Deformation Induced Molecular Behavior of Cis 1,4-Polyisoprene and Its Nanocomposites Monitored by Solid-State NMR

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Submitted to the Department of Materials Science and Engineering in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Polymer Science at the Massachusetts Institute of Technology
February 2005

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Abstract

Proton spin lattice ($T_1$) relaxation time constants were used to monitor changes in the molecular motion and architecture of polyisoprene, polyisoprene-clay composites and polyhedral oligomeric silsesquioxane (POSS) nanofillers. The high frequency relaxations monitored by NMR are sensitivity to changes in the environment of polyisoprene chains as a function of compressive strain. These are the first experiments to use magic angle spinning nuclear magnetic resonance techniques in situ with compression measurements to identify changes in the chain environment during compressive strain.

For the polyisoprene composites, in situ compression measurements were made during the acquisition of NMR relaxation measurements. Therefore, the architecture of polyisoprene-clay composites was monitored as a function of strain. Clay aggregates, composed of stacked clay platelets, were identified in the nanocomposites. Increases in strain resulted in an irreversible, increase in interfacial area between clay and the polymer as the aggregate broke apart. This increase in area could be easily quantified by NMR ($\sim 230\%$) and was verified with optical microscopy ($\sim 150\%$). The correlation between NMR and optical microscopy indicates, with certainty, that NMR relaxation measurements can be used to quantify differences in interfacial area of nanocomposites. With this being established, the techniques developed in this thesis could be applied to analyze strain induced changes in interfacial area for samples which are not optically clear or samples in which the particle dimensions make microscopy techniques difficult. The quantitative discrepancy between the two techniques suggests that NMR captures changes in the bulk whereas microscopy is confined to surface effects. Finally, these results point to the potential to design a composite in which this mechanism is halted, such as crosslinking the clay directly to the polymer matrix, in hopes of creating a higher energy mechanism of deformation and thereby improving the mechanical properties.

Octaethyl POSS was found to exhibit characteristics exemplified by plastic crystals. Phase transitions were identified with NMR and differential scanning calorimetry at $\sim 258$ K and $\sim 253$ K for partially deuterated and fully protonated ethyl POSS, respectively. For both derivatives at temperatures above the phase transition, the molecular motions of POSS were found to be on the order of nanoseconds ($\sim 30 \pm 2$ ns) and associated with molecular tumbling of the POSS molecule. After the phase transition, the molecular tumbling of POSS molecules slowed ($\sim 530 \pm 15$ ns) and became more asymmetric. These phase changes were characterized by a change in entropy of $20.2 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$, a typical value for plastic crystals. This plastic crystalline behavior suggests that in the high temperature phase, the POSS molecules will undergo plastic flow at relatively low levels of stress. Therefore, in the high temperature phase POSS will not enhance mechanical behavior in the same manner as other inorganic fillers, such as silica. In addition, the trends in the transition temperature suggest that the derivatives can be chemically altered to achieve the desired phase at a given operation temperature.
Finally, a compression device suitable for fitting inside the rotor of a magic angle spinning NMR probe was built. Although in situ NMR compression experiments have previously been investigated, these experiments were the first to be done while magic angle spinning. This allowed for increased specificity for assigning molecular mobility. Additionally, the magic angle spectra doubled the signal to noise, as compared to static proton NMR spectra. Thus, more rapid spectral acquisition was possible, allowing “snapshots” to be acquired under dynamic processes such as mechanical deformation. This led to a more detailed analysis of deformation than that possible from static spectra. For instance, using magic angle spinning the behavior of bulk polymer was separated from that adjacent to the clay. For this reason, the effect of the changes on the architecture of nanocomposites could be monitored through those protons in closest proximity to the clay surface. This enhanced selectivity resulted in an unambiguous determination of change in composite architecture and its time dependence.

