behind NMR and MRI with patience.

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Also I would like to thank all the guys in my research group who would never let me bash my husband in public. I need to thank Dave Hedrick who was instrumental in return to grad school and for his many political debates; Wayne Likavec for his great sense of humor, helping understand solids spectroscopy, and anointing me “bubble head”, John Waters, a polymer guru, for his writing and direction of our infamous NMR song and dance at the annual Christmas party and for being a great travel partner in San Francisco; Takeshi Saito for helping learn to use many software applications and for his interesting outlook on American culture; and finally Tony Wallner, my fellow liberal in the group, for helping relearn imaging and for listening to my bitching and moaning when I needed to vent. Also I needed to thank our adopted group member, Marnita Sandifer who always made me laugh, baby-sat me before my final oral, and showed me how to be true to my convictions. These fellow grad students made graduate life bearable.

There are several people who open my eyes to the fun of teaching. I must thank Dr. Ignacio Ocasio, my "second advisor," who taught me how to teach chemistry and make it interesting; Chris VanOrman who showed me the robes in teaching a chemistry lab my first semester of Chem 113; and Barbara Soltis, my mentor at Old Trail, who introduce me to the joy of teaching science to students of any age.

Finally I would like to thank my friends. First, thanks to my high school buddies, Vera Lillie Kitchen and Michelle Mehaliíc Pfeil, who even though our lives have moved in different directions have never let me forget what is really important in life. And a big thanks to my John
Carroll roommate, Wendy Wagner Clinger, for never allowing me to feel sorry for myself and for always giving me good advice during this stressful time. And to my special fiends from Tuesday Nite, Kim, Donna, Adrienne, Stella, and Betty, for showing how to regain my sanity and for showing me that there are many things in my life to be grateful for.
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LIST OF SYMBOLS AND ABBREVIATIONS

\( \chi \)  mass susceptibility
\( \phi \)  phase of magnetic resonance signal
\( \gamma \)  gyromagnetic ratio
\( \kappa \)  volume susceptibility
\( \Delta v_{1/2} \)  peak linewidth at half maximum
\( \theta_E \)  Ernst angle
\( \rho \)  density
\( \tau \)  a duration
\( \omega \)  Lamour frequency
2-D  two-dimensional
3-D  three-dimensional
\( A \)  maximum peak amplitude in CPMG experiment
\( B \)  magnetic field
\( B_0 \)  main magnetic field
\( C_{nv} \)  concentration of nuclei per voxel
CPMG  Carl-Purcell-Meiboom-Gill
\( D \)  diffusion coefficient in CPMG experiment
\( DR \)  digital resolution
DVB  divinylbenzene
\( E \)  amplitude of echo in CPMG experiment
\( \Delta F \)  frequency offset
FID  free induction decay
FLASH  fast low angle shot
FOV  field of view
FT    Fourier transform
G     spatial field gradient in CPMG experiment
G_x   frequency encoding gradient applied along the x-axis
G_y   phase encoding gradient applied along the y-axis
G_z   slice selection gradient applied along the z-axis
H     magnetic induction
hrs   hours
Hz    hertz
I     signal intensity
I_m   magnetization per unit volume of substance
k_e   normalization constant in CPMG experiment
kHz   kilohertz
μm    microns
mm    millimeters
ms    milliseconds
M     Molarity
MAS   magic angle spinning
MRI   magnetic resonance imaging
MW    molecular weight
N_x   number of complex points sampled along x-axis
N_y   number of phase encoding steps along y-axis
N_z   number of phase encoding steps along z-axis
NMR   nuclear magnetic resonance
PW    pulse width
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<td>SBR</td>
<td>styrene butadiene rubber</td>
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<td>SDVB</td>
<td>styrene-divinylbenzene</td>
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<td>S/N</td>
<td>signal to noise ratio</td>
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<td>$T_1$</td>
<td>spin-lattice relaxation time</td>
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<td>$T_2$</td>
<td>spin-spin relaxation time</td>
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<td>$T_2^*$</td>
<td>measurement of line broadening</td>
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<tr>
<td>$T_{ex}$</td>
<td>total experiment time</td>
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<tr>
<td>TE</td>
<td>echo time</td>
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<tr>
<td>TOSS</td>
<td>Total suppression Of Spinning Side bands</td>
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<td>repetition time</td>
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CHAPTER 1

INTRODUCTION TO THE THEORY OF MAGNETIC RESONANCE IMAGING
1.1 INTRODUCTION TO NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Magnetic Resonance Imaging is one of the techniques that evolved from Nuclear Magnetic Resonance (NMR) spectroscopy. In 1946, nuclear magnetic resonance was found in bulk materials by two independent groups. Purcell, Torrey, and Pound\textsuperscript{1} measured nuclear resonance absorption in solid paraffin, while Bloch, Hansen, and Packard\textsuperscript{2} discovered nuclear resonance in water. Within the next few years, it was discovered\textsuperscript{3-7} that the chemical environment of the nucleus affected its resonance frequency. Thus chemists looked to NMR as a technique to determine the structure of molecules.

An NMR spectrum of a substance can be obtained by continuous wave techniques\textsuperscript{8}. Usually the magnetic field is varied in a constant radio frequency signal. Sometimes the radio frequency is swept while the magnetic field is held constant. Because each resonance frequency in the spectrum is irradiated one at a time, these techniques are insensitive and time consuming.

In 1966, Ernst and Anderson\textsuperscript{9} showed that spectra could be obtained in relatively short times through the use of an intense radio frequency pulse and Fourier transform (FT) mathematics. All frequencies are irradiated at once through the use of a short radio frequency pulse. All Larmor frequencies are received simultaneously in the form of a free induction decay (FID). The information in the FID is transformed from a time domain into a frequency domain, or spectrum, via a Fourier transformation. FT-NMR allows for shorter overall experimental time
because all frequencies are irradiated at once. This rapid acquisition of a single response allows for time averaging of many repetitions to improve the signal to noise ratio (S/N). Thus the technique can obtain proton spectra of less concentrated samples -- in microgram quantities. It also allows for the routine study of less sensitive nuclei such as carbon-13, fluorine-19, phosphorus-31 and sodium-23. Also sensitivity increases with increasing magnetic field strength.

Two dimensional (2-D) NMR was proposed by Jeener in 1971. Two-dimensional NMR can be used to deconvolute complex one dimensional spectra of large molecules. A 2-D spectrum is obtained from the double Fourier transform of two time domains. Depending on the pulse program, the resulting 2-D plot could include homonuclear coupling constants and chemical shifts, heteronuclear coupling constants, or heteronuclear chemical shifts.

Until the mid 1970's, NMR spectroscopy was limited to substances in the liquid phase. NMR spectroscopy of solids was hampered by line broadening effects and long spin lattice relaxation times. As first shown by Schaefer and Stejskal in 1976, sharp line carbon-13 spectra of solid substances could be obtained by combining line narrowing techniques of magic angle spinning (MAS) and high power proton decoupling along with the signal enhancing technique of cross polarization.

Magic angle spinning was proposed independently by Andrew and co-workers and Lowe to remove line broadening caused by chemical shift anisotropy. This anisotropy is eliminated in liquids by
rapid, random motion. This behavior can be mimicked in solids by spinning the sample at an angle 54.7° to the main magnetic field.

However MAS is not an efficient method to eliminate line broadening due to dipole-dipole interactions. Samples mechanically can not be spun fast enough. High power proton decoupling can be used to narrow lines in carbon-13 spectra by eliminating dipolar interactions as was shown by Pines et al.\textsuperscript{16}

Long experimental times for solid carbon-13 spectra of hours or even days are due to long spin lattice relaxation times of the nuclei. Pines et al\textsuperscript{16} applied the idea of cross polarization. This process involves transferring spin polarization and energy between proton and carbon-13 nuclei. This results in decreased in relaxation time and an increase in signal intensity.

1.2 INTRODUCTION TO MAGNETIC RESONANCE IMAGING

The discovery of Magnetic Resonance Imaging (MRI) is credited to Lauterbur.\textsuperscript{17} In 1972, he produced the first two dimensional images of two 1 mm tubes containing water. The intensity of the first image was determined by the proton density. The intensity of the second image was determined by the spin lattice relaxation time due to the addition of an ionic species to one of the tubes. His technique combined the radio frequency of the magnetic field needed for nuclear resonance and linear magnetic field gradients which spatially mapped the spin density of the
nuclei. Thus he labeled this technique zeugmatography which is derived from the Greek $ζυγμα$ -- that which is used for joining.

1.3 MAGNETIC FIELD GRADIENTS

The generation of a magnetic resonance image depends upon the interaction of nuclei with a homogeneous magnetic field and linear magnetic field gradients. In a homogeneous magnetic field, chemically equivalent nuclei resonate at the same frequency that is designated as the Larmor frequency, $\omega$:

$$\omega = \gamma B_0$$

(1.3.1)

The Larmor frequency is directly proportional to the main magnetic field, $B_0$, and the gyromagnetic ratio of the nuclei, $\gamma$.

When a linear field gradient is applied along the $x$-axis, nuclei at different positions along this axis will resonate at different frequencies. As the field gradient increases along the $x$-axis, the nuclei resonate at higher frequencies. Thus the Larmor frequency is now spatially dependent on the strength of the applied gradient, $G_x$:

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

(1.3.2)

Consider a model consisting of two water tubes. When an FID is acquired of the model in a homogeneous magnetic field, the resulting Fourier transform of this signal would produce a single frequency line. If the FID is acquired in the presence of a linear field gradient applied along the $x$-axis, the resulting spectrum will consist of two broader lines because the nuclei are resonating at different frequencies. The FID is
said to have been frequency encoded, and the spectrum is a projection of the proton spin density along the x-axis.

1.4 BACK PROJECTION RECONSTRUCTION IMAGING

An image of the prementioned model can be constructed by combining several projections each taken along a different axis. This technique was proposed by Lauterbur.\textsuperscript{17} A second projection perpendicular to the first can be produced by applying a gradient along the y-axis. A series of projections at various angles can be acquired by combining the x and y gradients. See Figure 1.4.1. An image of the model can be produced from the projections through standard back projection reconstruction methods. The major drawback to this technique is that image quality is very dependent on the linearity of the applied gradients. A nonlinear gradient causes complex geometrical artifacts in the image.\textsuperscript{18,19} This technique is also sensitive to instrumental imperfections and large time requirements for data acquisition and processing. Because of these drawbacks, back projection reconstruction is not commonly used in routine clinical imaging.\textsuperscript{18,20}
Figure 1.4.1: Back projection reconstruction technique (from reference 18).
1.5 THE SPIN ECHO IMAGING TECHNIQUE

Current multi-dimensional imaging methods, such as the spin-echo technique, were based on NMR Fourier Zeugmatography that was proposed by Kumar, Weli, and Ernst.21 Like the back projection reconstruction method, this technique involves frequency encoding of the signal but only along one, defined as the x, axis. The signal along the second axis, defined as the y, is encoded by phase, $\phi$.

$$\phi = \gamma G_y y \cdot \tau$$

(1.5.1)

The phase of the signal is dependent on the strength of the gradient, $G_y$, the duration of the gradient, $\tau$, and the position of the spins, $y$, with respect to the gradient.

Both in Lauterbaur's and Ernst's techniques, the signal sampled was in the form of an FID. The initial data points of the FID can be corrupted by eddy currents produced by the rapid switching of the field gradients.20 Instead an echo signal can be sampled. In a spin echo pulse sequence, developed by Hahn 22, the echo is generated through the use of a 90° pulse follow by a 180° pulse. See Figure 1.5.1.23 The 90° pulse applied along the x-axis takes the longitudinal magnetization from the z-axis and places it into the transverse of x-y plane. The spins dephase in the transverse plane due to natural relaxation processes, main field inhomogeneities and applied gradients. After a time, $\tau$, a 180° pulse is applied along the x-axis. This pulse rotates the spins. After a second duration equivalent to the first value of $\tau$, the spins are refocused. This signal which is sampled is called a spin echo.

If only a frequency encoding gradient and a phase encoding
Figure 1.5.1: Spin-echo pulse sequence (from reference 23).

a) $90^\circ$ pulse  
b) Dephasing of spins  
c) $180^\circ$ refocusing pulse  
d) spins refocus
gradient are applied during an imaging sequence, the resulting image will contain information from that part of the object within the radio frequency coil. One method to decrease the volume of the object that is sampled is to define a slice within the object. Slice selection is achieved by applying a gradient along the z-axis, $G_z$, while the 90° pulse is applied. Since slice thicknesses of a centimeter or less are selected, longer, softer pulses (on the order of milliseconds) are used in imaging as compared with the shorter, harder pulses (on the order of microseconds) used in spectroscopy. The actual size of the slice, $\Delta z$, depends on the duration of the soft pulse, $PW$, and the strength of the gradient, $G_z$.24

$$\Delta z = \frac{1}{\gamma \cdot PW \cdot G_z} \quad (1.5.2)$$

Stronger gradients and longer pulses produce thinner slices.

A schematic of a spin echo imaging sequence is shown in Figure 1.5.2. First, a 90° pulse and a slice selection gradient in the z-direction are applied in order to excite the spins and select a slice. Second, a phase encoding gradient is applied in the y-direction. The gradient can be incremented in duration,21 or as Edelstein and coworkers25 suggested, incremented in strength. The latter method was given the name spin-warping. Concurrently, two rephasing gradients are applied in both the z and x-directions to rephase the spins that are dephased while the slice and frequency encoding gradients are applied.26 Third, a 180° refocusing pulse is applied along with a slice selection gradient. Fourth, a frequency encoding gradient is applied in the x-direction. During this time a spin echo occurs and n data points are collected.
Figure 1.5.2: Spin-echo imaging sequence.
The entire imaging sequence is repeated \( m \) times. Each time, the strength of the phase encoded gradient is incremented. (Typical values for \( n \) and \( m \) are 128, 256 and/or 512.) Thus a two-dimensional data set is produced where the variable along the \( x \)-axis is frequency, and the variable along the \( y \)-axis is phase. A double Fourier transform produces an image of intensity with axes defined by the frequency and phase encoding gradients. One of the main advantages of using Fourier transformation instead of back projection reconstruction is that there is a homogeneous error distribution over the whole frequency range.\(^{21}\)

Several parameters are defined by the pulse sequence. The duration between the \( 90^\circ \) pulse and the middle of the spin echo is termed the echo time (TE). The time between successive \( 90^\circ \) pulses is defined as the repetition time (TR). The duration of these parameters can, in part, determine the signal intensity of the image. Also the strength and duration of the gradients affect both the signal intensity and the resolution of the image.

1.6 IMAGE APPEARANCE - SIGNAL INTENSITY AND RESOLUTION

The appearance of an image depends on the resolution and signal intensity. Both are affected by the voxel size of the image. The voxel size depends upon the duration and strength of the three orthogonal gradients. As mentioned before, the size of the voxel in the slice direction is inversely dependent on the duration of the soft pulse and strength of the \( z \)-gradient.
In the frequency encoding direction, the field of view, FOV, is inversely proportional to the x-gradient, G_x, and the time between two sampled points, Δτ_x, in the digitized sample.

\[ \text{FOV}_x = \frac{2\pi}{\gamma \cdot G_x \cdot \Delta \tau_x} \]  \hspace{1cm} (1.6.1)

The digital resolution, DR_x, in this dimension is determined by the field of view and the number of complex points, N_x, sampled during the digitization of each echo.

\[ \text{DR}_x = \frac{\text{FOV}_x}{N_x} \]  \hspace{1cm} (1.6.2)

Commonly 128, 256, or 512 data points are collected.

In the phase encoding direction, the field of view is inversely related to the change in the strength of the γ-gradient, ΔG_y, in successive experiments and the duration of the gradient, τ_y.

\[ \text{FOV}_y = \frac{2\pi}{\gamma \cdot \Delta G_y \cdot \tau_y} \]  \hspace{1cm} (1.6.3)

The digital resolution in this direction, DR_y, is dependent on the field of view and the number of phase encoding steps required, N_y.

\[ \text{DR}_y = \frac{\text{FOV}_y}{N_y} \]  \hspace{1cm} (1.6.4)

Again, this gradient is incremented in strength 128, 256, or 512 times.  \(^20\)

Hence the voxel volume is the product of its three dimensions.  \(^26\)

\[ \text{voxel volume} = \Delta z \cdot \frac{\text{FOV}_x}{N_x} \cdot \frac{\text{FOV}_y}{N_y} \]  \hspace{1cm} (1.6.5)
In acquiring an image with a spin-echo pulse sequence with slice selection, the slice thickness is much larger (millimeters) when compared to the transverse plane dimensions (microns). Thus the term pixel resolution is use in discussing resolution in the x-y plane.

Generally, the pixel size can be decreased if the strength or duration of the x or y gradient is increased, the number of points sampled is increased, and/or the number of phase encoding steps is increased. However, if the resolution is increased, the signal to noise ratio (SNR) is decreased. Increasing the resolution by a factor of two reduces the SNR by a factor of four. Also increasing the duration of any gradient will increase the repetition time of the pulse sequence.

The signal received from a particular voxel depends upon the intrinsic sensitivity, abundance, concentration, spin-lattice and spin-spin relaxation times of the nuclei under study. Due to the high sensitivity and abundance of hydrogen, proton imaging is routine. Although imaging of other nuclei such as $^2$H, $^{13}$C, $^{17}$O, $^{19}$F, $^{23}$Na, $^{31}$P is possible.

Signal averaging can be used to overcome the problem of low concentration or short spin-spin relaxation time. However increasing the number of scans, $n$, will only increase the S/N by a factor of $\sqrt{n}$. This may have an adverse effect on the total experiment time, $T_{ex}$, which also depends on the number of phase encoding steps, $N_y$, and on the repetition time, TR.

$$T_{ex} = n \cdot N_y \cdot TR \quad (1.6.6)$$
Thus increasing the number of scans to improve S/N (or improving resolution by increasing the number of phase encoding steps or increasing the duration of a gradient) may make the length of the experiment too long to be practical.

The intensity of an image can be contrasted to reflect the spin density, spin-lattice or spin-spin relaxation times of the sample. The signal intensity, I, is dependent on concentration of nuclei per voxel, \( C_{NV} \), repetition time, TR, spin-lattice relaxation time, \( T_1 \), echo time, TE, and spin-spin relaxation time, \( T_2 \), as follows:

\[
I = C_{NV} (1 - \exp(-TR/T_1)) (\exp(-TE/T_2))
\]  

(1.6.7)

If the intensity of the image is to reflect only the spin density, two pulse sequence parameters must be set in accordance with the relaxation times of the nuclei under study. First, the repetition time should be set at least equal to five times the spin-lattice relaxation time of the sample. At "5\(T_1\)", 99% of the longitudinal magnetization has recovered through spin-lattice relaxation processes. Second, the echo time should be less than the spin-spin relaxation time of the sample. After the longitudinal magnetization has been tipped into the transverse plane by the 90\(^\circ\) pulse, the spins loose phase coherence due to spin-spin relaxation processes, in addition to, main field inhomogeneities and applied gradients. Thus the signal needs to be sampled before it completely dephases.

An image of a heterogeneous sample can be contrasted to reflect different relaxation times. If a sample is heterogeneous in that substances have different spin-lattice relaxation times, a \( T_1 \)-weighted
image can be obtained by selecting a repetition time that meets the "5-
T<sub>1</sub> rule" for only some substances. Thus substances with short T<sub>1</sub>'s will
appear bright; substance with longer T<sub>1</sub>'s will appear darker. If a
heterogeneous sample contains substances that have different spin-spin
relaxation times, a T<sub>2</sub>-weighted image can be acquired. An echo time is
chosen that is shorter than only some of the T<sub>2</sub>'s of the substances.
Thus substances with T<sub>2</sub>'s less than the echo time will appear as dark
regions in the image.

1.7 OTHER IMAGING TECHNIQUES

In addition to the spin-echo imaging sequence, there are other
sequences that are commonly used. One of these is the gradient-echo
sequence<sup>28</sup> shown in Figure 1.7.1. The main difference between the
sequences is that the gradient-echo does not employ a 180° pulse.
Instead, the sequence employs a negative gradient along the x-axis to
refocus spins that are dephased in the transverse plan. The echo formed
is due to this gradient hence the name gradient-echo. However, the
refocusing gradient does not refocus dephasing due to main field
inhomogeneities. Thus the main disadvantage is an increase in signal
loss especially at the interface of substances with different magnetic
susceptibilities. The main advantage to this sequence is that shorter
echo times can be utilized due to the absence of the 180° pulse. An
application of this imaging sequence will be discussed in Chapter 3.
Figure 1.7.1: Gradient-echo imaging sequence.
A variation of the gradient-echo sequence allows for a shorter overall experiment time. It incorporates a shorter repetition time and an excitation pulse of less than 90°.28 A reduction only in the repetition time would cause a decrease in signal intensity due to saturation. However, Ernst and Anderson9 discovered almost thirty years ago that the overall experiment time could be reduced without decreasing the S/N by also reducing the excitation pulse to a value less than 90°. The relationship between the reduced angle or Ernst angle, \( \theta_E \), the reduced repetition time, TR, and the spin-lattice relaxation time of the sample, \( T_1 \), is the following:

\[
\theta_E = \cos^{-1}\left( \exp\left(-\frac{TR}{T_1}\right) \right) \tag{1.7.1}
\]

However there is a reduction in the ability to acquire a \( T_1 \)-weighted image. The incorporation of this angle with the gradient-echo imaging sequence has come to be called fast low-angle shot (FLASH) or gradient-recalled acquisition in the steady state (GRASS).28 In medical imaging, this sequence is used in motion freezing techniques and the study of dynamic effects such as flow.

A multi-slice imaging technique29 permits imaging of several contiguous slices in a sample. In a spin-echo imaging sequence, one must wait approximately 5\( T_1 \) for the return of longitudinal relaxation. Instead of wasting this time, several other slices can be selected and imaged. The total number of slices that can be sampled is limited by the echo time of the sequence. The position of the excited slice is determined by the radio frequency’s carrier frequency. The frequency
offset, \( \Delta F \), needed to excite a slice at a position along the z-axis, \( Z \), is:

\[
\Delta F = \frac{\gamma}{2\pi} \cdot G_Z \cdot Z
\]  \hspace{1cm} (1.7.2)

If the carrier frequency coincides with the resonance frequency of the sample, the slice selected is at the iso-center of the slice gradient. However, the spin-echo pulse sequence does excite spins outside the selected slice. To avoid the potential problem of saturation of neighboring slices, they are excited in an interleaved method: first odd slices then even slices are excited. An application of this imaging sequence will be shown in Chapter 2.

The spin-echo pulse sequence used in multi-slice imaging produces slice thicknesses on the order of millimeters. Another technique, three-dimensional (3-D) imaging, allows for the acquisition of very thin slices through a second phase encoding gradient which replaces the slice selection gradient. See Figure 1.7.2. A nonselective 90° pulse is positioned before the gradients to excite the spins through the sample. (A gradient can still be applied along the z-axis to select a slab.) However the trade off for a thinner slice is an increase in total experiment time:

\[
T_{ex} = n \cdot N_y \cdot N_z \cdot TR
\]  \hspace{1cm} (1.7.3)

where \( N_z \) is the number of phase encoding steps in the z-direction. Data is collected from the entire volume instead of one slice resulting in an increase in signal. However, noise is produced from the entire volume no matter how the signal is collected. Thus another advantage of 3-D imaging a higher S/N ratio. One can sacrifice the improvement in
Figure 1.7.2: Three-dimensional imaging sequence.
signal to noise by reducing the repetition time - smaller signal due to saturation - to achieve a shorter experimental time. Also the 180° pulse can be eliminated reducing S/N but allowing for a shorter echo time.

1.8 INSTRUMENTATION

There are four major components needed for a nuclear magnetic imaging system: a magnet that can produce a homogeneous field within its bore, a set of coils that can generate linear gradients, a transceiver system that can produce and receive radio frequency signals, and a computer system for image processing.

There are three types of magnets that can be used in magnetic resonance imaging: permanent, electromagnetic, and superconducting. The type of magnet used depends upon the type of imaging - medical diagnostic, medical or materials research - being conducted. Permanent magnets produce the weakest fields while superconducting magnets produce the strongest fields. As field strength increases, the homogeneity of the magnetic field and the signal to noise ratio also increases. The Table 1.8.1 shows the uses of magnets at different field strengths. A Bruker superconducting magnet operating at 9.4 Tesla was used for the research for this thesis. The inner bore of the magnet measures 70 millimeters.

Permanent magnets consist of ferromagnetic material that can generate fields up to 1 Tesla. This type of magnet concentrates the field flux between the poles and produces little stray field. However, as the
Table 1.8.1 Uses of Magnets at Different Field Strengths

<table>
<thead>
<tr>
<th>USE</th>
<th>MAGNETIC FIELD (Tesla)</th>
<th>HYDROGEN FREQUENCY (MHz)</th>
<th>BORE SIZE (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectroscopy</td>
<td>17.6</td>
<td>750</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>14.1</td>
<td>600</td>
<td>50</td>
</tr>
<tr>
<td>Microscopy</td>
<td>11.7</td>
<td>500</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>9.4</td>
<td>400</td>
<td>70</td>
</tr>
<tr>
<td>Small animal MRI</td>
<td>7.0</td>
<td>300</td>
<td>180</td>
</tr>
<tr>
<td>Research Medicine MRI</td>
<td>4.7</td>
<td>200</td>
<td>400</td>
</tr>
<tr>
<td>Radiological MRI</td>
<td>4.0</td>
<td>170</td>
<td>125</td>
</tr>
<tr>
<td>Low Field Medical MRI</td>
<td>1.5</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>Experimental Low Field MRI</td>
<td>0.094</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.015</td>
<td>0.680</td>
<td></td>
</tr>
</tbody>
</table>
pole pieces are moved apart to accommodate human specimens, the strength of the field decreases to approximately 0.05 Tesla.\textsuperscript{34} Also permanent magnets are heavy and are limited in their design flexibility.\textsuperscript{18} These low field magnets may have a use in trauma units of hospitals because there is less risk of them attracting surrounding metal medical equipment.\textsuperscript{34}

In electromagnets, the field is generated by the flow of electrical current through coils of conducting wires. The simplest method to produce a linear magnetic field is to pass current through a solenoid. However, the field is not homogeneous since it decreases towards the ends of the solenoid.\textsuperscript{18} Instead, a set of four to six coils is oriented with respect to each other as if they were on the surface of a sphere.\textsuperscript{35} This design increases the uniformity of the magnetic field and field strengths of 0.2 Tesla can be attained.\textsuperscript{36} Another design which increases field homogeneity is to place the coils within the poles of iron cores. The magnetic field is increased, to approximately 0.5 Tesla, and stray fields are reduced due to the ferromagnetic material. But this type of electromagnet is extremely heavy. Electromagnets have a low initial cost and easy access to the coils in case of repair. However, the coils must be water cooled since heat is generated when current is passed through the coils due to the resistivity of the material.\textsuperscript{34} In addition, they have high power requirements and the fields can be unstable.\textsuperscript{36}

In a superconducting magnet, the field is furnished by the passage of current through coils that are shaped into a solenoid. The coils are made of superconducting material which can conduct current without
electrical resistance at extremely low temperatures. Extremely homogeneous fields can be generated over large bore sizes: 0.5 - 2.0 Tesla over 1 meter\textsuperscript{34} to 17.6 Tesla over 51 millimeter.\textsuperscript{37} The superconducting coils are placed in a bath of liquid helium which is enclosed in a cryostat.\textsuperscript{18} The cryostat system consists of head shields and a liquid nitrogen bath to prevent radiational heating. If the helium and thus the coil material reaches a temperature above the superconducting temperature, the coil will become resistive via local heating. Thus the magnet will rapidly deenergize which is a process known as quenching.\textsuperscript{34} Heating by conduction is reduced by using materials for the shields and baths that have low thermal conductivity. Convection heating is eliminated by placing the magnetic coils and the other materials in a vacuum.\textsuperscript{18} In addition to improved signal to noise ratio due to higher field strengths, superconducting magnets offer field stability and inexpensive daily operation costs. However, the magnets have a high start up cost that includes energizing the coils. Also the coils are not accessible for repairs and the magnet requires regular liquid cryostat fills.\textsuperscript{36}

The homogeneity of the magnetic field can be improved through the use of shim coils. The magnet is fitted with two sets of electromagnetic coils. By adjusting the amount of current in each of the coils, the homogeneity of the main field is improved. A set of cryoshims which are in the liquid helium bath are adjusted once - after the energization of the main field. A set of shim coils that reside in the inner bore wall are adjusted for regular fine tuning of the main field before a
This process of shimming can be done on a model with one chemical shift and monitoring the linewidth at half maximum, $\Delta v_{1/2}$, of the single peak:

$$\Delta v_{1/2} = \frac{1}{\pi \cdot T_2^*} \quad (1.8.1)$$

where $T_2^*$ is a measurement of line broadening due to spin-spin relaxation and magnetic field inhomogeneity. Actually it is easier to monitor the size and shape of the free induction decay. The larger the size and the more symmetrical the shape of the decay, the narrower the peak with a cleaner baseline upon Fourier transformation.

Linear field gradients are produced in three orthogonal directions by a set of coils located within the imaging probe. The simplest coil design is shown in Figure 1.8.1 a. The coil consists of two solenoids in which current flows in opposite directions. This type of coil design is used to generate gradients parallel to the main magnetic field. Gradient coils utilized to produce gradients perpendicular to the main field in the $x$ and $y$ directions are of a more complicated arrangement. They have a Golay or saddle shape geometry. See Figure 1.8.1b. The strengths of the linear gradients are dependent on the amount of current and the number of turns in the gradient coil. The strengths are measured in Gauss per centimeter. (One Tesla is equal to ten thousand Gauss.) The power to each gradient coil is supplied by a computer-controlled gradient amplifier. Since the gradients are switched on and off for a duration dictated by the imaging sequence, the amplifier must be capable of short rise times. A preamplifier may be used to correct the gradient
Figure 1.8.1: Gradient coil designs (from reference 39).

a) Solenoid gradient coil  b) Golay type gradient coil
voltages for less than satisfactory rise times. The switching on and off of gradients produces eddy currents in the surrounding material which can deteriorate image quality. To correct for these electronic currents, the gradient coils are driven by complex waveforms.

The transceiver system includes radio frequency coils which are used to produce oscillating magnetic fields in the megahertz range that excite nuclei. These were referred to earlier as excitation pulses. If quadrature excitation is employed, these coils generate rotating magnetic fields. The frequency ranges of the excitation pulses are generated by a synthesizer and soft pulses are shaped via a selective excitation unit. Hard and soft pulses are enhanced through a broad band or linear amplifier, respectively, before being sent to the radio frequency coil. These coils also detect the resulting signal, a spin or gradient echo, produced by the imaging sequence. These coils are located in the imaging probe, between the gradient coils and the sample, so that the fields that are transmitted or received are perpendicular to the main magnetic field. The different designs for these coils are shown in Figure 1.8.2. The Helmholtz design is used in the Bruker imaging probe. Several sizes of coils are available from 5 to 25 millimeters. If a sample would fit into a 5 mm NMR tube, then in theory a 5 mm coil should be used to achieve the best possible filling factor. The filling factor is the ratio of the coil volume to the volume occupied by the sample. If the smaller 5 mm coil was chosen, radio frequency artifacts would appear in the image. Thus in practice a 10 mm coil is used. After the transceiver has received a signal, it is sent to a low-
Figure 1.8.2: Types of radio frequency coils (from reference 18).

a) solenoid  b) Helmholtz  c) bird cage  d) surface
noise preamplifier and then to an amplifier. The radio frequency signal is converted to an audio frequency signal by a phase sensitive detector. The audio signal is transformed into binary data by using a conventional analog to digital converter. This binary data is then processed by the computer system.

The computer system consists of several components linked by a network. The central processing unit will have enough core memory to store operating software, pulse programs, imaging sequences, waveforms and raw image data sets. An array processor is employed to construct an image from a two or three dimensional data set. The processor must have buffered memory access so incoming data is not lost during image sequence execution. Actually, this processor converts the digital data into analog data so the image can be displayed on a cathode ray tube. This display screen is capable of displaying a 512 x 512 matrix and a continuous gray scale. Due to limits in the CPU core memory, raw data sets are archived on magnetic tape. Files can be transferred from the CPU to a VAX system and then backup copies are made.