Thesis Supervisor: Karen K Gleason
Title: Professor of Chemical Engineering
Acknowledgement

I would like to thank my advisors, Prof. Karen Gleason and Prof. Robert Cohen, for funding and guidance for this thesis work. Thanks to both for their patience and willingness to keep reading and reviewing various drafts of this thesis. In addition, I would like to thank the group members in both labs for their help with various aspects of this project. In particular, I would like to thank my NMR predecessors Prof. Leslie Loo and Prof. Kenneth Lau for teaching me the various experimental nuances of NMR spectroscopy. Thanks to Prof. Jeff Abes for help with the art of transmission electron microscopy and Prof. Yonathan Thio for many discussions about mechanical behavior. Finally, thanks to the Haddad Group at the Edwards Air Force Base for supplying the POSS material I requested and Prof Wuensch and Joe Adario for helpful suggestions and conversations about X-ray spectroscopy.
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Chapter 1

Background and Introduction
Introduction

For many years, researchers have attempted to understand the structure-property relationship of polymers and composites. It has been theorized that bulk macroscopic properties such as the glass transition temperature (T_g), mechanical modulus and wear resistance are all controlled by the molecular level mobility, often associated with only a few repeat units on the polymer chains.\(^1\text{-}^4\) In order to explore these theories atomic level simulations were used to reproduce bulk property measurements from dielectric or dynamic mechanical experiments.\(^5\text{-}^6\) However, more recently researchers have designed in situ experiments, for instruments such as atomic force microscopy and nuclear magnetic resonance, which allow for molecular level observation of the polymer during mechanical deformation.\(^7\text{-}^9\)

There has been a surge in the research of nanocomposite materials in the recent years. Nanocomposites are generally defined as a two component material system in which one of the components has at least one dimension on the nanoscale. The applications of these materials have been far reaching into essential all the fundamental scientific fields of research; such as biology, materials science and chemistry.\(^10\) For instance, biological applications include biosensors and biomaterials composed of nanocomposite materials.\(^11\text{-}^13\) Researchers in the field of material science have explored the utility of nanocomposites for alternatives to traditional packaging materials and as lightweight alloys.\(^10,^14,^15\) Finally, chemists have synthesized nanocomposites with a variety of chemical architectures to be used in solid state battery application and sensors.\(^10,^16,^17\) Therefore, as researchers look for medical, scientific and industrial applications for nanocomposites there is a desire to explore and understand the relationship between molecular level architecture and macroscopic behavior. In order to properly specify the macroscopic properties of nanocomposites it is essential to control and design the composite on a molecular level.

This need to understand the atomic and molecular level interactions of a nanocomposite makes observations by nuclear magnetic resonance (NMR) ideal. Solid-state NMR is a nondestructive molecular level characterization technique, which can be used to observe the molecular level interactions and mobility of different parts of a composite. The relationship between structure and function can be determined with the use in situ mechanical techniques. Historically, quasi-static mechanical stress or strain has been applied to the polymers while monitored by static solid-state NMR.\(^18\text{-}^20\) This work illustrates the advantages of monitoring quasi-static deformation with magic angle spinning (MAS) solid-state NMR.
**NMR Background**

Previous NMR work has primarily used deuterium (\(^2\text{H}\)) NMR to monitor in situ deformation of polymers and polymer composites.\(^{21-23}\) However, the low relative abundance of this nucleus results in low signal to noise, which can only be overcome with the acquisition of numerous scans. In addition, the researcher must either incur the cost of synthesizing a deuterated polymer or work with a substance which has an exchangeable functionality, such as an alcohol or an amine. This work involves the use of proton (\(^1\text{H}\)) NMR which has a high relative abundance and therefore requires fewer scans in order to acquire a spectrum with large signal to noise. In addition, the high abundancy of the isotope means there is no isotopic labeling necessary. Therefore, \(^1\text{H}\) NMR is time and cost effective relative to observation of other nuclei.

As mentioned earlier, this work explores the use of magic angle spinning with in situ mechanical deformation. Magic angle spinning (MAS) is a solid-state NMR technique used to resolve the powder pattern to the isotropic chemical shifts of the chemically distinguishable nuclei. When a proton experiment is done statically the observed behavior describes the collective motions of all the protons on the polymer. With MAS the observed behavior can be assigned to each chemically distinguishable nucleus. The increased specificity of MAS will be contrasted to static experiments throughout the following chapters.