1.9 APPLICATIONS OF MRI TO MEDICINE

Since its discovery in 1972 by Lauterbur, magnetic resonance imaging may have been associated with medical research because of a discovery by Damadian in 1971. He observed that spin-lattice relaxation times were elevated for tumourous tissues. In 1976, Mansfield and
Maudsley\textsuperscript{41} imaged a cross-section of a human finger. Then in 1977, Hinshaw, Bottomley and Holland\textsuperscript{42} produced an image of a human wrist with an X-ray comparable in plane resolution of 0.4 mm. Since these discoveries, magnetic resonance imaging has grown into a medical diagnostic tool for several reasons. The human body consists of 55 percent water overall, while soft tissue in the body contains 60 to 90 percent water.\textsuperscript{43} The tissues could be distinguished due to a difference in water content along with variances in both spin-lattice and spin-spin relaxation times.\textsuperscript{43,44} Some applications of imaging in medicine are the detection of tumors in the brain, along the spinal column, and in the muscle tissue. MRI is a tool used in the study of cerebrovascular disease, abnormalities of brain white matter, effects of epileptic seizures, spinal cord trauma, vertebral disk herniation, joint injuries, bone marrow disorders and congenital heart disease. Also MRI can be used to visualize blood vessels (angiography), to measure tissue blood flow (perfusion), and to measure a change in water content of tissue (diffusion). Research continues in these areas as well as applications of MRI to disorders of the beast, chest, abdomen and pelvis, the development of new contrast agents for relaxation-weighed images, and neurological and psychological disease.\textsuperscript{45-47}

\section*{1.10 APPLICATIONS OF MRI TO MATERIALS RESEARCH}

Although not as extensive as medical imaging, MRI has been used to study the properties of several different types of materials such as
ceramics. For example, Ackerman, Garrido and co-workers\textsuperscript{48,49} used MRI to study the porosity, organic binder distribution, and void distribution in green-state ceramics. Samples of ceramics were filled with a protonated solvent to map out areas devoid of ceramic material in the image. Several groups\textsuperscript{49,50} have looked at the process of slip casting ceramics via imaging the water present in the material. Wallner and Ritchey\textsuperscript{51} used both spin-echo and gradient echo image sequences to observe porosity, void distribution, and bore hole uniformity in solvent filled ceramics.

Several imaging studies have been conducted to analyze properties of other porous material. Komoroski et al\textsuperscript{52} qualitatively studied the porosity of sintered glass disks filled with water. Defects were enhanced in images by employing a gradient-echo pulse sequence. Fordham and co-workers\textsuperscript{53} observed simulated voids in cement slurries. However the iron contained in the cement attenuated the signal intensity. Watson et al\textsuperscript{54} have studied the multiphase flow of water in porous limestones and sandstones, while Osment and co-workers\textsuperscript{55} studied porosity and void distribution in wet samples of natural limestone and sandstone.

Recently, MRI has been applied to study the characteristics of soil, rock, and coal. For example, Tollner and co-workers\textsuperscript{56} tried to quantify the effect of iron content in wet and dry soil samples on image quality. Fordham et al\textsuperscript{57} examined the depth filtration of clay in rock cores. Only qualitative one-dimensional images were used for this study. Botto and co-workers have imaged sample of coal swollen with solvent using
various three-dimension techniques\textsuperscript{58} and imaged a solid sample of coal itself using a solid imaging technique.\textsuperscript{59}

Another area of interest for MRI is the investigation of plants and wood. Southern and Johnson\textsuperscript{60} utilized both spin-echo and gradient echo pulse sequences to image the water content of the roots of an oat plant and the surrounding soil. Also Walter and co-workers\textsuperscript{61} have used MRI as a tool to investigate the water content and binding of plants and leaf growth under conditions of high salinity. McCain and Markley\textsuperscript{62} imaged tulip tree and cottonwood leaves to determine water content, thickness, and changing morphology. McDougall et al\textsuperscript{63} have observed two different growth morphologies of the stems in flax plants using MRI, while Johnson and co-workers\textsuperscript{64} have used spin density, T\textsubscript{1}-weighted and T\textsubscript{2}-weighted images to distinguish different types of tissue in squash stems. In the study of wood, Chang et al\textsuperscript{65} used MRI to differentiate different types of tissue based on water content on samples of white oak and black cherry. While Olson and co-workers\textsuperscript{66} studied the drying process in oak samples by monitoring moisture content via MRI. And finally, Morris et al\textsuperscript{67} examined the three stages of germination of a castor bean by monitoring the water uptake through T\textsubscript{1}-weighted images.

Magnetic resonance imaging has also been employed to noninvasively study the structure and properties of food itself and during processing. Duce, Carpenter, and Hall\textsuperscript{68} used a spin-echo technique to obtain images of various types of chocolate bars contained in their wrappers. Since signal intensity was derived from lipids, different
components (such as nuts, raisins, and chocolate) were distinguished. A modified imaging technique was used by Heil, Perkins, and McCarthy\textsuperscript{69} to determine the percentage of vegetable oil in French salad dressing. The proton density projection of the oil phase and water phase were obtained with a spin echo sequence with the phase encoding gradient turned off. Song and Litchfield\textsuperscript{70} measured the change in the moisture distribution in corn while drying using both a three-dimensional and a multi-slice two-dimensional spin-echo method. Ruan et al\textsuperscript{71} employed a two-dimensional spin-echo sequence to acquire proton density images of potatoes during drying and absorption of water. These images were used in the mapping of the internal moisture distribution and the calculation of the effective moisture diffusion coefficient.

Also magnetic resonance imaging has been used to study the morphology of, diffusion in, and polymerization of polymers. Several groups have developed solid imaging techniques to image polymers that have not been swollen with solvent or do not have elastic properties and thus cannot be imaged with conventional imaging techniques. A review of this research will serve as an introduction to Chapter 2.

1.11 CONCLUSION

Magnetic resonance imaging, along with two-dimensional and solids spectroscopy, has its beginnings in nuclear magnetic resonance spectroscopy. This technique combines the radio frequency of the magnetic field and magnetic field gradients to produce images that
spatially map the spin density of the nuclei in a selected region in the sample. Also relaxation-weighted images can be produced by picking proper timing parameters in the imaging sequence. There are many methods used to obtain images such as back projection reconstruction, spin-echo, gradient-echo and three-dimensional imaging. Each has advantages and disadvantages. The four major components needed for an imaging system are a magnetic, gradient coils, a transceiver and a computer system. One of the main advantages of MRI is that it is a noninvasive method. That is a major reason why it is used as a medical diagnostic tool. Although the majority of research is conducted in the field of medicine, some are using this nondestructive tool to study the properties of materials with a high liquid content or that are filled with a solvent. These materials include ceramics, soils, plant life, food, elastomers and more rigid polymers.
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CHAPTER 2

UTILIZING MAGNETIC RESONANCE IMAGING TECHNIQUES TO STUDY THE PROPERTIES OF ELASTOMERS
2.1 INTRODUCTION TO ELASTOMERS

An elastomer is a type of polymer that is distinguished by its elasticity. Characteristically, this kind of polymer can be mechanically stretched to at least double its length at room temperature. Upon release of the stress, the material will return to its original shape. Also, an elastomer can be defined as a polymer that is at a temperature between its glass transition temperature and melting point. The elasticity can be enhanced by crosslinking of the polymer chains which increases the melting point.¹

The common name for an elastomer is rubber. Elastomers can occur naturally such as natural rubber and gutta percha. However during both World Wars, supply routes to Asian and South American countries that furnished natural rubbers were blocked. Thus research was conducted to produce synthetic rubber. Early synthetic materials were made from starting materials of dimethylbutadiene (methyl rubber), butadiene (Buna rubber), butadiene and styrene (Buna-S or Government Rubber). Today, there are several types of synthetic rubber including the styrene-butadiene copolymer (SBR), isobutene-isoprene copolymer (butyl rubber), cis-polybutadiene, and cis-polyisoprene which matches natural rubber in structure and properties. Rubber is used primarily in the manufacture of tires and tubing. Rubber materials are also used in mechanical devices, clothing, toys, and adhesives.²

Actually raw rubber material is not an elastomer but a thermoplastic which flows when exposed to heat or pressure. Thus to increase the elasticity of the rubber, crosslinks are introduced between
polymer chains by a process called vulcanization. This sulfur-induced crosslinking of natural rubber was discovered independently by Charles Goodyear in 1839 and Thomas Hancock in 1843. Crosslinking can be accomplished by other chemical substance such as peroxides. Other substances, such as fillers like carbon black, anti-aging compounds, dyes and plasticizers, are added to the raw material during compounding to adjust the final product's chemical and physical properties.

2.2 REVIEW OF STUDYING ELASTOMER PROPERTIES VIA MRI

Several methods are used to study the properties of elastomers including thermal techniques such as differential scanning calorimetry and thermogravimetric analysis, separation methods such as gas and size exclusion chromatography, and spectroscopic techniques such as infrared and nuclear magnetic resonance. Within the last decade, magnetic resonance imaging has been employed to study the spatial structures of materials. The main advantage of MRI is that it is noninvasive.

Many materials cannot be imaged by imaging techniques used in medical diagnosis due to their short spin-spin relaxation times. However, polymers with longer spin-spin relaxation times, such as elastomers, can be imaged with conventional techniques. Chang and Komoroski used a two-dimensional spin-echo technique to image samples of bulk cis-polyisoprene, natural rubber, and cured, carbon filled cis-polyisobutylene. It was shown that image intensity is affected by chain segment mobility,
which is a determinate in the spin-spin relaxation time, and the echo time of the pulse sequence. In a continuation of this work, Sarkar and Komoroski obtained images of diblends of cis-polybutadiene and styrene-butadiene rubbers through a multi-slice spin-echo technique. As the amount of styrene-butadiene increased in the blend, the signal intensity of the image decreased due to an overall decrease in spin-spin relaxation time. They also employed a three-dimensional multi-slice sequence to image the elastomeric components of a section of a non-steel-belted bias-ply tire. A three-dimensional pulse sequence has the advantage over a two-dimensional sequence of employing a shorter echo time. This allows for the imaging of samples with shorter spin-spin relaxation times. The spin-spin relaxation time of the tire elastomer was decreased due to the addition of fillers such as carbon black.

Void distribution in different elastomers were studied. Blumler and Blumich obtained two-dimensional spin-echo images of natural rubber to determine the location of defects in the material as well as to follow the aging of the sample. Webb and co-workers employed a two-dimensional spin-echo imaging sequence to detect the defects in samples of natural and epoxidated natural rubber. Regions of low signal intensity were attributed to voids or areas of concentrated crosslinking. Both would have shorter spin-spin relaxation times as compared to the elastomeric material. The natural rubber was saturated with cyclohexane and again imaged to distinguish voids from crosslinked areas. Smith and Koenig obtained proton images of cured, cis-1,4-polybutadiene swollen with deuterated cyclohexane with both a single and a multiple spin-echo
pulse sequence. Swelling of the elastomer allowed enhancement of voids and other defects above the image resolution which in part was determined by gradient strength.

Distribution of substances in filled elastomers can be studied through imaging. For instance, Garrido et al.\textsuperscript{9} obtained both two-dimensional gradient-echo and spin-echo images of crosslinked polybutadiene. The homogeneity of the signal intensity was used to judge the uniformity of crosslinks and filler distribution in the material. Kapadia\textsuperscript{10} obtained two-dimensional spin-echo images of styrene butadiene rubber that contained varying amounts of carbon black. It was found that signal intensity decreased as the amount of carbon black increased. This was attributed to restricted polymer chain motion.

\section*{2.3 Review of Solid Imaging Techniques}

As mentioned before, more rigid polymers are not imaged by conventional imaging techniques because of their short spin-spin relaxation times. However several groups have used solvent ingress to circumvent this problem to study void distribution in several types of polymers. Hoh and co-workers\textsuperscript{11} studied the void distribution in three different composites (polyester, high catalyst content nylon, and low catalyst content nylon) with two-dimensional imaging. The proton density images display the content of water that had been soaked up by the composites. The imaging results correlated with the measured increase in weight of the samples. Jezzard et al.\textsuperscript{12} have used both two-
dimensional and three-dimensional imaging to detect voids in carbon fiber reinforced composites. The samples were exposed to water so any surface connected voids would fill. The appearance of the water signal in the two-dimensional images corresponds to the results from ultrasound measurements. Krejsa and Koenig\textsuperscript{13} employed two-dimensional spin-echo technique to obtain images of solvent swollen cured elastomers. Cured butyl rubber was swollen with different solvents, benzene and cyclohexane. The areas of low signal intensity or low solvent uptake were associated with areas of high crosslink density.

However, there are two main disadvantages to the solvent ingress technique. Swelling of the material may change the original shape of voids. Also there is the possibility of an interaction between the solvent and the material which could affect the appearance of the image.

Acquiring images of a solid material itself using conventional imaging techniques is difficult due to line broadening caused by chemical shift anisotropy and dipolar coupling. Broad line widths decrease both the resolution and signal to noise ratio of an image. Solid imaging methods used to decrease line broadening can be divided into three broad categories. First, large magnetic field gradients are used in a brute force method. Second, solid NMR spectroscopy line narrowing techniques such as multiple pulse sequences or magic angle spinning can be used with smaller gradient strengths. Third, echo pulse sequences are used with phase encoding gradients.

An example of using large gradients was presented by Carpenter, Hall and Jezzard\textsuperscript{14} who developed a modified gradient system which
allows for imaging of solids that have spin-spin relaxation times ≥ 0.5 ms. This system allows for gradient rise times on the order of 100 μs which, in turn, reduces the echo time of the imaging sequence. Also conventional imaging pulse sequences can be used with this system. Three-dimensional images of a solid polyisoprene sample with man-made voids were obtained in thirty minutes.

Several other groups are using multiple pulse sequences for line narrowing in order to image solids. Tokarczuk and McDonald\textsuperscript{15} have presented a detailed theoretical discussion of the zigzag sequence which consists of a series of 90° pulses separated by equal duration times. This multiple pulse sequence when used with sinusoidally driven field gradients offers a smaller time span for the refocusing of chemical shift, susceptibility, and main field inhomogeneity line broadening. Cory and co-workers\textsuperscript{16} have developed a solid imaging technique which involves a phase shifted version of the MREV-8 multiple pulse cycle. The pulse cycle in itself eliminates dipolar line broadening and reduces chemical shift interactions. By phase shifting certain pulses, chemical shift and susceptibility shifts are eliminated by second averaging. In this technique, gradients are applied between the longer durations amid the pulses which avoids gradient interference with solid echoes produced by the pulse sequence. A two-dimensional image of a poly(methyl methacrylate) model was produced with the above sequence and calculated from a back projection reconstruction method. No slice selection was employed. A spatial resolution of approximately 100 μm was reported. Cory, Miller and Garroway\textsuperscript{17} have developed a one-
dimensional imaging technique which combines a 48-pulse homonuclear dipolar decoupling cycle and a time-dependent magnetic field gradient. This multiple pulse sequence, in addition to eliminating dipolar line broadening, refocuses chemical shifts. This technique allows for modest gradient strengths. Thus sensitivity is not lost to large detection bandwidths. One-dimensional images of ferrocene (spatial resolution of 30 μm) and pressure crystallized polyethylene (spatial resolution of 300 μm) were obtained with this technique which has been named CMG-48.

An example of imaging solids with echo pulse sequences is given by Rommel, Hafner, and Kimmich\(^\text{18}\) who proposed imaging of solid material through a Jeener-Broekaert phase encoding imaging (JEPHI) technique. The phase encoding gradients, in two or three dimensions, are turned on between the first and second pulse of the Jeener-Broekaert pulse sequence. Between the second and third pulse, signal information is conserved in the dipolar order state. The third pulse produces an echo which contains the signal information. Two dimensional images of hexamethylbenzene and polytetrafluoroethylene were obtained using this technique without slice selection. A spatial resolution in both dimensions of 1.7 mm was reported. A LOSY (localized spectroscopy of solid samples) pulse sequence was investigated as a means of slice selection. Demco, Hafner, and Kimmich\(^\text{19}\) have developed a magic echo phase encoding imaging (MEPSI) technique. The formation of magic echoes provides longer evolution intervals and the coherences are refocused completely in comparison to the Jeener-Broekaert phase encoding signals or solid echoes. Two dimensional images of a plastic plug and of a
cylindrical hexamethyl-benzene tetrafluoroethylene sandwich sample using the MEPSI technique are shown. No slice was employed, but the use of a LOSY pulse is suggested. They further discuss\textsuperscript{20} the theory of MEPSI technique as well as a newly developed technique: the rotary-echo phase-encoding solid imaging (REPSI) technique which permits phase encoding in the rotating frame through a rotary echo.