Finally, there are numerous NMR methods to measure molecular mobility; however, the spin lattice relaxation time constants (\(T_1\)) were used in these experiments. Motions which cause this type of nucleus relaxation are on the order of the Larmor frequency \(^{24}\), for these experiment that is 270 MHz. Previous, in situ NMR and mechanical experiments rarely monitor this type of relaxation because such a high frequency cannot be readily compared to dynamic mechanical or dielectric measurements. However, as will be illustrated in the following chapters, mechanical deformation does change the mobility detected at this frequency. Specifically, the spectral density of motion, which dictates the spin-lattice relaxation, may be centered at a much higher frequency than other techniques, but the tail of the spectral density distribution can influence the \(T_1\) experiments. In addition, the paramagnetic theory is well established for this relaxation, making it an attractive parameter for measurements of paramagnetic containing nanocomposites.
NMR of Polyisoprene

Molecular level theories to describe the macroscopic mechanical properties of polyisoprene were widely hypothesized by the academic community in the 1940's. Specifically, Doi and Edwards explained the macroscopic exponential decay of stress as chains slipping out of physical entanglements. However, Mooney, et. al. suggested stress relaxation in a vacuum can be described by a two term equation: one term describes a transient relaxation caused by the molecular level rupture of secondary bonds and a second term describes the exponential decay caused by the molecular level chain rupture and slippage. In comparison, extensive work by Tobolsky and Razumovski identified oxidative scission of the polyisoprene chains as the molecular mechanism for stress relaxation in air, at elevated temperatures.

Approximately a decade latter in the 1950's, the NMR community began to publish studies characterizing the molecular motions of static, undeformed polyisoprene. Gutowsky, et. al. found, using static proton NMR, that the activation energy associated with internal repeat units was larger than for the methyl groups; furthermore, these barriers changed as a function of crosslink density. In Gutowsky's study, it was noted that interchain crosslinks, caused by back biting of the sulfur radical, could be identified by a decrease in the mobility of the methyl substituents. Odajima, et. al. found that the spectral distribution used to describe the proton spin-lattice relaxations of polyisoprene was best described by a distribution of correlation times rather than the single correlation time suggested by the Bloomberg, Pound and Purcell model. This distribution describes the range of motions occurring along the polymer chain due to the slight differences in the motions of each repeat unit. Despite the complexity of the underlying spectral density calculation, Yager, et. al. noted that static proton experiments of polyisoprene only required a single spin-lattice relaxation time constant due to the extensive dipolar communication in the sample.

Building on this characterization of the static undeformed polyisoprene, various groups investigated the changes in molecular mobility of strained polyisoprene. For instance, Von Meerwall, et. al. discovered small changes in the spin-lattice relaxations but large changes in the lower frequency spin-spin relaxations of tensile strained crosslinked polyisoprene. Only at large tensile strains, greater than 200%, did the polyisoprene chains became static increasing the dipolar interaction and decreasing the spin-spin relaxation. In fact, the theory, suggested by Mooney and Tobolsky a decade earlier, was best
described by these low frequency motions. For this reason, Kariyo, et. al. also measured the effects of tensile deformation using relaxometry. Proton relaxometry allowed for a simultaneous monitoring of a range of motions occurring at various frequencies from $10^{-5}$ to $10^2$ MHz. They found the largest differences in the spin-lattice relaxation occurred at low frequencies, $10^{-2}$ to $10^0$ MHz, when strain was above 300%. Extending beyond tensile deformation, various groups, have designed in situ static compression devices. For instance, Hedden, et. al. noted decreased mobility and increased asymmetry of methyl group rotations when using deuterium NMR to monitor compressed polydimethylsiloxane. However, none of these compression studies have spoken to the polymer communities past interest in stress relaxation by focusing on a time dependence of the induced molecular motions.

**NMR of Polyisoprene-Nanocomposites**

Due to the increased industrial importance of composites, the polymer community has recently been interested in the casual relationship between the microscopic architecture and macroscopic strength. For instance, Kraus, et. al. used electron microscopy to identify the effect of the carbon black-polyisoprene interface on mechanical strength. However, Kraus acknowledges microscopy is best suited for observing particle size not molecular level mobility at the interface. Indeed, Kraus notes the measured particle size alone could not be used to completely describe the observed mechanical behavior. Furthermore, as interests in polyisoprene-nanocomposites increases, the dimensions for the fillers become smaller and microscopic techniques become challenging and time consuming. For instance Vu, et. al. investigated the correlation between the degree of exfoliation and the mechanical properties of cis 1,4-polyisoprene-montorillonite composites; however, dispersion techniques were limited to x-ray diffraction and transmission electron microscopy. In their experiments a sample contained both regions of clay exfoliation and intercalation making characterization with these techniques tedious and difficult. Therefore, there is a need to design convenient techniques to monitor interfacial effects and an averaged composite architecture.

NMR is particularly well suited to study nanocomposites since it is a nondestructive technique, sensitive to molecular level architecture and mobility. Since nanocomposites are a presently expanding field of interest, NMR studies of nanocomposites have not been as extensive as those of homopolymers. However, some researchers have developed NMR techniques to characterize nanocomposites.
instance, both VanderHart, et. al. and Asano, et. al. noted that the amount of clay would alter the spin-lattice relaxation of nanocomposites due to the presence of natural occurring paramagnetic centers, Fe$^{3+}$, in the clay structure.\textsuperscript{41,42} In fact, VanderHart used the presence of the iron to identify that the usually unstable gamma crystallites are stabilized by the clay and form in close proximity to the surface.\textsuperscript{41} Therefore, most of the NMR done on nanocomposites has centered on characterizing structures using the natural occurring paramagnetic centers as markers. No studies have applied in situ NMR deformation techniques to nanocomposites. Therefore, this thesis intends to apply that previous knowledge of in situ NMR techniques to this new field of interest.

\textit{NMR of Nanofillers}

A critical element of designing nanocomposites is to identify the independent behavior of each constituent of the composite prior to blending. Therefore, there is a need to fully characterize the behavior of nanofillers, prior to blending them in homopolymers, in order to accurately predict the properties of the composite. Gates, et. al. and others have used solid state NMR to measure the effect of the oxidation state of iron on the relaxation of various nuclei, $^{29}$Si and $^{27}$Al, in the clay.\textsuperscript{44} The spin-lattice relaxation time of the nuclei decreases with an increase in the oxidation state.\textsuperscript{43} In addition, the absorption mechanisms of small molecules on clay platelets were monitored with solid-state NMR by numerous investigators. Concerning natural occurring montmorillonite,\textsuperscript{46-49} Xiong, et. al. used deuterium NMR to determine the orbitals of deuterated benzene used for absorption with the interatomic Ca$^{+2}$ ion in montmorillonite.\textsuperscript{48} In addition, the effect of absorption was a decrease in the molecular tumbling about the $C_6$ axis. He, et. al. used carbon-13 NMR to analyze the ordering of alkyl groups on tallow surfactants in between sheets of clay. It was found that the substituents became ordered, forming a trans configuration, when proximal to the surface. Furthermore, the amount of ordering depended on the packing density of the surfactant.\textsuperscript{47} However, the conclusions of both groups were subject to speculation because the results were masked by the paramagnetic centers contained in the clay structure.

The other nanofiller of current widespread interest is polyhedral oligomeric silsesquioxane (POSS), a fused cage of cyclic siloxane with a molecular radius on the order of a nanometer. Although NMR has been used to characterize various POSS-polymer nanocomposites,\textsuperscript{50,51} unlike the clays, no NMR has been done solely on the POSS nanofiller. Therefore, this thesis will use solid state NMR to characterize
the properties of POSS crystals, with the premise that understanding the nanofiller properties will allow us to better predict the composite properties.

Project Goals

The primary goal of this work is to develop in situ mechanical and NMR methodology which will aid in the understanding the molecular level changes in the polymers and polymer nanocomposites during macroscopic deformation. These techniques were developed and tested on the model systems of polyisoprene homopolymers and polyisoprene nanocomposites.

Synthetic cis 1,4-polyisoprene was a desirable homopolymer for this study for three reasons: it is a structurally simple system in comparison to natural occurring polyisoprene, due to its inherent molecular mobility small amounts of MAS are required to resolve the spectrum, and the low modulus means a lightweight compression device can be used to create in-situ deformation (Table 1, Appendix 1). First, in the 1970's and 1980's, work by Tanaka, et. al. centered on the complete characterization of natural polyisoprene. They attempted to fully characterize the role of fatty acids on the mechanical behavior of the polymer, as well as characterize the polymer so that it could be synthetically reproduced. Later, both groups led by Tanaka and Smith found that the uniaxial extensibility of the polymer was dependent on the degree of crystallinity formed by fatty acids. Due to this complexity, synthetic cis 1,4-polyisoprene was an ideal choice for study because it avoided the complications introduced by proteins and fatty acids occurring in natural polyisoprene. Second, a decrease in dipolar interactions increases spectral resolution. The high mobility of elastomers creates a internal decrease in dipolar interactions; therefore, elastomers only require small amounts of MAS to further resolve spectra into their isotropic chemical shifts. Finally, elastomers have a relatively low modulus (~ 0.5 MPa) which can be easily deformed using a lightweight nylon screw. Therefore, a lightweight compression device could be designed and used in a MAS rotor.