Another avenue for solids imaging has been proposed. Jezzard and co-workers\textsuperscript{21} suggested imaging at elevated temperatures using standard pulse sequences and hardware used for liquid imaging. The increase in temperature lengthens the spin-spin relaxation time of the solid so spin-echo sequences with an echo time of 1.5 ms can be employed. Also the sample size is only limited by the bore size. This is an advantage over magic angle spinning and multiple pulse techniques since sample sizes are limited to approximately 0.5 cm due to sample rotation and the requirement of intense homogeneous radio frequency pulses, respectively. An image of a sample of commercial poly(vinyl acetate) at 62°C was obtained. Also Jackson\textsuperscript{22} has used elevated temperature imaging to observe the curing process of a continuous carbon-fiber reinforced epoxy resin. A series of two-dimensional images, obtained with a spin-echo sequence, were taken of a multi-laminate sample at a range of temperature between 40 and 90°C. At 60°C, the first image of the resin is seen due to an increase in the spin-spin relaxation time. After the sample reached 90°C, the intensity of the images decreases over time due to a decrease in molecular motion because of curing.
2.4 OBJECTIVES OF RESEARCH

There were four main goals of the following research. The first was optimizing the operating parameters of the spin-echo and multi-slice pulse programs currently in use. Second was employing the multi-slice technique to follow how the morphology changed in a sample of filled polyisoprene and to quantify the defect sizes. Third was to improve the signal to noise ratio of images of several samples of styrene butadiene rubber (SBR) with a variable temperature technique. (The structure of both elastomers are shown in Figure 2.4.1.) The increase in image quality was compared to changes in relaxation parameters. And finally the multi-slice and variable temperature technique was used in combination to study the morphology of a commercial tire tread.

2.5 EXPERIMENTAL

All images were obtained with a Bruker MSL 400 with micro imaging accessories operating at a frequency of 400.13 MHz. The nucleus of interest was proton. The proton signal in the images of the polyisoprene and styrene butadiene rubber is most likely due to the methyl group and phenyl group, respectively, attached to the carbon backbone. The pulse sequences, spin-echo and multi-slice, used in this study were developed by Martine Ziliox and Sam Gravina, respectively, of Bruker Instruments (Billerica, Massachusetts). Both pulse sequences employed selective 90° and 180° pulses. The vertical artifact along the frequency encoding axis in the images is due pulse breakthrough. This
Figure 2.4.1 a: Structure of polyisoprene.

b: Structure of styrene butadiene rubber.
radio frequency interference overwhelms the signal from the sample. Signal which is erroneously not phase encoded manifests itself as a horizontal artifact along the phase encoding axis. This type of artifact appears in the multi-slice images. The largest radio frequency coil available, 25 mm, was used to obtain maximum signal to noise ratio. Samples were placed in a 20 mm NMR tube to reduce the possibility of radio frequency artifacts. Additional equipment (a heater, thermocouple, and air line) was needed for the variable temperature experiments. Samples that were imaged at an elevated temperature were placed in the probe approximately thirty minutes before the initiation of the imaging sequence to allow samples to achieve thermal equilibrium. Figure 2.5.1 shows how this equipment is integrated into the micro imaging probe.

For the spin-echo images, the image pixel dimensions were 256 x 128 (frequency encoding versus phase encoding). For the multi-slice images the number of pixels in the frequency encoding direction was reduced to 128 to reduce the overall experimental time. The field of view is determined by the inner diameter of the NMR sample tube which was 18 mm. Hence the pixel resolution of the spin-echo images was 70 μm x 140 μm, while the multi-slice pixel resolution was 140 μm x 140 μm. The slice thickness for every image was 1 mm. The slice gradient is applied along the z-axis which is defined as being collinear to the main magnetic field. The phase encoding gradient is implemented along the y-axis, while the frequency encoding gradient is applied along the x-axis.

Gradient strengths and timing parameters vary slightly from image to image due to the fact that optimal imaging parameters were also being
Figure 2.5.1: Imaging probe with variable temperature capabilities.
determined during these studies. A summary of these parameters can be found in Tables 2.5.1 - 2.5.3. Also before every imaging session, a water model is used to shim the main magnetic field and to select parameters which ensure that the image shape is circular and the screen field of view is filled. The model consists of a 10 mm NMR tube containing distilled water that was fitted into a 20 mm NMR tube containing doped water (0.004 M CuSO₄). Because the doped water has shorter relaxation times than distilled water, the model also can be used to check the timing parameters of echo and repetition time.

All elastomer samples that were used were obtained from James Visintainer of The Goodyear Tire & Rubber Company (Akron, Ohio). The polyisoprene sample contained 10% carbon black by weight. A total of four SBR samples were used in this study, two were uncured and two were cured by irradiating the samples with 70 megarads of Cobalt-60. Also one of the uncured and one of the cured samples contained 10% carbon black by weight. The samples were supplied in sheets. Pieces of the sheets were cut with scissors to a size of approximately 30 mm x 17 mm x 3 mm to fit the inner diameter of the 20 mm NMR tube. Refer to Figure 2.5.2 for a pictorial view of how the sample was placed in the tube and how the slice selection was made.

The relaxation study was performed on the SBR samples using a Carl-Purcell-Meiboom-Gill software package provide by Bruker. The timing parameters can be chosen by the operator. The resulting peak heights were measured manually. A Windows compatible graphics
Table 2.5.1 Experimental Parameters for Polyisoprene Study

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>SPIN-ECHO SINGLE SLICE</th>
<th>MULTI-SLICE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slice Thickness</td>
<td>1 mm</td>
<td>1 mm</td>
</tr>
<tr>
<td>Gradients Z</td>
<td>2.34 G/cm</td>
<td>2.34 G/cm</td>
</tr>
<tr>
<td>Y</td>
<td>2.22, 2.54 G/cm</td>
<td>4.76 G/cm</td>
</tr>
<tr>
<td>X</td>
<td>3.43, 2.88 G/cm</td>
<td>3.30 G/cm</td>
</tr>
<tr>
<td>Echo Time</td>
<td>11.2, 9.4 ms</td>
<td>5.1 ms</td>
</tr>
<tr>
<td>Repetition Time</td>
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<td>0.125 sec</td>
</tr>
<tr>
<td>Overall Experiment Time</td>
<td>14.2, 17.1 hrs</td>
<td>17.1 hrs</td>
</tr>
<tr>
<td>Image Size</td>
<td>256 x 128</td>
<td>128 x 128</td>
</tr>
<tr>
<td>Digital Resolution</td>
<td>70 µm x 140 µm</td>
<td>140 µm x 140 µm</td>
</tr>
<tr>
<td>PARAMETER</td>
<td>SPIN-ECHO SINGLE SLICE</td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------------</td>
<td></td>
</tr>
<tr>
<td>Slice Thickness</td>
<td>1 mm</td>
<td></td>
</tr>
<tr>
<td>Gradients</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>2.34 G/cm</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>2.54 G/cm</td>
<td></td>
</tr>
<tr>
<td>X</td>
<td>2.88 -3.20 G/cm</td>
<td></td>
</tr>
<tr>
<td>Echo Time</td>
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</tr>
<tr>
<td>Repetition Time</td>
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<td></td>
</tr>
<tr>
<td>Overall Experiment Time</td>
<td>17.1 hrs</td>
<td></td>
</tr>
<tr>
<td>Image Size</td>
<td>256 x 128</td>
<td></td>
</tr>
<tr>
<td>Digital Resolution</td>
<td>70 μm x 140 μm</td>
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Table 2.5.3 Experimental Parameters for Tire Tread Study

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>SPIN-ECHO MULTI-SLICE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slice Thickness</td>
<td>1 mm</td>
</tr>
<tr>
<td>Gradients Z</td>
<td>2.34 G/cm</td>
</tr>
<tr>
<td></td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Echo Time</td>
<td>5.1 ms</td>
</tr>
<tr>
<td>Repetition Time</td>
<td>2 sec</td>
</tr>
<tr>
<td>Overall Experiment Time</td>
<td>17.1 hrs</td>
</tr>
<tr>
<td>Image Size</td>
<td>128 x 128</td>
</tr>
<tr>
<td>Digital Resolution</td>
<td>140 μm x 140 μm</td>
</tr>
</tbody>
</table>
Figure 2.5.2: Sample position in NMR tube with relation to slice selection.
package, ORIGIN, was used to calculate spin-spin relaxation times from timing parameters and peak heights.

The commercially available tire tread was also provided by Dr. Visintainer, however it was not a Goodyear product. Pieces of the tread of approximately 30 mm x 12 mm x 12 mm in size were cut with an exacto blade. Pieces were cut so to include both carbon filled elastomer and cording.

2.6 RESULTS AND DISCUSSION OF POLYISOPRENE - MULTI-SLICE STUDY

A polyisoprene sample with 10% carbon black by weight was used for this study. Figure 2.6.1a shows a spin echo image of the sample. The repetition time was 0.5 s, while the echo time was 11.2 ms. (These timing parameters were routinely used to image liquid samples.) Three areas of intensity are seen along with a distribution of small circular areas of low intensity. The small circular areas may be attributed to agglomerates of carbon black and/or small air pockets. Also present are two large voids appearing on the upper and lower left side of the image. Another spin echo image, shown in Figure 2.6.1b, was taken of the second slice position but with a longer repetition time, 2.0 s, and a shorter echo time, 9.4 ms. These timing parameters better reflected the longer spin-lattice and the shorter spin-spin relaxation times of elastomers as compared to liquids. The sample in this image appears as
Figure 2.6.1 a: Spin echo images of a polyisoprene sample with 10% carbon by weight.
b: This image was taken with a longer TR, shorter TE and at a different slice position.
one general area of high intensity with small circular areas of low intensity and one large void in the upper right corner.

The differences in image appearance may be due to the fact that the carbon black and/or void distribution varies throughout the sample. One could repeat the two experiments at the two different slice positions to show data reproducibility. However each image using the second set of timing parameters would take approximately 17 hours. This is probably not a wise use of instrument time. The alternative is to use a multi-slice technique. As explained in Chapter 1, several slices are selected and imaged while one waits for the first slice to relax. Thus several images can be acquired with the multi-slice technique in the time it takes to image one slice with the spin-echo method.

A multi-slice experiment was performed to confirm the different appearances of the spin-echo images. A 16 slice experiment (repetition time of 2.1 s and echo time of 5.1 ms) was run in the same amount of time that it took to run one spin-echo experiment. These images are shown in Figure 2.6.2 and 2.6.3. Slice positions 1 through 8 resemble the spin echo image in Figure 2.6.1a in that three general areas of varying intensity are seen. Slice positions 10 through 16 resemble the spin echo image in Figure 2.6.1b in that only one general area of intensity is seen throughout the sample. The multi-slice images confirms what is seen in the two spin-echo sequences. The sample has a heterogeneous morphology due to uneven mixing of the carbon black. Also a large void in the upper right corner can be followed through slice positions 9 to 14. Thus it is at least 6 mm long, 2 mm in diameter, and
Figure 2.6.2: Multi-slice of the polyisoprene sample.

a: Slice positions 1 through 4.

b: Slice positions 5 through 8.
Figure 2.6.3: Multi-slice of the polyisoprene sample.

a: Slice positions 9 through 12.

b: Slice positions 13 through 16.
cylindrical in shape based on the facts that the slice thickness is 1 mm and the field of view is 18 mm. Multi-slice imaging allows for a three dimensional size analysis of defects.

2.7 RESULTS AND DISCUSSION OF STYRENE BUTADIENE RUBBER - VARIABLE TEMPERATURE STUDY

Four different samples of styrene butadiene rubber (SBR) were used in this study: an uncured and a cured sample without carbon black, an uncured and a cured sample with carbon black. Each sample was imaged with a spin-echo pulse program at room temperature, 25°C, and then at 50°C. The experiment time for these proton images was approximately 17 hours. The images of these samples at the two different temperatures are shown in Figures 2.7.1 through 2.7.4, respectively.

The only sample that could be imaged at room temperature was the SBR that contained no carbon black and was not cured. As expected the samples that contained carbon black and/or were cured could not be imaged at room temperature. Addition of fillers to and curing of an elastomer decreases the polymer chain segmental mobility which in turn decreases the spin-spin relaxation time. This type of relaxation is due to excess potential energy associated with nuclear spins in a magnetic field being redistributed among the nuclei. The decrease in chain mobility allows for an increase in the exchange of energy between nuclei.
Figure 2.7.1 a: Uncured SBR without carbon black imaged at 25°C.
b: Uncured SBR without carbon black imaged at 50°C.
Figure 2.7.2 a: Cured SBR without carbon black imaged at 25°C.
b: Cured SBR without carbon black imaged at 50°C.
Figure 2.7.3 a: Uncured SBR with 10 % carbon black imaged at 25°C.
b: Uncured SBR with 10 % carbon black imaged at 50°C.
Figure 2.7.4 a: Cured SBR with 10 % carbon black imaged at 25°C.
b: Cured SBR with 10 % carbon black imaged at 50°C.
Signal intensity and spin-spin relaxation time are directly proportional: 

$$\text{Signal} \propto \exp \left( -\frac{\text{TE}}{T_2} \right)$$  \hspace{1cm} (2.7.1) 

Thus the overall signal intensity of an image would be diminished if $T_2$ is decreased. Increasing the temperature of the sample increases the segmental mobility and the image intensity. At $50^\circ \text{C}$, the signal intensity is greatly increased for the cured SBR (Figure 2.7.2b) and the SBR with carbon black (Figure 2.7.3b), while the signal intensity is only somewhat enhanced for the cured SBR sample with carbon black (Figure 2.7.4b).

Spin-spin relaxation ($T_2$) measurements were taken of each sample at $25^\circ \text{C}$ and $50^\circ \text{C}$ with a Carl-Purcell-Meiboom-Gill (CPMG) experiment. A $90^\circ$ pulse is applied along the $+x$ axis. After time, $\tau$, a $180^\circ$ pulse is applied along the $+y$ axis. After a second time, $\tau$, an echo with positive amplitude is formed. The time between pulses, $\tau$, is increased, and as a result the amplitude of the resulting echoes, $E$, is diminished since the strength of the echo is inversely proportional to $\tau$: 

$$E = k_e \exp \left[ - \left( \frac{2\tau}{T_2} \right) - \left( \frac{2}{3} G^2 D^2 \tau^3 \right) \right]$$  \hspace{1cm} (2.7.2) 

where $k_e$ is a normalization constant. Also the amplitude of the echo is dependent upon the diffusion that occurs during this experiment; $G$ represents the spatial field gradients while $D$ represents the diffusion coefficient. If very short duration times are chosen, then effects from the diffusion term can be diminished.

The duration values chosen are listed in Table 2.7.1. The resulting data was Fourier transformed, spectrums were phased, and the
### Table 2.7.1 Duration Times for CPMG Relaxation Experiment

<table>
<thead>
<tr>
<th>NUMBER</th>
<th>DURATION TIME (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.010</td>
</tr>
<tr>
<td>2</td>
<td>0.100</td>
</tr>
<tr>
<td>3</td>
<td>0.500</td>
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<td>4</td>
<td>1.000</td>
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<td>6</td>
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</tr>
<tr>
<td>7</td>
<td>7.500</td>
</tr>
<tr>
<td>8</td>
<td>10.000</td>
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</tbody>
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### Table 2.7.2 Spin-Spin Relaxation Values for SBR Samples*

<table>
<thead>
<tr>
<th>SBR SAMPLE</th>
<th>$T_2$ - 25°C (ms)</th>
<th>$T_2$ - 50°C (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncured, No Carbon Black</td>
<td>1.6</td>
<td>2.3</td>
</tr>
<tr>
<td>Cured, No Carbon Black</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>Uncured, 10% Carbon Black</td>
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<td>2.1</td>
</tr>
<tr>
<td>Cured, 10% Carbon Black</td>
<td>1.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

* Experimental Error ± 0.2 ms
amplitude of the strongest peak was recorded. Graphs of peaks heights versus duration were made in order to determine the value of $T_2$ for each sample using the following function:

$$y = A \exp\left(-x / T_2\right)$$

(2.7.3)

where $A$ is a variable function representing the maximum peak amplitude. The results are shown in Table 2.7.2. These measurements confirm that increasing the temperature of the sample increases $T_2$. However the shortest $T_2$ was measured for the cured unfilled sample instead of the cured filled sample. This unexpected measurement may not be due to the condition of the sample but due to the fact that measurements were taken with an imaging probe instead of a solids probe. The imaging probe was used in order to take relaxation measurements of intact samples. Also the effect of diffusion was not taken into account. However the smallest change in $T_2$ was measured for the cured filled sample while the largest change was exhibited by the uncured filled sample. This result suggests that curing reduces the polymer segment chain mobility to a greater extent than the carbon black filler.

In imaging the samples at an elevated temperature, the morphology differences between the filled and unfilled SBR were seen. The unfilled samples appear as layers of elastomer with air in between. The filled uncured SBR appears to have an even distribution of carbon black. The filled cured SBR appears to have small circular defects distributed throughout. These could be attributed to agglomerates of carbon black or areas of high crosslink density.
2.8 RESULTS AND DISCUSSION OF TIRE TREAD - VARIABLE TEMPERATURE MULTI-SLICE STUDY

A commercially available tire tread was used for this study. Because the tread contained fillers including carbon black as well as fiber cording, the sample was imaged at an elevated temperature of 50°C. Since the objective was to determine the nature of defects throughout the sample, a multi-slice imaging sequence was employed. The portion of tire tread that contained an even distribution of cording was chosen to be imaged.

The multi-slice images are shown in sequential order in Figures 2.8.1 and 2.8.2. The elastomer material is high in intensity while the fiber cord is low in intensity. The overall cord pattern is consistent throughout the slices. A large void can be seen in slice 4 and continuing through to slice 8 where it is smaller in size, thus it is at least 5 mm long. The void diameter ranges from 4.5 mm to 1.5 mm and is conical in shape. Upon further examination, smaller defects can be seen throughout the sample. For example, a small defect can be seen on the middle right side of the tread in slice positions 13 and 14. Also there is a variance in the image appearance on the right side at the second and third fiber layer. This could be due to small agglomerates of carbon black or mislaid cord fiber.

There was concern that the signal from the tire tread was not produced from the polymer but the wax surrounding the fiber cording. To determine the source of the signal, a second variable temperature multi-slice experiment was run on a different piece of the tire tread. This
Figure 2.8.1: Multi-slice of tire tread.

a: Slice positions 1 through 4.
b: Slice positions 5 through 8.
Figure 2.8.2: Multi-slice of tire tread.

a: Slice positions 9 through 12.

b: Slice positions 13 through 16.
portion of tread, cut in the shape of a trapezoid contained an uneven
distribution of cording. The cording only ran through half of the sample.
Figure 2.8.3 shows four images which correspond to slices five through
eight. The upper right side of the image shows alternating areas of high
and low intensity. This represents the cording running through the
elastomeric material. The lower left side of the image consists mainly of
an area with high intensity with a varying pattern of low intensity. This
is the elastomeric material without cording that contains defects or
voids.
Figure 2.8.3: Multi-slice of tire tread, second portion.

Slice positions 5 through 8.
2.9 CONCLUSIONS

Magnetic resonance imaging is a noninvasive technique that can be utilized to study the morphology of elastomers. Timing parameters of an imaging sequence should be chosen to maximize signal intensity. Since elastomers have longer spin-lattice and shorter spin-spin relaxation times than liquids, shorter echo times and longer repetition times should be used.

There are several advantages in using the multi-slice sequence instead of a spin-echo sequence. Several images can be taken in the same time as one spin-echo image. Data collection is simultaneous for all images. The changes in morphology in an elastomer can be seen. Also if the elastomer contains carbon black, the distribution of the substance can be determined. The size and shape of a defect within the material can be calculated in three dimensions without actually cutting open the material.

With variable temperature imaging, filled and/or cured elastomers with short spin-spin relaxation time can be imaged. The increase in spin-spin relaxation time of elastomers at elevated temperatures can be confirmed with conventional NMR relaxation experiments. The major advantage that this technique has over previously mentioned solids imaging techniques is that rather sophisticated pulse sequences or hardware adjustments are not required.

Some future research studies could include finding the optimal imaging temperature for certain types of elastomers. How the elastomer and hardware are effected by repeated exposure to heat would need to
be determined. Thus MRI and relaxation experiments would be used to yield complimentary data. Also MRI could be used as a technique not only to locate defects but also determine their identity. This question is the subject of the next chapter.
REFERENCES


27. Farrar, T. C. An Introduction to Pulse NMR Spectroscopy; The Farragut Press: Chicago, 1897, Chapter 2.
CHAPTER 3

UTILIZING SUSCEPTIBILITY ARTIFACTS TO IDENTIFY DEFECTS WITHIN ELASTOMERS
3.1 INTRODUCTION TO SUSCEPTIBILITY ARTIFACTS

In medical imaging, there are many different types of artifacts that are patient-related. These include motion, flow, chemical shift, and susceptibility.\textsuperscript{1} This chapter will focus on the last type of artifact. Magnetic susceptibility is defined as the ratio of magnetization of a material to the magnetic field strength. In patients, artifacts occur at the interface of two substances that differ greatly in susceptibility. Artifacts can occur between air and tissue such as in the lungs\textsuperscript{2} and sinus cavities,\textsuperscript{3} and between bone and tissue such as in the area surrounding the spinal column.\textsuperscript{4} It has been suggested that susceptibility artifacts may serve as a means to differentiate between diseased and healthy tissue.\textsuperscript{5} Also, imbedded metal objects, such as dental fillings and medical implants, cause artifacts.\textsuperscript{1,6,7} The appearance of the artifact depends upon main magnetic field strength, gradient strength, type of pulse sequence used, and magnetic properties of the materials.

3.2 THEORY OF SUSCEPTIBILITY ARTIFACTS

Substances are defined by their chemical and physical properties including magnetic properties. In introductory chemistry, students learn that diamagnetic substances are repelled by a magnetic field whereas paramagnetic substances are drawn into the field.\textsuperscript{8} When a substance is placed in a magnetic field, \( B \), the magnetic induction within a substance, \( H \), is defined as

\[
H = B + 4\pi I
\] (3.2.1)
where I is defined as the magnetization per unit volume of substance. For diamagnetic substances, the values of I are negative; for paramagnetic substances, the values of I are positive. The volumetric susceptibility, \( \kappa \) is defined as the ratio of the magnetization per unit volume to the applied magnetic field strength:

\[
\kappa = \frac{I}{B}
\]  
(3.2.2)

The specific or mass susceptibility, \( \chi \), is defined as:

\[
\chi = \frac{\kappa}{\rho}
\]  
(3.2.3)

where \( \rho \) is the density of the substance. The molar susceptibility, \( \chi_M \), is defined as

\[
\chi_M = MW \cdot \frac{\kappa}{\rho}
\]  
(3.3.3)

where MW is the molecular weight of the sample.\(^9,10\) A list of molar susceptibility values for inorganic and organic substances is given in Table 3.2.1.\(^10,11\)

Magnetic susceptibility differences in heterogeneous samples can cause artifacts in magnetic resonance images. These artifacts appear at the interface of two substances. Artifacts take the form of geometric distortions and signal losses. The type of artifacts that are seen depends on what type of MRI pulse sequence was used to obtain the image.

The major artifact produced in a spin-echo image is a geometric distortion. In a heterogeneous sample, a variation in magnetic susceptibility between two substances creates a local field gradient. The
<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>$\chi_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled Water</td>
<td>-12.96</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>-68.13</td>
</tr>
<tr>
<td>Copper Sulfate</td>
<td>+1460.0</td>
</tr>
<tr>
<td>Silicon Oxide</td>
<td>-29.6</td>
</tr>
<tr>
<td>Argon</td>
<td>-19.6</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-12.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>+3349</td>
</tr>
<tr>
<td>Air</td>
<td>+680.2</td>
</tr>
<tr>
<td>Graphite</td>
<td>-5.9</td>
</tr>
<tr>
<td>Benzene</td>
<td>-54.84</td>
</tr>
<tr>
<td>2-Methyl-2-butene</td>
<td>-54.14</td>
</tr>
</tbody>
</table>
pixels containing the interface experience a magnetic field gradient which is greater or less than what would be experienced in the presence of the applied imaging gradients. Because of this difference, the effected pixels are mismapped along the frequency encoded axis. The direction and amount of the shift of pixel intensity depends proportionally on the susceptibility difference of the substances involved and inversely to the intensity of the applied magnetic gradients.

The major artifact produced in a gradient-echo image is a signal loss artifact. Again, at the interface between two substances that have different magnetic susceptibilities, a gradient is created. Because of the additional gradient, spins lose phase coherence. In a spin-echo pulse sequence, this loss in phase coherence would be refocused by the 180° pulse. In a gradient echo image, a negative read gradient replaces the 180° pulse hence an echo still forms. However, this gradient is inefficient in refocusing the dephased spins, and signal losses occur at the interfaces in a heterogeneous sample.

Both types of artifacts are theoretically thought to be seen along the read and slice selection directions. Posse and Aue state that artifacts in the phase-encoding direction would be slight because image intensity is determined by the central echo which is formed when the phase encoding gradient is equal to zero. They suggest that susceptibility artifacts may be reduced by using a second phase encoding gradient for slice selection instead of selective excitation. Ludeke and co-workers suggest that geometric distortions may be reduced in spin-echo images by increasing the strength of the read and slice selection
gradients but at a cost of reduced signal to noise. They also show mathematically that the shift of the artifact is directly proportional to the main magnetic field. Posse and Aue\textsuperscript{13} state theoretically that signal loss artifacts in gradient-echo images increase with decreasing particle size. Also they state that these artifacts can be diminished by increasing the read gradient, reducing voxel size, and reducing the echo time of the experiment. The latter however limits the ability of obtaining a $T_2$-weighted image.

3.3 REVIEW OF RESEARCH

In medical imaging, susceptibility artifacts are seen as a nuisance. The artifacts interfere with a diagnosis based, in part, on an MRI scan. In materials imaging, sometimes it is advantageous to rid an image of artifacts. For example, Kinchesh, Randall, and Zick\textsuperscript{15} have used the STRAFI (stray field imaging) technique with two-dimensional reconstruction to reduce artifacts due to local magnetic susceptibility variations of a liquid contained in a solid lattice. The model used in this study consisted of a sealed capillary tube of water surrounded with nickel sulfate crystals. It is suggested that this technique could be used to investigate water or oil entrapped in wood, rocks and minerals, clays and soils.

Several groups view susceptibility artifacts as an advantage instead of a nuisance in image quality. For instance, Chang and Komoroski\textsuperscript{16} suggest that signal loss artifacts, which occur at
susceptibility interfaces in gradient-echo images, could be used to detect defects in elastomers. The defect would appear larger than actual size which would allow for detection of defects smaller than pixel resolution. Kapadia\textsuperscript{17} showed that defects in samples of styrene butadiene rubber could be enhanced using a FLASH imaging sequence. Krejsa and Koenig\textsuperscript{18} suggest that susceptibility artifacts can be used to distinguish if voids in elastomer samples are filled with air or solvent. Spin-echo images were obtained of samples of cured and air aged butyl rubber swollen in benzene. The bright region next to the air aged sample may be due to the susceptibility difference between the entrapped air and solvent. Sarkar and Komoroski\textsuperscript{19} also suggest that susceptibility artifacts, appearing in spin-echo images of elastomers, may be useful in identifying defects in the material. The model that was studied consisted of a glass capillary tube filled with air, a glass capillary tube filled with carbon black, and a graphite pencil tip embedded in commercial vegetable shortening. The only artifact that appears in a spin-echo image of the model is at the interface of the graphite and shortening. In a gradient-echo image of the model, the largest signal loss artifact is also seen at this same interface.

The defects in green ceramics and a ceramic of known porosity were magnified through gradient-echo imaging by Wallner and Ritchey.\textsuperscript{20} The defects, which are below resolution in spin-echo images, can be seen in gradient-echo images due to signal loss artifacts which occur at the interfaces of two substances (ceramic and air or binder) which differ in susceptibility. Wallner\textsuperscript{10} also showed that the amount of
signal loss in a gradient echo image is determined by the substance that causes the defect. Models used in this study consisted of air bubbles entrapped in cyclohexane and doped water. The signal loss between the cyclohexane/air interface was smaller than the signal loss at the doped water/air interface. When compared to a spin-echo image, the signal losses could be quantified. The identity of a defect in a green state ceramic filled with cyclohexane was determined to be air because of a similar signal loss factor.

3.4 OBJECTIVES OF RESEARCH

Defects in elastomers used in the manufacture of rubber products can shorten the life of that product. Thus identifying the source of the defects is desirable. The goal of this research is to identify defects in elastomers through susceptibility artifacts. One method investigated is quantifying signal loss artifacts in models. Another is to determine if the shift direction of a geometric distortion depends on the magnetic properties of the substance in the defect.

3.5 EXPERIMENTAL

All images were obtained with a Bruker MSL 400 with micro imaging accessories operating at a frequency of 400.13 MHz. The nucleus of interest was proton. The gradient-echo imaging sequence used in this study was developed by Sam Gravina of Bruker Instruments
The spin-echo imaging sequence was rewritten so that the determination of the echo time was independent of the duration of the linear gradients. Both pulse sequences employed selective 90° and 180° pulses. The largest radio frequency coil available, 25 mm, was used to obtain maximum signal to noise ratio. Samples were placed in a 20 mm NMR tube to reduce the possibility of radio frequency artifacts.

For all images, the image pixel dimensions were 256 x 128 (frequency encoding versus phase encoding). The field of view is determined by the inner diameter of the NMR sample tube which was 18 mm. Hence the pixel resolution of the spin-echo images was 70 μm x 140 μm. The slice thickness for every image was 1 mm. The slice gradient is applied along the z-axis which is defined as being collinear to the main magnetic field. The phase encoding gradient is implemented along the y-axis, while the frequency encoding gradient is applied along the x-axis. A summary of imaging parameters is listed in Table 3.5.1.

All elastomer and carbon black samples used in this study were obtained from James Visintainer of The Goodyear Tire & Rubber Company (Akron, Ohio). The polyisoprene sample used for the signal loss models was unfilled and uncured. The polyisoprene sample mentioned in the geometric distortion artifact observations was filled with 20% carbon black by weight. The agar gel powder (Agarose Low EEO) was obtained from the Biology Department at Case Western Reserve. The agar gel, 1% by weight, was prepared with distilled water.
<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>SPIN-ECHO</th>
<th>GRADIENT-ECHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slice Thickness</td>
<td>1 mm</td>
<td>1 mm</td>
</tr>
<tr>
<td>Gradients Z</td>
<td>2.34 G/cm</td>
<td>2.34 G/cm</td>
</tr>
<tr>
<td>Gradients Y</td>
<td>5.07 G/cm</td>
<td>5.07 G/cm</td>
</tr>
<tr>
<td>Gradients X</td>
<td>3.29 G/cm</td>
<td>3.29 G/cm</td>
</tr>
<tr>
<td>Echo Time</td>
<td>7.6 ms</td>
<td>5.4, 6.5, 7.6, 8.8 ms</td>
</tr>
<tr>
<td>Repetition Time</td>
<td>1, 2 sec</td>
<td>1, 2 sec</td>
</tr>
<tr>
<td>Image Size</td>
<td>256 x 128</td>
<td>256 x 128</td>
</tr>
<tr>
<td>Digital Resolution</td>
<td>70 μm x 140 μm</td>
<td>70 μm x 140 μm</td>
</tr>
</tbody>
</table>
3.6 RESULTS AND DISCUSSION OF SIGNAL LOSS ARTIFACTS

The goal of this study was to determine whether the identity of defects in elastomer samples can be distinguished through susceptibility signal loss artifacts. These artifacts occur at the interfaces of different substances in gradient echo images. The interfaces studied were an air/polyisoprene interface and a carbon black/polyisoprene interface. These interfaces were chosen because defects in the samples in the previous chapter were attributed to voids or agglomerates of carbon black. The uncured, unfilled polyisoprene was chosen because it would have a longer $T_2$ than any sample used previously. This longer $T_2$ results in a higher signal to noise ratio. Thus an image with acceptable intensity can be acquired in a shorter amount of time (approximately six hours).

The model used in this study was made of polyisoprene that was cut to form two rectangular holes. It would have been preferable to make circular defects since the defects seen previously had a round shape. Attempts at making circular defects were frustrating. Both manual and machine methods were tried: boring holes with a dissecting needle, cork bore, and machine bit. The polyisoprene was frozen in liquid nitrogen before each attempt. However insertion of any type of object warmed the polyisoprene, making further drilling impractical.

Finally rectangular defects were made by cutting the polymer at room temperature with an exacto blade. Liquid soap was used as a lubricant. Two pieces were cut: one in the shape of an E and the other in the shape of a rectangle. The overall size of the model was 15 mm x
12 mm x 20 mm. A diagram of this model is shown in Figure 3.6.1  The left hole was filled with carbon black while the right hole was filled with air.