Table 1: Characteristics of the Synthetic Cis 1,4-Polyisoprene Used in the Majority of this Thesis

<table>
<thead>
<tr>
<th>Structure*</th>
<th>Tg**</th>
<th>Stabilizer</th>
<th>Initiator</th>
<th>Modulus***</th>
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<tr>
<td>97% cis 1,4-polyisoprene, 3% trans 1,4-, 1,2- and 3,4-polyisoprene</td>
<td>-67 °C</td>
<td>2,6-di-tert-butyl-4-methylphenol</td>
<td>Sec-butyl lithium</td>
<td>0.5 MPa</td>
</tr>
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* verified with 1H NMR; **measured by DSC; ***measured by compression tests

Polyisoprene-nanocomposites have been a topic of recent research due to the widespread industrial uses of polyisoprene and the recent commercialization of polyisoprene-clay nanocomposites. Therefore,
information about the structure-property relationships for these nanocomposites could aid in designing composites with desired macroscopic properties.

In order to perform these measurements while the sample was spun at the magic angle a novel compression device was made. This device included a rod of Teflon with a hole in the middle large enough for the placement of the polymer or polymer composite. Strain was placed on the polymer with successive turns of a nylon screw. The entire device was housed in a ceramic rotor so that the sample could be spun by the NMR probe. As mentioned above it was important that the materials used be lightweight so that the probe could easily spin the sample; therefore, these in situ techniques are limited to elastomeric materials.

The description of this thesis work is divided into: two chapters concerned with the deformation mechanisms occurring in clay polyisoprene nanocomposites, a chapter which uses NMR to explore the crystallographic phase transition of polyhedral oligomeric silsesquioxane (POSS), a commercially available nanofiller and a chapter concerning the in situ mechanical behavior of polyisoprene
References


32. Yager Physics 1939, 7, 434.


Chapter 2

Strain Behavior of Cis 1,4-Polyisoprene-Montmorillonite Clay Nanocomposites Monitored by Solid-State NMR

(Submitted to Journal of Applied Polymer Science, G.M. Poliskie, R.E. Cohen, K.K. Gleason)
Abstract

Previous work has focused on the use of microscopy to explore the mechanisms of deformation in polymer nanocomposites. That technique creates a qualitative representation which may not be statistically representative of the bulk properties. This paper illustrates the utility of solid-state NMR, which inherently measures bulk behavior, to both identify and quantify mechanisms of deformation. Specifically, in this study, increases in the interfacial area of various modifications of Cloisite® clay in 1,4-cis polyisoprene nanocomposites were monitored during uniaxial compression. Interaction of the Fe$^{3+}$ in the clay with the polymer decreases the polymer's $^1$H spin-lattice relaxation time constant ($T_1$). In some of the nanocomposites, the increase in the interfacial area of the clay platelets was observed by a decrease in the polymer's $T_1$ with successive amounts of strain. The observation of these changes with static $^1$H NMR is limited by the dispersion of the clay.

Introduction

Transmission electron microscopy (TEM) of elongated nylon-6 montmorillonite composites indicated that individual clay layers of the aggregate could be pulled apart with macroscopic tensile strain. TEM allows for the qualitative observation of microscopic deformation; however, each individual micrograph is not necessarily representative of the bulk composite. Furthermore, in order to quantitatively determine changes in the interfacial area between the clay and the polymer, multiple micrographs would have to be taken over the entire sample. In contrast, NMR is a technique which inherently averages the bulk properties of the composite. Therefore, it is useful to explore the utility of NMR to identify and quantify this mechanism of deformation in polymer nanocomposites.

Polyisoprene and polyisoprene composites have been the subject of a large number of studies aimed at improving their mechanical properties due to their widespread industrial uses. In particular, clay nanocomposites have found a niche in the automotive and sporting good industries. Clay has an advantage over traditional fillers due to their larger aspect ratio, which allows for more interfacial contact with the polymer. As a result of this higher aspect ratio, a clay nanocomposite has the capability of improving strength with lower loadings than that used for traditional composites.