The design of this model has several advantages over previous work. Since the elastomer is not swollen with a solvent, there is no unseen damage to the material itself or shape changes of voids. Also the interfaces of interest are not separated by a glass capillary tube.

A spin-echo image acquired with an echo time of 7.6 ms is shown in Figure 3.6.2. Four gradient-echo images of the model are shown in Figures 3.6.3 and 3.6.4. Each gradient-echo image was acquired with a different echo time to determine if the amount of signal loss depended on the echo time. The echo times were 5.4, 6.5, 7.6, 8.8 ms respectively. The holes appear larger in the gradient-echo image due to signal loss artifacts at the interfaces of the polyisoprene and carbon black or air.

The areas of both holes in all five images were measured by taking three widths and three heights and averaging them. These heights and widths were measured from the monitor display to insure the same rows and columns were measured for each image. The gradient echo areas were compared to the spin echo area to determine the hole enlargement. These results are given in Table 3.6.1 and are shown graphically in Figure 3.6.5.

Several conclusions can be drawn from this data. First, there is a larger signal loss at an air/polyisoprene interface than at a carbon black/polyisoprene interface. This correlates with the magnetic susceptibility differences between the substances. Polyisoprene and
Figure 3.6.1: Schematic of two hole polyisoprene model.
Figure 3.6.2: Spin-echo image of model. The left hole filled with carbon black. The right hole filled with air.
Figure 3.6.3: Gradient-echo images of two hole polyisoprene model.

a: Echo time of 5.4 ms.  

b: Echo time of 6.5 ms.
Figure 3.6.4: Gradient-echo images of two hole polyisoprene model.
a: Echo time of 7.6 ms. b: Echo time of 8.8 ms.
Table 3.6.1 How Interface Type and Echo Time Affect Signal Loss

<table>
<thead>
<tr>
<th>DEFECT FILLER</th>
<th>CARBON BLACK* (mm²)</th>
<th>AIR* (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signal Loss</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SE vs GE - 5.4 ms</td>
<td>0.28</td>
<td>0.77</td>
</tr>
<tr>
<td>SE vs GE - 6.5 ms</td>
<td>0.39</td>
<td>2.97</td>
</tr>
<tr>
<td>SE vs GE - 7.6 ms</td>
<td>1.20</td>
<td>6.24</td>
</tr>
<tr>
<td>SE vs GE - 8.8 ms</td>
<td>1.51</td>
<td>8.95</td>
</tr>
</tbody>
</table>

* Experimental error ± 0.07 mm.

Figure 3.6.5: Graph of signal loss vs. echo-time - first polyisoprene model.
carbon black are both diamagnetic substances while air can be
considered a paramagnetic substance since oxygen is a major
component.\textsuperscript{11} Although susceptibility values were not readily available
for carbon black and polyisoprene, values for similar materials were
compared: graphite and 2-methyl-2-butene, respectively. (Refer to Table
3.2.1 for molar susceptibility values.) Carbon black is considered an
amorphous form of carbon while graphite is a crystalline form. Carbon
black consists of graphite platelets that are random in orientation.\textsuperscript{21}
Also 2-methyl-2-butene is similar to the repeating unit in polyisoprene.
The difference in magnetic susceptibility between graphite and 2-methyl-
2-butene is approximately 50 while the difference in magnetic
susceptibility between air and 2-methyl-2-butene is approximately 735.
Second, signal loss increases as echo time increases which was
predicted in theory. Third, the signal loss occurs at a faster rate at the
air/polyisoprene interface than for a carbon black/polyisoprene interface
(2.46 mm\(^2\)/ms vs. 0.40 mm\(^2\)/ms). Also it should be noted that no
geormetric artifacts were seen in the spin echo images. This lack of
artifact may be due to the large size and/or rectangular shape of the
defect.\textsuperscript{13}

This model had defects in the design. First, there was an
additional air/polyisoprene interface where the two pieces of polymer
came together. Also the right defect opened to the outside in gradient-
echo images with longer echo times. This might have been due to the
air/polyisoprene interface at the perimeter of the model. Both unwanted
interfaces could have corrupted the signal loss data.
A second model used in the study was redesigned to eliminate unwanted polyisoprene/air interfaces. The redesigned model was again made out of polyisoprene, and the same interfaces were studied. Two square pieces of elastomers were cut to dimensions of 20 mm x 12 mm x 4 mm. Two smaller pieces of double sided poster tape were cut and placed in between the elastomer pieces as spacers to create a defect with a thickness of approximately 2 mm. A diagram of this model is shown in Figure 3.6.6.

With the void being filled with air, one spin-echo image and three gradient-echo images were obtained. The spin-echo image had an echo time of 7.6 ms while the gradient-echo images had echo times of 5.4, 6.5, 7.6 ms respectively. Data from the third gradient-echo image was not used due to the poor signal to noise. The spin-echo and one of the gradient-echo images are shown in Figure 3.6.7.

A second set of images was taken of the model with the void filled with carbon black. Again one spin-echo image and three gradient-echo images were obtained. The spin-echo image had an echo time of 7.6 ms while the gradient-echo images had echo times of 5.4, 6.5, 6.5 ms respectively. Although the last two gradient echoes did not differ in echo time they did differ in the strength of the read refocusing gradient. The spin-echo and one of the gradient-echo images are shown in Figure 3.6.8. The signal loss seen in the polyisoprene itself in both gradient-echo images is due to entrapped air.

Signal losses at the interfaces were measured in the following manner. Six heights of the void were measured in the spin-echo images.
Figure 3.6.6: Schematic of one hole polyisoprene model.
Figure 3.6.7: One hole polyisoprene model, the hole filled with air.

a: Spin-echo image, echo time of 7.6 ms.

b: Gradient-echo, echo time of 5.4 ms.
Figure 3.6.8: One hole polyisoprene model, the hole filled with carbon black.  
a: Spin-echo image, echo time of 7.6 ms.  
b: Gradient-echo, echo time of 5.4 ms.
Then the same height positions were measured in the gradient-echo images. These heights were measured from the monitor display to insure the same columns were measured for each image. The heights were larger due to the signal loss artifact seen in gradient echo image. The gradient-echo heights were compared to the spin-echo heights to determine an average signal loss.

This study confirmed two conclusions from the first study. First, the data indicated that the carbon black/polyisoprene interface had a lower signal loss than the air/polyisoprene interface. Second, the signal losses increased with increased echo time. Also the two gradient-echo images of the carbon filled defect, that had the same echo times but different read reversal gradients, exhibited almost identical signal losses. These results are listed in Table 3.6.2 and displayed in Figure 3.6.9.

Also the model was turned at a 90° angle so the defect was parallel with the phase encoding gradient. This was done to see if any geometric artifacts would be seen in a spin-echo image. No artifacts of this type were seen whether the void was filled with air or carbon black. This lack of geometric artifacts may be due to the large size and/or rectangular shape of the defect.13

The findings from this model were not conclusive. First, only two gradient-echo images could be acquired with an adequate amount of signal. Thus only two data points could be compared. Second the data for the air/polyisoprene and the carbon black/polyisoprene interfaces were taken at different times due to the model's design. A third model was designed that included two rectangular holes instead of one. The
Table 3.6.2 How Interface Type and Echo Time Affect Signal Loss

<table>
<thead>
<tr>
<th>DEFECT FILLER</th>
<th>CARBON BLACK (mm)</th>
<th>AIR (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signal Loss</td>
<td>0.42</td>
<td>0.57</td>
</tr>
<tr>
<td>SE vs GE - 5.4 ms</td>
<td>0.84</td>
<td>1.09</td>
</tr>
<tr>
<td>SE vs GE - 6.5 ms</td>
<td>0.83</td>
<td>----</td>
</tr>
</tbody>
</table>

* Experimental error ± 0.07 mm.

Figure 3.6.9: A graph of signal loss vs. echo time for one-hole polyisoprene model.
redesigned model was again made out of polyisoprene. Three rectangular pieces of elastomer were cut to dimensions of approximately 20 mm x 12 mm x 3 mm. Four smaller pieces of double sided poster tape were cut and placed in between the elastomer pieces as spacers to create voids with a thickness of approximately 2 mm. A diagram of this model is shown in Figure 3.6.10.

Before any experiments were run with this model, one hole was filled with carbon black. The other defect was filled with air. A spin-echo image and three gradient-echo images were obtained. The spin-echo image had an echo time of 7.6 ms while the gradient-echo images had echo times of 5.4, 6.0, 6.5 ms respectively. The spin-echo image and one of the gradient-echo images are shown in Figure 3.6.11. However it appeared that neither defect experienced a signal change. Although initial results were promising, it appears that they were influenced by problems in the design of the models.

At this point, a new direction was taken in model design. The uncured, unfilled polyisoprene was difficult to cut and only rectangular defects could be made. However, the shape of the defects in the elastomer samples studied previously were circular. Agar gel was chosen as an alternative due to its availability and ease of preparation. Round defects could be made in the gel material by using glass rods. A model containing four circular voids was made in the following manner. Agar powder was added to boiling distilled water contained in a 5 ml beaker. The beaker contained four glass rods that were glued to its bottom. This size beaker had a diameter that measured approximately
Figure 3.6.10: Schematic of second two hole polyisoprene model.
Figure 3.6.11: Second two hole polyisoprene model, the top hole filled with air, the bottom hole filled with carbon black.

a: Spin-echo image, echo time of 7.6 ms.

b: Gradient-echo, echo time of 5.4 ms.
Thus the round model could slide down the 20 mm NMR tube that had an inner diameter of 18 mm. As the agar gel was cooling, the four glass rods, that were approximately 2 mm in diameter, were held in place with masking tape. The gel cooled for twenty-four hours. At this time the glass rods were removed. The agar model was removed from the beaker before carbon black was placed in two of the rod shaped defects. A notch was cut into the gel between the defects containing air so identification could be made while viewing images. A diagram of this model is shown in Figure 3.6.12.

The only drawback with this model is the type of interfaces being examined. Since the primary ingredient in agar is distilled water, the interfaces in this model were air/water and carbon black/water. One would expect the signal loss between the carbon black/water interface to be smaller than the signal loss between the air/water interface because both materials are diamagnetic. A spin-echo image and five gradient-echo images were obtained. The spin-echo image had an echo time of 7.6 ms while the gradient-echo images had echo times of 5.4, 6.5, 7.6, 8.8, and 10.0 ms respectively. The repetition time of the imaging sequence was reduced to one second because the signal came from water which has a shorter spin-lattice relaxation time. Also the total experiment time only took nine minutes because of the strong signal to noise ratio. The images are shown in Figures 3.6.13 through 3.6.15.

The defects containing carbon black had a much larger signal loss in the gradient-echo images. The signal losses were quantified by measuring their areas. The areas of both holes in five images were
Figure 3.6.12: Schematic of agar gel model.
Figure 3.6.13: Agar gel model, top holes filled with carbon black, bottom holes filled with air.  

a) Spin-echo image, echo time of 7.6 ms.  
b) Gradient-echo image, echo time of 5.4 ms.
Figure 3.6.14: Agar gel model.

a) Gradient-echo image, echo time of 6.5 ms.

b) Gradient-echo image, echo time of 7.6 ms.
Figure 3.6.15: Agar gel model.

a) Gradient-echo image, echo time of 8.8 ms.

b) Gradient-echo image, echo time of 10.0 ms.
measured by taking a width and a height and calculating the area. The area was not measured for the last gradient echo image because the signal loss from the gel itself made this difficult. These heights and widths were measured from the monitor display to insure the same rows and columns were measured for each image. The gradient echo areas were compared to the spin echo area to determine the hole enlargement. These results are given in Table 3.6.3 and are shown graphically in Figure 3.6.16.

Several conclusions can be drawn from this data. First, signal loss increases as echo time increases which was predicted in theory. Second, there is a larger signal loss at a carbon black/water interface than at an water/air interface. This does not correlate with the magnetic susceptibility differences between the substances. (Refer to Table 3.2.1 for susceptibility values.) The difference in magnetic susceptibility between graphite and water is approximately 7 while the difference in susceptibility between air and water is approximately 690. Also when the carbon black was placed into the cylindrical defects, the material soaked up water from the gel. The result was a heterogeneous matrix of carbon black, water and entrapped air. This would cause a large signal loss defect due to the many different interfaces.
Table 3.6.3 How interface Type and Echo Time Affect Signal Loss

<table>
<thead>
<tr>
<th></th>
<th>DEFECT FILLER</th>
<th>CARBON BLACK (mm²)</th>
<th>AIR (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Left</td>
<td>Right</td>
<td>Left</td>
</tr>
<tr>
<td>SE vs GE - 5.4 ms</td>
<td>2.86</td>
<td>2.36</td>
<td>0.34</td>
</tr>
<tr>
<td>SE vs GE - 6.5 ms</td>
<td>3.67</td>
<td>2.83</td>
<td>0.56</td>
</tr>
<tr>
<td>SE vs GE - 7.6 ms</td>
<td>5.29</td>
<td>4.63</td>
<td>0.56</td>
</tr>
<tr>
<td>SE vs GE - 8.8 ms</td>
<td>7.41</td>
<td>5.18</td>
<td>0.56</td>
</tr>
</tbody>
</table>

* Experimental error ± 0.07 mm.

Figure 3.6.16: Graph of signal loss vs. echo time for agar gel model.
3.7 RESULTS AND DISCUSSION OF GEOMETRIC ARTIFACTS

One difficulty that may occur when the above technique is applied to samples of filled and/or cured elastomers, is that signal loss during a gradient-echo image may be so severe that an image cannot be acquired. However geometrical artifacts seen in spin-echo images may be instrumental in determining the identity of defects in elastomer samples.

Komoroski and Sarkar have stated that geometric distortions are common in elastomers filled with carbon black. They attribute the artifacts to coke - carbon black that is in crystalline or graphitic phase.\textsuperscript{22} In their model, which was mentioned previously, an arrowhead artifact was only seen at the vegetable shortening/graphite interface.\textsuperscript{19}

One may conclude that if a susceptibility artifact is seen in a spin-echo image of a carbon black filled elastomer, the defect is not entrapped air but an agglomerate of carbon black. Figure 3.7.1 shows a spin-echo image of a polyisoprene sample filled with 20 % carbon black. A large defect with a geometric distortion shifted to the left is seen. This suggests carbon black is the source. If one refers back to Figure 2.8.1 in Chapter 2, one can see a large void in the tire tread in slices 4 through 8. Via microscopy conducted at The Goodyear Tire & Rubber Company, it was determined that the defect was an agglomerate of carbon black. However a geometrical distortion was not seen around the defect in any of the images. Figure 3.7.2 shows two spin-echo images of a different tire tread at two different slice positions. A geometric distortion shifted to the left is seen around the small void in the center of the tire tread in the first image as well as the bend in the perimeter in the second image.
Figure 3.7.1: Spin-echo image of polyisoprene with 20% carbon black by weight.
Figure 3.7.2: Spin-echo images of tire tread at different slice positions.
The interface in the second image is tire tread and air. This contradicts the hypothesis of Komoroski and Sarkar. An increase in the susceptibility difference may be due to the fact that the image of the tread was taken at 50°C with a variable temperature set-up. Warm air was pumped around the sample continuously. This would have increased the average molecular energy of the air molecules around the tire which in turn would increase the number of collisions of the air molecules with the tread.

In Figure 3.6.13a, the spin-echo image of the agar gel, there is an appearance of a geometric distortion around the left hole of carbon black and to the right of the right hole of carbon black. However no artifacts appear at or around the air filled holes. The absent of artifacts at the air/water interface does not concur with what was found by Ludeke and co-workers. They have seen arrowhead artifacts at the interface of water and air and of water and a solution of copper sulfate.

Through these comparisons, geometrical distortions may not be a simple means of identifying the substance within a defect. The appearance of artifacts at interfaces of known defects are not consistent. The appearance of artifacts may also depend upon the shape and size of the defect. The appearance may also depend upon gradient strengths.
3.8 Conclusions

Although geometric distortions may not aid in the identification of defects in elastomer sample, quantification of signal loss artifacts could provide a solution. Initial work with models consisting of polyisoprene and rectangular defects consisting of air and carbon black looked promising. The amount of signal loss around the defects was calculated by comparing gradient-echo measurements to spin-echo measurements. As predicted, a greater signal loss was seen at the air/polyisoprene interface than at the carbon black/polyisoprene interface. Also as the echo time of the gradient-echo image was increased, the signal loss around the defects also increased. A model consisting of agar and circular defects was also used to better resemble the round voids seen in previous elastomer samples. The voids containing only air exhibited a smaller signal loss than the defects containing the wet clumps of carbon black. Again as the echo time of the gradient-echo image increased, the signal attenuation around the defects also increased.