NMR has recently been used not only to identify structural changes in the polymer, but to determine how these changes influence the macroscopic mechanical properties. In situ and quasi-static
experiments on a number of semi-crystalline and elastomeric polymers have explored the changes in structure as a function of stress or strain. Little work has focused on the mechanical and structural effects of the addition of montmorillonite clay to polyisoprene. What has been reported has focused on the well dispersed, surface modified clay in a crosslinked polyisoprene matrix. NMR work on composites has been limited to studies of the structural changes of the matrix polymer upon the addition of clay. Since polyisoprene is an elastomeric and not a semicrystalline polymer, the addition of clay should not significantly alter the morphology of the matrix. Furthermore, no NMR in situ mechanical measurements have been reported on clay filled polyisoprene nanocomposites. Therefore, this study investigates the use of NMR to better understand the behavior of uncrosslinked polyisoprene nanocomposites under deformation. Understanding this behavior will aid in optimizing the design of a mechanically desirable polyisoprene nanocomposite. Furthermore, this study will illustrate the utility of solid-state NMR to quantitate changes in the interfacial area between the clay and polyisoprene when the composite is deformed.

**Experimental**

Aldrich 97% cis 1,4-polyisoprene with weight average molecular weight 800,000 g/mol was used as received. Cloisite®, a montmorillonite clay with varying surfactant modifications, was purchased from Southern Clay Products. The surfactants on the clays included: methyl, tallow, bis-2-hydroxyethyl quaternary ammonium (30B), dimethyl, dehydrogenated tallow quaternary ammonium (20A) and dimethyl, hydrogenated tallow, 2-ethylhexyl quaternary ammonium (25A). All blends were solvent cast from a 1.1 wt% solution of polyisoprene in THF to which was added 0.15 wt% of the corresponding clay. After solvent evaporation, the clay made up 13 wt% of the polymer nanocomposite. For those blends which contained varying amounts of Na+ exchanged clay, the solution of polyisoprene in THF remained 1.1 wt% and the solution of clay consisted of 0.23 wt%, 0.34 wt% and 0.45 wt% to make a 20 wt%, 30 wt% and 40 wt% blends upon solvent evaporation, respectively.

Wide angle x-ray diffraction (WAXD) measurements were made on Riguku Ru300 x-ray generator with Cu Kα radiation. The operating voltage was 60 kV with a current of 300 mA. Spectra were taken, from thin films cast upon glass sides, in reflection mode at room temperature.

Transmission electron microscopy (TEM) was performed on a Joel 2000FX instrument. This instrument had a lanthanum hexaboride filament operating at 200 kV. Samples were cryomicrotomed at –
130 °C to a thickness of 50 nm using a MT-X Ultramicrotome and a diamond knife. The samples were collected on 400 mesh copper grids.

The mechanical data were acquired with an Instron Model 4201 operated in compression mode at room temperature. The specimens were rectangular with dimensions: 0.2 in. x 0.2 in. x 0.4 in. Both the top and bottom of the polymer specimen had a Teflon-polymer interface allowing for equal slip on both sides. The deformation rate was 0.5 mm/min. A 5 kN compression load cell was used for all tests.

All NMR spectra were taken with an Oxford 6.3 T magnet (with a 270 MHz ¹H resonance frequency) using a Tecmag dual resonance pulse generator and receiver. Static ¹H experiments were performed on a home built probe with a 2 μs π/2 pulse width. Spectra were acquired with a 10 μs dwell time and a 5 s recycle delay. The static spectra, represented in Figure 3, were taken at room temperature and the spin lattice relaxation times were taken at -10 °C (± 1°C), unless otherwise noted. The nanocomposites were compressed at room temperature and then the temperature was decreased for NMR acquisition. These spectra were taken after a 10 minute wait for temperature equilibration and stress relaxation (Appendix 2). The lower temperature was regulated with a N₂ gas stream submerged in a dewar containing liquid N₂.

The device used for static spectra in the presence of compressive strains was a Teflon rod 0.25 in. in diameter and 1.00 in. in length. The polymer was placed in a threaded 0.18 in. diameter hole and compression was induced by successive turns of the nylon screw. A Teflon spacer between the polymer and screw allowed for slip at one end of the specimen while the bottom of the Teflon device created slip at the other. Accordingly, the polymer specimens were rectangular with the dimensions of 0.09 in. x 0.09 in. x 0.30 in.. After 40% compressive strain, there was clearance between the specimen’s circumference and the sides of the compression cell.