However more work is needed. In future models, circular defects should be employed due to their symmetrical shape. Also this is the main shape of defects in carbon black filled elastomer samples. Instead of agar gel, which is primarily composed of water, an elastomer system that can be polymerized around glass rods should be used. Two elastomers that may be utilized are dimethyl siloxane and a polyethylene glycol polyurethane copolymer. The sizes of the glass rods could be varied to determined if signal loss increases with decreasing defect size. The slice size should be decrease because sensitivity varies with
position. However, a decrease in slice thickness would result in a decrease in signal to noise. Also experiments could be run at different temperatures to examine the change in appearance in susceptibility artifacts. Interfaces involving a paramagnetic substance may be diminished at higher temperatures since the susceptibility decreases at higher temperatures for paramagnetic substances. Finally, relaxation measurements of the interface through NMR microscopy may help in determining if a paramagnetic species is present. Paramagnetic substances moderately decrease the spin-lattice and spin-spin relaxation time of a material.
REFERENCES


CHAPTER 4

STUDYING ION-EXCHANGE RESINS
VIA MAGNETIC RESONANCE IMAGING
4.1 INTRODUCTION TO ION CHROMATOGRAPHY

About 5,000 years ago, Moses threw a decomposed log into a pool of brackish water at Marah.\textsuperscript{1} Apparently the water was made drinkable due to an exchange of ions because the log acted as an ion exchange resin.\textsuperscript{2} Ion exchange is defined as the reversible exchange of ions of similar charge between an ionic solution and an insoluble solid.\textsuperscript{3} It was not until the early 1960's that ion-exchange chromatography became automated with the routine introduction of amino acid analysis.\textsuperscript{4} However this separation technique could not detect non-ultra violet absorbing ionic species. Conductivity is a universal detector for ions, but the conductivity response due to the analyte would be swamped by the mobile phase electrolyte. In 1975, Small, Stevens and Bauman\textsuperscript{5} solved this problem by using an ion exchange column along with a second suppressor column. The suppressor column contains an ion-exchange resin which converts the background electrolyte to a molecular species of limited ionization. Thus sample ions can be detected by a simple conductivity cell. The separation of dissolved ions by this process has been labeled ion chromatography. A schematic of an ion chromatography instrument is shown in Figure 4.1.1.\textsuperscript{6}

Ion chromatography is used to determine the identity of metal cations, common inorganic anions, and organic substances in a variety of areas. Environmental applications include the measurement of sodium and potassium levels in brine water.\textsuperscript{7} Nitrogen and phosphorus containing anions in industrial plant water discharge can be separated.\textsuperscript{8} This technique is also used to determine the ionic content of natural...
Figure 4.1.1: Schematic of ion chromatography instrument. (from reference 5).
and drinking waters\textsuperscript{10,11} as well as a tool to study the problem of acid rain.\textsuperscript{12,13}

There are several applications involving geological samples. The chloride content can be determined in silicate rock\textsuperscript{14}, while sulfur amounts can be determined in coal and oil shale\textsuperscript{15}. In the field of agronomy, this technique is used to ascertain the sulfur and chloride levels\textsuperscript{16} as well as potassium, sodium, calcium, and magnesium levels in plant material\textsuperscript{17}. The urea content in fertilizer can be determined by cationic exchange after conversion to ammonium\textsuperscript{18}.

Ion chromatography is used by industry and in medicine to monitor ionic levels. Electroplating baths can be tested for transition metals.\textsuperscript{19} In the pulp and paper industry, a large variety of anions and cations are monitored including hypochlorite and sulfate.\textsuperscript{20,21} In the food industry, this type of chromatography is used to determine the levels of sodium, potassium, calcium and nitrates in a variety of foods,\textsuperscript{22} as well as the carbohydrate content in beer.\textsuperscript{23} Organic acids can be determined in plasma and urine.\textsuperscript{24} Ion chromatography is still routinely used in the determination of amino acids.\textsuperscript{25}

\subsection*{4.2 ION EXCHANGE RESINS}

An exchange resin contains a functional group with a fixed ionic charge bonded to its surface. An exchangeable counterion ion is present to provide charge neutrality. See Figure 4.2.1. Because analyte ions have different affinities to the functional group, they can be separated.\textsuperscript{26}
Figure 4.2.1: Schematic of ion exchange resin (from reference 26).
The ion exchange capacity of the stationary phase is defined as the number of ion exchange sites per gram of resin.\textsuperscript{27} The main difference between ion-exchange and ion chromatography is the type of exchange resin used in the separator column. There are three main types of ion exchange resins: bonded phase pellicular, bonded phase porous, and polymeric porous.\textsuperscript{4}

Pellicular particles consist of a nonporous glass or polymeric bead that is coated with a synthetic exchange resin.\textsuperscript{4,6,28} Due to their structure, these beads do not contract or expand when different mobile phases are used.\textsuperscript{27} This type of packing provides improved column efficiency but has a lower ion exchange capacity than the other two types of beads.\textsuperscript{4,28} Bonded phase porous particles are made of silica microparticles with exchange resin bonded to the surface of porous silica gel\textsuperscript{4,28} or with exchange resin polymerized into the pores.\textsuperscript{6} These types of beads also have improved column efficiency,\textsuperscript{4,26} however they are unstable in alkaline and in highly acidic solutions.\textsuperscript{28,29}

In ion chromatography, the stationary phase usually consists of polymeric porous beads. One of the advantages that these beads have over silica beads is their stability over a wide pH range. See Figure 4.2.2. The most common polymeric material used is a copolymer of styrene and divinylbenzene. See Figure 4.2.3.\textsuperscript{4} The styrene molecules join together to form a carbon backbone chain while divinylbenzene (DVB) molecules crosslink the chains together. Crosslinking makes the bead more rigid and thus mechanically stronger. Commercially styrene-divinylbenzene (SDVB) beads are made with 2 to 16\% DVB.\textsuperscript{3} The
Figure 4.2.2: Effect of pH on exchange capacity of porous polymeric exchange resins (from reference 4).
\[
\begin{align*}
&\text{CH} = \text{CH}_2 \\
&\sigma \\
&\text{STYRENE} \\
\end{align*}
\]

\[
\begin{align*}
&\text{CH} = \text{CH}_2 \\
&\sigma \\
&\text{DIVINYLBENZENE} \\
\end{align*}
\]

\[
\begin{align*}
&\cdots \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 \cdots \\
&\sigma \text{SO}_3\text{H} \\
\end{align*}
\]

\[
\begin{align*}
&\cdots \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 \cdots \\
&\sigma \text{SO}_3\text{H} \\
\end{align*}
\]

\[
\begin{align*}
&\cdots \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 \cdots \\
&\sigma \text{SO}_3\text{H} \\
\end{align*}
\]

\[
\begin{align*}
&\cdots \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH} - \text{CH}_2 \cdots \\
&\sigma \text{SO}_3\text{H} \\
\end{align*}
\]

\[
\begin{align*}
&\text{CROSS LINKED SULFONATED} \\
&\text{POLYSTYRENE-DIVINYLBENZENE} \\
\end{align*}
\]

Figure 4.2.3: SDVB monomers and sulfonated copolymer.
percentage indicates the mole percent of DVB in the monomer mixture.³⁰

The SDVB copolymers can be polymerized by two different methods: bead or suspension polymerization. Bead polymerization consists of copolymerizing the monomers in the presence of a free radical catalyst like benzoyl peroxide. A liquid mixture of the monomers and catalyst is poured into water containing a small amount of surfactant. Beads start to form; the size of the beads is controlled by the amount of surfactant and the rate of stirring. Also DVB reacts faster than styrene, so the initial polymer will contain more of this monomer. As the polymerization continues, the liquid beads turn into small solid spheres.³ These beads are considered microporous, hence column efficiency is decreased with increased crosslinking.³⁰

Bead polymerization differs from emulsion polymerization. In emulsion polymerization, enough surfactant is added for micelle formation. Also a water-soluble initiator, like hydrogen peroxide, is used. A dispersion of very small particles called a latex is formed.³

Macroporous beads can be made through suspension polymerization. A miscible substance is added to the monomer/catalyst aqueous mixture that is a poor solvent for the polymer. As polymerization proceeds, polymer chains become entangled due to immiscibility with the solvent. The solid polymer bead will consist of an aggregate of sub-micron size particles with the immiscible solvent filling the space in between particles forming relatively large pores. The size of the beads is controlled by suspending and dispersing agents.³,³⁰
After polymerization, functional groups are bonded chemically to the polymer. In a cationic resin, a common functional group is the sulfonate group, \( \text{SO}_3^- \). The aromatic rings in the SDVB resin can be monosubstituted with the functional group. First, the beads are placed in a liquid, like nitrobenzene, that will cause the beads to swell. Then the beads are placed into concentrated fuming sulfuric acid or chlorosulfonic acid. The acid is allowed to diffuse the polymer at low temperature to ensure uniform sulfonation. Then the temperature is raised so that the chemical bonding of sulfonated groups can commence.\(^3\) Because of the uniform distribution of functional groups, the beads will have a high exchange capacity. If beads with low exchanged capacity are needed, only the surface of the bead is sulfonated. The beads are not swollen before exposure to the acid.\(^{30}\) The beads function as a strong acid that will exchange hydrogen ions for other cations. The carboxylic group, \( \text{COO}^- \), is also used as a cationic functional group however it is weakly acidic.\(^{28}\)

In an anionic resin, quaternary ammonium groups serve as the principle functional group.\(^{28}\) The resin beads are treated first with chloromethyl ether which results in the -CH\(_2\)Cl group being monosubstituted onto the benzene ring. The product is reacted with a tertiary amine to produce a quaternary ammonium chloride, a strong base, that will exchange its chloride for other anions. Also primary, secondary, and, tertiary amines can function as weakly basic anionic exchange resins.\(^{3,30}\)
Resins with strong functional groups are effective, remain highly ionized, over a wide pH range. However, resins with weak functional groups are affected by the pH of the mobile phase.\textsuperscript{30} Refer to Figure 4.2.2.\textsuperscript{4} A weakly acidic cation exchange resin's exchange capacity increases with increasing pH, while a weakly basic exchange resin's exchange capacity increases with decreasing pH. Thus the affinity of the resin for analyte ions can be varied under different pH conditions.\textsuperscript{30}

\section*{4.3 PREVIOUS RESEARCH}

Previously, the morphology of polymeric beads has been studied by invasive techniques. Several groups\textsuperscript{31-34} have used transmission electron microscopy (TEM) to study the morphology of poly(methyl methacrylate) - styrene copolymer made through an emulsion polymerization. In some of the TEM studies\textsuperscript{32-34}, the double bonds in the polystyrene domains were stained with ruthenium (IV) oxide. In these studies, the beads are cut with an ultramicrotome before being scanned. The different conditions included pH, initiator, and viscosity. Polymeric beads containing a hydrophilic carboxyl containing core and a hydrophobic polystyrene shell were also examined by TEM. Scanning electron microscopy (SEM) has also been used to examine poly(methyl methacrylate) - styrene copolymer beads\textsuperscript{32}, as well as styrene divinylbenzene containing terpolymer made via suspension polymerization.\textsuperscript{36} With the latter, the microscopy showed that the beads were macroporous.
Recently, Wallner\textsuperscript{37} has shown that MRI can be used as a noninvasive technique to examine the morphology of SDVB chromatography resins. A single bead was prepared in a capillary mounting method. Results using this type of mount displayed the least effect from susceptibility differences. Beads that showed homogeneous and heterogeneous swelling could be viewed with a spin-echo imaging sequence. Unsulfonated and sulfonated beads, having different spin-lattice relaxation parameters, could be distinguished through $T_1$-weighted images.

### 4.4 Objectives of Research

There were two main objectives of this research. First was to develop a mount that would allow one to determine the uniformity of a sample of exchange resin beads. Second was to determine if the resins under went morphological changes when exposed to extremely acidic and alkaline conditions.

### 4.5 Experimental

All images were obtained with a Bruker MSL 400 with micro imaging accessories operating at a frequency of 400.13 MHz. The nucleus of interest was proton. The proton signal did not originate from the material itself but from the liquid contained in the pores of the material. The spin-echo imaging employed in this study used a selective
90° pulse and a nonselective 180° pulse. Samples were placed on a multiple bead mount which was inserted into a 5 mm NMR tube. A 10 mm radio frequency coil was used to reduce the possibility of radio frequency artifacts.

For all images, the image pixel dimensions were 256 x 128 (frequency encoding versus phase encoding). The field of view is determined by the inner diameter of the NMR sample tube which was 4.2 mm. Hence the pixel resolution of the spin-echo images was 16 μm x 33 μm. The slice thickness for every image was 1 mm. The position of the slice was adjusted to ensure that the beads were within the slice. The adjustment was made by changing the carrier frequency of the pulses at the computer console. The slice gradient is applied along the z-axis which is defined as being collinear to the main magnetic field. The phase encoding gradient is implemented along the y-axis, while the frequency encoding gradient is applied along the x-axis. A summary of imaging parameters is listed in Table 4.5.1.

All but one of the resin samples were obtained from Charles Gaw of Rohm and Haas (West Chester, Ohio). All five Rohm and Haas beads were styrene divinylbenzene resins. Information concerning exchange type, exchange group, and % DVB in the monomer mixture\textsuperscript{38} is listed in Table 4.5.2. The beads were received packed in water. The size of the beads ranged from 16 to 50 US mesh (1.18 to 0.300 mm in diameter). Beads that measured 0.600 mm or larger were sifted out with a machined sieve. The other SDVB exchange resin was obtained from Patrick Smith of The Dow Chemical Company (Midland, Michigan).
Table 4.5.1 Experimental Parameters - Ion Exchange Resin Studies

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>SPIN-ECHO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slice Thickness</td>
<td>1 mm</td>
</tr>
<tr>
<td>Gradients</td>
<td></td>
</tr>
<tr>
<td>Z</td>
<td>2.34 G/cm</td>
</tr>
<tr>
<td>Y</td>
<td>22.2 G/cm</td>
</tr>
<tr>
<td>X</td>
<td>14.3 G/cm</td>
</tr>
<tr>
<td>Echo Time</td>
<td>7.6 ms</td>
</tr>
<tr>
<td>Repetition Time</td>
<td>1 sec</td>
</tr>
<tr>
<td>Overall Experiment Time</td>
<td>2 hrs</td>
</tr>
<tr>
<td>Image Size</td>
<td>256 x 128</td>
</tr>
<tr>
<td>Digital Resolution</td>
<td>16 μm x 33 μm</td>
</tr>
</tbody>
</table>
Table 4.5.2: Styrene - Divinyl Benzene Resins Characteristics

<table>
<thead>
<tr>
<th>BEAD</th>
<th>TYPE</th>
<th>EXCHANGE GROUP</th>
<th>% DVB</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR-120</td>
<td>Cationic</td>
<td>Sulfonate</td>
<td>8%</td>
</tr>
<tr>
<td>IR-122</td>
<td>Cationic</td>
<td>Sulfonate</td>
<td>10%</td>
</tr>
<tr>
<td>IR-200</td>
<td>Cationic</td>
<td>Sulfonate</td>
<td>20%</td>
</tr>
<tr>
<td>IR-94</td>
<td>Anionic</td>
<td>Weak Base</td>
<td>N/A</td>
</tr>
<tr>
<td>IR-900</td>
<td>Anionic</td>
<td>Quaternary Amine</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Beads were tested in distilled water, 9M sulfuric acid, 1M sulfuric acid, and 1M NaOH. The sulfuric acid solutions diluted from concentrated acid (Fisher Scientific). The sodium hydroxide solution was made from solid NaOH (Fisher Scientific).

Relaxation studies were performed on the SDVB samples using a Carl-Purcell-Meiboom-Gill software package provided by Bruker. The timing parameters can be chosen by the operator. The resulting peak heights were measured manually. A Windows compatible graphics package, ORIGIN, was used to calculate spin-spin relaxation times from timing parameters and peak heights.

The C-13 solid spectra were also obtained on the Bruker MSL 400. A TOSS (Total suppression Of Spinning Side bands) pulse sequence, implemented by John Waters, was used which eliminated spinning side bands while allowing cross polarization. A 90 pulse of 4.81 μs, a delay time of 2 s, and a spin rate of 3 kHz was used. Four sets of cation exchange resin with 8% divinylbenzene were placed in distilled water, 9 M H₂SO₄, 1 M H₂SO₄ or 1 M NaOH overnight. However wet beads were difficult to place into the rotor and the rotor would not spin. So before being placed into the spinner, the beads were rinsed with distilled water and vacuum filtered to dryness.

4.6 DISCUSSION AND RESULTS

Previously, a cation exchange resin obtained from DOW was imaged in a single bead mount developed by Anton Wallner. The spin-
echo images of this bead showed conflicting results. In some images, the bead showed heterogeneous morphology. In other images, the sample showed a homogeneous morphology.\textsuperscript{39} These results could be real or could be instrumental because the images were acquired on different days. A multiple mount needed to be developed so that several beads from a sample could be imaged at the same time. Figure 4.6.1 shows a multiple bead mount. A piece of double sided poster tape was cut with a 4 mm cork bore and placed on top of a portion of 4 mm glass rod. Five beads were placed on top of the poster tape. The tape provided enough adhesion so the beads did not roll off the mount when it was slid down a 5 mm NMR tube. The spin-echo images of the resins are shown in Figure 4.6.2. The second image is the same as the first only shown at a lower monitor brightness setting. All five beads appear to be homogeneous in the first image. At the lower monitor setting, the three beads in the upper right appear to have a heterogeneous morphology. Thus the different morphologies seen before with the single bead mount were real and not caused by different imaging conditions.

The multiple bead mount was used to examine the changes in morphology of exchange resins when exposed to extremely acidic and alkaline environments. Even strongly acidic (basic) exchange resins lose exchange capacity at extremely acidic (basic) environments. Refer to Figure 4.2.2. Five different exchange resins were imaged: three strongly acidic cationic exchange resins with sulfonic acid functional group, one strongly basic anionic resin with a quaternary ammonium functional group, and a weakly basic anionic resin. All the resins were reported by
MULTIPLE BEAD MOUNT

Figure 4.6.1: Schematic of multiple bead mount.
Figure 4.6.2: a) Spin-echo image of SDVB beads that show varying morphology. b) Same image at a lower monitor brightness setting.
the manufacturer to have a homogeneous morphology. The cationic resins contained different amounts of divinylbenzene in the monomer mixture: 8, 10, and 20%. Four to seven beads from each group was placed in distilled water for twenty-four hours then imaged with a spin-echo sequence. The same beads were placed in 9M H₂SO₄ for twenty-four hours and then imaged. A concentrated solution of sulfuric acid, an oxidizing reagent, was chosen because SDVB resins with a high content of divinylbenzene are more resistant to oxidation. Five sets of images are shown in Figures 4.6.3 through 4.6.7. An average cross-sectional signal area of the resins in each image was measured in the following manner. A height and a width for each bead was measured directly off the monitor. A signal area for each bead was calculated. These areas were averaged for each image. The results are reported in Table 4.6.1.

All the cationic beads exhibited a decrease in signal area, while the anionic beads showed an increase in size. This implies that the functional group may be interacting with the strongly acidic solution.

A decrease in signal area in the cationic resins could be due to an actual shrinkage in the size of the bead. Also the outer perimeter of the bead could be deteriorating due to oxidation by the sulfuric acid. Thus only the inner portion of the bead would still retain liquid. The cationic exchange resins would exchange a sodium ion for a hydronium ion thus transferring the bead from salt to acidic form. A cationic resin in the acidic form should also be larger than in the salt form; but the cationic resins in the images shrank in signal area when exposed to the
Figure 4.6.3: a) Cationic exchange resins (8% DVB) swollen with distilled water. b) Same resins swollen with 9 M H$_2$SO$_4$. 
Figure 4.6.4: a) Cationic exchange resins (10% DVB) swollen with distilled water. b) Same resins swollen with 9 M H$_2$SO$_4$. 
Figure 4.6.5: a) Cationic exchange resins (20% DVB) swollen with distilled water. b) Same resins swollen with 9 M H₂SO₄.
Figure 4.6.6: a) Weakly basic anionic exchange resins swollen with distilled water. b) Same resins swollen with 9 M $\text{H}_2\text{SO}_4$. 
Figure 4.6.7: a) Strongly basic anionic exchange resins swollen with distilled water. b) Same resins swollen with 9 M H₂SO₄.
Table 4.6.1 Changes in Cross-Sectional Areas of Resins Exposed to 9 M Sulfuric Acid

<table>
<thead>
<tr>
<th>BEAD</th>
<th>AREA $\text{H}_2\text{O}$ (mm$^2$)*</th>
<th>AREA $9\text{ M H}_2\text{SO}_4$ (mm$^2$)*</th>
<th>CHANGE IN AVERAGE SIGNAL AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cationic - 8 % SDVB</td>
<td>0.25</td>
<td>0.21</td>
<td>Decrease 16%</td>
</tr>
<tr>
<td>Cationic - 10 % SDVB</td>
<td>0.36</td>
<td>0.35</td>
<td>Decrease 3%</td>
</tr>
<tr>
<td>Cationic - 20 % SDVB</td>
<td>0.42</td>
<td>0.38</td>
<td>Decrease 10%</td>
</tr>
<tr>
<td>Anionic - Weakly Basic</td>
<td>0.29</td>
<td>0.35</td>
<td>Increase 21%</td>
</tr>
<tr>
<td>Anionic - Strongly Basic</td>
<td>0.29</td>
<td>0.39</td>
<td>Increase 34%</td>
</tr>
</tbody>
</table>

* Experimental Error ± 0.02 mm
acid solution. However cationic resins are converted to the acid form with hydrochloric, not sulfuric acid.41

Even though the anionic beads showed an average increase in size, some of the beads appear to have a smaller signal area. This may be due to the oxidation of the outer portion of the beads. The anionic exchange resin functional group may undergo an acid-base reaction with the concentrated sulfuric acid.

Also as the amount of DVB in the monomer mixture increases, the amount of crosslinking increases in exchange resins. If one compares the average cross-sectional area with percentage DVB in the cationic resin when swollen with distilled water, the opposite is true. The bead with the largest percentage of DVB is the largest bead. This could be explained by two factors. First the 8% and 10% DVB beads are microporous while the 20% DVB beads are macroporous.38 The larger pore size beads would allow for the absorption of liquid. Also the latter 20% DVB beads chosen could have had a larger initial mesh size.

These experiments were repeated in solutions of 1 M H2SO4 and 1 M NaOH to observe if this trend is seen again. However only three of the five beads were exposed to these solutions due to a restriction in instrument time. The cationic resin with 8% DVB, the cationic with 20% DVB, and the strongly basic anionic resin were chosen because they exhibited the largest change in average signal area. The six sets of images are shown in Figures 4.6.8 through 4.6.13. The average areas and changes in the areas are reported in Tables 4.6.2 and 4.6.3.
Figure 4.6.8: a) Cationic exchange resins (8% DVB) swollen with distilled water. b) Same resins swollen with 1 M H₂SO₄.
Figure 4.6.9: a) Cationic exchange resins (20% DVB) swollen with distilled water. b) Same resins swollen with 1 M H₂SO₄.
Figure 4.6.10: a) Strongly basic exchange resins swollen with distilled water. b) Same resins swollen with 1 M H₂SO₄.
Figure 4.6.11: a) Cationic exchange resins (8% DVB) swollen with distilled water. b) Same resins swollen with 1 M NaOH.
Figure 4.6.12: a) Cationic exchange resins (20% DVB) swollen with distilled water. b) Same resins swollen with 1 M NaOH.
Figure 4.6.13: a) Strongly basic anionic exchange resins swollen with distilled water. b) Same resins swollen with 1 M NaOH.
<table>
<thead>
<tr>
<th>BEAD</th>
<th>AREA ( \text{H}_2\text{O} ) ( (\text{mm}^2)^* )</th>
<th>AREA ( 1 \text{ M H}_2\text{SO}_4 ) ( (\text{mm}^2)^* )</th>
<th>CHANGE IN AVERAGE SIGNAL AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cationic - 8 % SDVB</td>
<td>0.30 *</td>
<td>0.20 *</td>
<td>Decrease 33%</td>
</tr>
<tr>
<td>Cationic - 20 % SDVB</td>
<td>0.45 *</td>
<td>0.27 *</td>
<td>Decrease 40%</td>
</tr>
<tr>
<td>Anionic - Strongly Basic</td>
<td>0.46 *</td>
<td>0.21 *</td>
<td>Decrease 54%</td>
</tr>
</tbody>
</table>

\* Experimental Error ± 0.02 mm
Table 4.6.3 Changes in Cross-Sectional Areas of Resins Exposed to 1 M Sodium Hydroxide

<table>
<thead>
<tr>
<th>BEAD</th>
<th>AREA H₂O (mm²)*</th>
<th>AREA 1 M NaOH (mm²)*</th>
<th>CHANGE IN AREA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cationic - 8 % SDVB</td>
<td>0.35</td>
<td>0.36</td>
<td>Increase 3%</td>
</tr>
<tr>
<td>Cationic - 20 % SDVB</td>
<td>0.42</td>
<td>0.45</td>
<td>Increase 7%</td>
</tr>
<tr>
<td>Anionic Strongly Basic</td>
<td>0.49</td>
<td>0.52</td>
<td>Increase 6%</td>
</tr>
</tbody>
</table>

* Experimental Error ± 0.02 mm
All three types of beads showed a large increase in size in the weaker acidic solution and a small decrease in size in the basic solution. This suggests that the bead material and not the functional group is interacting with the solutions.

After the resins were imaged for the second time, they were placed in distilled water again for twenty-four hours and imaged for a third time. The beads that were exposed to 9 M sulfuric acid could not be imaged due to lack of a signal. The cationic beads that were exposed to 1 M sulfuric acid also could not be imaged due to lack of a signal. However, the anionic bead exposed to 1 M sulfuric acid as well as all the beads exposed to 1 M NaOH could be imaged after a second exposure to distilled water. This may be further evidence that the beads are deteriorating via oxidation due to sulfuric acid left in the pores. The 8% and 10% DVB cationic beads become brittle and would easily break under pressure.

The beads that appear to shrink may in actuality be the same size but the signal may be attenuated. The signal received from the resins may be decreasing due to a decrease in spin-spin relaxation. T2 relaxation times were measured with the Carl-Purcell-Meiboom-Gill pulse program described in Chapter 2. The cation exchange resin with 8% DVB was chosen. Four sets of beads were observed. Before being divided into sets, the beads were soaked for twenty-four hours in distilled water. Then each set was soaked in a different solution for twenty-four hours: distilled water, 9M and 1M sulfuric acid, and 1 M sodium hydroxide. Before the beads were packed into the 5 mm NMR
tube, they were air dried. This was to ensure that the signal measured in experiments was from solution entrapped in the beads. Also the beads that were soaked in the acidic or alkaline solutions were reexposed to distilled water for twenty-four hours and air dried so the relaxation experiment could be repeated. The duration values for the experiment are listed in Table 4.6.4. The results are listed in Table 4.6.5.

The relaxation times of the beads do decrease in the acidic solution (13 ms) but recover somewhat after the beads have been reexposed to water, (15 - 17 ms). However the decrease in T₂ is not enough to attenuate the signal because the echo time of the experiment was 7.6 ms. Since signal loss is not due to a decrease in T₂, the shrinkage of the bead may be real or due to a lack of solution in the outer shell of the beads.

Carbon-13 solid spectra were obtained of the cationic resins with 8% DVB soaked in each of the four solutions. These spectra are shown in Figures 4.6.14 and 4.6.15. The spectra of the beads soaked in 1 M NaOH have a poorer signal to noise signal because the beads were not completely dried when placed into the spinner. The peak and shoulder at approximately 58 ppm are attributed to the methine and methylene carbons along the carbon backbone. The peaks at approximately 130 ppm and 148 ppm are attributed to the phenyl carbons.42,43 The peak height of the peak at 58 ppm increases by approximately 15% in the 9 M and 1 M H₂SO₄ spectra. The heights of the other peaks due not change appreciably. Also a peak at 100 ppm becomes apparent in the 9 M and
Table 4.6.4 Duration Times for CPMG Relaxation Experiments

<table>
<thead>
<tr>
<th>NUMBER</th>
<th>DURATION TIME (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>5.0</td>
</tr>
<tr>
<td>3</td>
<td>10.0</td>
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<tr>
<td>4</td>
<td>20.0</td>
</tr>
<tr>
<td>5</td>
<td>30.0</td>
</tr>
<tr>
<td>6</td>
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</tr>
<tr>
<td>7</td>
<td>50.0</td>
</tr>
<tr>
<td>8</td>
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</tr>
<tr>
<td>9</td>
<td>70.0</td>
</tr>
<tr>
<td>10</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Table 4.6.5 Spin-Spin Relaxation Values for Cationic (8% DVB) Resins

<table>
<thead>
<tr>
<th>SOLUTION</th>
<th>SPIN-SPIN RELAXATION TIME (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>22</td>
</tr>
<tr>
<td>9 M H$_2$SO$_4$</td>
<td>13</td>
</tr>
<tr>
<td>1 M H$_2$SO$_4$</td>
<td>13</td>
</tr>
<tr>
<td>1 M NaOH</td>
<td>20</td>
</tr>
<tr>
<td>H$_2$O after 9 M H$_2$SO$_4$</td>
<td>15</td>
</tr>
<tr>
<td>H$_2$O after 1 M H$_2$SO$_4$</td>
<td>17</td>
</tr>
<tr>
<td>H$_2$O after 1 M NaOH</td>
<td>21</td>
</tr>
</tbody>
</table>

* Experimental Error ± 1 ms
Figure 4.6.14: C-13 spectra of cationic (8% DVB) exchange resins.

a) after being soaked in distilled water.

b) after being soaked in 9 M $\text{H}_2\text{SO}_4$. 
Figure 4.6.15: C-13 spectra of cationic (8% DVB) exchange resins.

a) after being soaked in 1 M H₂SO₄.

b) after being soaked in 1 M NaOH.
1 M H$_2$SO$_4$ spectra. These changes also suggest a chemical change, oxidation, of the beads when exposed to the acidic solutions.

4.7 CONCLUSION

Magnetic resonance imaging is a technique that can investigate the consistency of the morphology of a sample of chromatographic exchange resins. A multiple bead mount was developed for the purpose. Thus several beads can be imaged at the same time and their morphologies compared.

Also MRI can be used to examine the changes in size for homogeneous SDVB exchange resins when they are exposed to extremely acidic and basic environments. Five different exchange resins were imaged: three strongly acidic cationic exchange resins (8, 10, 20% DVB in the monomer mixture) with sulfonic acid functional group, one strongly basic anionic resin with a quaternary ammonium functional group, and a weakly basic anionic resin. The average signal area of cationic exchange resins decreased when exposed to 9 M H$_2$SO$_4$, while the area of the anionic exchange resins increased. This suggests that the functional group may be interacting with the acidic solution.

Three of the resins (two cationic, 8% and 10% DVB, and the strongly basic anionic) were exposed to 1 M H$_2$SO$_4$ and 1 M NaOH solutions. All of the beads decreased in average signal area in the acidic solution, but slightly increased in average signal area in the basic
solution. This suggests that the bead material and not the functional group is interacting with the solutions.

Spin-spin relaxation experiments were conducted on one of the resins: the cationic with 8% DVB. Although a slight decrease in $T_2$ was seen for samples of the resin exposed to acidic conditions, it was not shorter than the echo time of the imaging sequence. Hence $T_2$-weighted images were not produced. Since signal loss in the images is not due to a decrease in $T_2$, the shrinkage of the bead may be real or due to a lack of solution in the outer shell of the beads.

Changes in peak intensity of C-13 spectra of the cationic exchange resin with 8% DVB, suggest that the beads are being oxidized by the sulfuric acid solutions. This bead could not be imaged when reexposed to distilled water after exposure to either acidic solution. This would also suggest a deterioration of the bead due to oxidation.

A future study could involve exposed the beads to a variety of acids like nitric, sulfuric, hydrochloric, and phosphoric. This would provide a range of oxidizing and acid strengths. For example, would one be able to produce an image of resins that were exposed to nitric acid, or would the resin deteriorate due to oxidation. Also maximum operating temperatures are given by the manufacturer for exchange resins. \(^{38}\) Morphology changes of the beads at elevated temperatures could be observed by variable temperature imaging.
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CHAPTER 3


CHAPTER 4

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