Spin-lattice relaxation time constants were measured using an inversion recovery sequence (π-τ_d - π/2-Acq). A single least square exponential was fitted to the peak intensity (M) versus delay time (τ), resulting in a two parameter fit yielding: the equilibrium peak intensity (M₀) and the spin-lattice relaxation time constant (T₁) (Eq 1).²⁰

\[
\text{Eq 1: } M = M_0(1 - 2\exp(-\tau/T_1))
\]

Applying this single exponential, for the nanocomposites, resulted in an R² value ≥ 0.99 in all cases. Each fit consisted of 15 points from equally spaced delay times. All T₁ time constants are reproducible within
7% error. Simulations of line shapes for the static spectra were performed with the use of GRAMS® software with three peaks used to represent the three chemically distinguishable protons. For the homopolymer, simulated peaks were Gaussian with the full width half mass (FWHM) line widths extracted from the simulation. A Lorentzian peak was used to simulate the lineshape for the various nanocomposites.

Results

There was no clear difference in the type of clay tactoids seen in the TEM as a function of surfactant modification. Representative micrographs from the blend with the 30B surfactant are presented in Figure 1. Figure 1a shows sheets of clay clustering in micron sized clumps. In Figure 1b, single exfoliated clay sheets can be observed surrounding smaller clusters.

*Figure 1: TEM images of the cis 1,4-polyisoprene blended with 13 wt% 30B montmorillonite prior to deformation*

Figure 2 and Table 1 provide more quantitative details of the clay tactoids in the various blends.

*Table 1: Comparison of WAXD spacing of cis 1,4-polyisoprene montmorillonite nanocomposites*

<table>
<thead>
<tr>
<th>Type of nanocomposite</th>
<th>Clay d₀₀₁ spacing (nm)</th>
<th>Nanocomposite d₀₀₁ spacing (nm)</th>
<th>Change in d₀₀₁ spacing (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>1.16</td>
<td>1.28</td>
<td>0.12</td>
</tr>
<tr>
<td>30B</td>
<td>1.80</td>
<td>1.95</td>
<td>0.15</td>
</tr>
<tr>
<td>20A</td>
<td>2.35</td>
<td>2.68</td>
<td>0.33</td>
</tr>
<tr>
<td>25A</td>
<td>2.08</td>
<td>2.20</td>
<td>0.12</td>
</tr>
</tbody>
</table>
In Figure 2, shifts in the wide angle x-ray diffraction spectra indicate that there is some intercalation of polyisoprene chains into the galleries of the clay structure, with the amount depending on the nature of the surfactant. The largest change in spacing shown in Table 1 indicates that the surfactant 20A is the most compatible with polyisoprene.

*Figure 2. WAXD of cis 1,4-polyisoprene-montmorillonite nanocomposites*

![WAXD of cis 1,4-polyisoprene-montmorillonite nanocomposites](image)

Figure 3 is a representative static spectrum of polyisoprene with and without montmorillonite filler. The static spectrum of polyisoprene is resolved into the methine (a) resonance and the combined methylene (b) and methyl (c) resonances (see Figure 4). In the case of the homopolymer, the FWHM was ~200 Hz for the methine resonance and ~400 Hz for the combined methyl and methylene resonance. The
broadening in the presence of clay causes a loss of spectral resolution of the methine versus the methylene and methyl protons and increases the FWHM. The linewidths of the nanocomposites cluster into the two groups consisting of: the less polar surfactants 20A and 25A, FWHM ~3200 Hz, and the more polar surfactant 30B and Na⁺ exchanged clay, FWHM ~2800 Hz.

Figure 3: Static $^1$H NMR of cis 1,4-polyisoprene and cis 1,4-polyisoprene containing 13 wt% Na⁺ exchanged montmorillonite

![Figure 3](image)

Figure 4: Structure of cis1,4-polyisoprene

![Figure 4](image)

Figure 5 is a plot of the inverse of the measured $T_1$ time constants versus the weight percent of Na⁺ exchanged clay. The $T_1$ value decreased with increasing weight percent of clay at both temperatures of −10 °C and 0 °C.
Figure 5: Plot of $T_1$ time constants as a function of amount of clay added for Na$^+$ exchanged clay nanocomposites

Figure 6 and Figure 7 are the magnetization recovery plots at three different values of strain for the nanocomposites containing Na$^+$ exchanged and 30B surfactant, respectively. In the case of the Na$^+$ exchanged clay, there is a steady decrease in the $T_1$ from 0% to 40% strain. For the 30B surfactant containing nanocomposite, there is an initial drop in the $T_1$ after strain but no further drop after 20%.
Figure 6: Magnetization recovery curve for cis 1,4-polyisoprene nanocomposites containing 13 wt% Na$^+$ exchanged clay under compressive strains at -10°C

Figure 7: Magnetization recovery curve for cis 1,4-polyisoprene nanocomposites containing 13 wt% 30B
exchanged clay under compressive strains at $-10 \degree C$

The $T_1$ time constants for all four cis 1,4-polyisoprene nanocomposites are represented in Figure 8. The initial value of $T_1$, prior to compression, is smaller for the less polar surfactants. The nanocomposites containing the two more polar surfactants, Na$^+$ and 30B, have the same initial $T_1$ of $\sim 1$ s and the two nanocomposites containing the less polar surfactant, 20A and 25A, have an initial $T_1$ of $\sim 0.7$ s. The nanocomposites containing Na$^+$ and 30B are the only samples showing a significant drop in $T_1$ with increasing compressive strain.

Figure 8: $T_1$ time constants of cis 1,4-polyisoprene and cis 1,4-polyisoprene-montmorillonite nanocomposites under compressive strains at $-10 \degree C$

The addition of clay to polyisoprene had a statistically significant, but small effect, on the compression modulus as indicated in Figure 9. Specifically, there was a small drop in the compression modulus for the 20A and 25A modified nanocomposites.
Homopolymer and Clay Modification in the Nanocomposite

Discussion

Using solid-state NMR to determine changes in the interfacial area of the nanocomposite requires that the clay contain paramagnetic Fe$^{3+}$ centers, which are used as markers. In addition, it requires that there be unexposed Fe$^{3+}$ centers in the aggregate in order to observe changes with an increase in strain. Therefore, TEM and WAXD were used to differentiate composites with unintercalated aggregates, with unexposed paramagnetic centers, from composites in which extensive intercalation makes changes in interfacial area difficult to observe. Furthermore, the bulk macroscopic modulus was related to the microscopic architecture of the composite.

As seen in Figure 1, different sized clusters could be identified in the TEM in all specimens. Because, a single platelet has dimensions of 1 nm to 75-100 nm, the micron sized aggregates must be composed of multiple platelets. It is important to establish the presence of aggregates, with unexposed clay surface area, in order to interpret the NMR as an increase in interfacial area during deformation.

Montmorillonite clay contains paramagnetic Fe$^{3+}$ in its galleries; the Fe$_2$O$_3$ comprises 3.11-4.28 atomic weight percent of the clay depending on the source. The presence of these paramagnetic centers
has important implications for the acquisition of NMR spectra. The linewidth is inversely related to the inhomogeneous spin-spin relaxation, which is influenced by the homogeneity of the local magnetic field around the observed nucleus. As noted in other systems, each paramagnetic center alters the local magnetic field around it, increasing the linewidth. Figure 3 indicates that these local field gradients broaden the spectrum, decreasing the spectral resolution of chemically inequivalent nuclei. Because of the broadening, the $T_1$ time constants could not be assigned to a particular proton moiety. Instead the $T_1$ values describe the collective behavior of all the protons on the polymer.

The nanocomposites with the nonpolar surfactants, 20A and 25A, are expected to disperse better in the polyisoprene matrix since their chemical structures more closely match that of the polymer. Consistent with this logic, these two composites had a larger FWHM due to the greater distortion of the local field created by the larger amount of exposed $Fe^{3+}$ centers. This illustrates the utility of NMR to identify improved dispersions caused by adding the appropriately modified clay.

For the nanocomposites, the $T_1$ time constant is a linear combination of variety of factors which include, but are not limited to: paramagnetic centers, dipolar coupling, and chemical shift anisotropy (Eq 3).

\[ \frac{1}{T_1} = \frac{1}{T_{1\text{para}}} + \frac{1}{T_{1\text{anisotropy}}} + \frac{1}{T_{1\text{dipolar}}} \]

The chemical shift anisotropy for protons is small; therefore, the dipolar coupling and the paramagnetic effect are the two largest contributions to the $T_1$ parameter. The paramagnetic contribution for a system with spin diffusion has been worked out by others, the spin-lattice relaxation can be related to the concentration of paramagnetic sites (N), the diffusion barrier length (b), and the spin diffusion constant (D) (Eq 4). Therefore, as the polymer is exposed to more $Fe^{3+}$ centers (N), within the diffusion barrier of 0.5 nm, the contribution from the paramagnetic effect will increase and the measured $^1H\ T_1$ time constant of the polymer will decrease.

\[ \frac{1}{T_{1\text{para}}} = 4\pi NbD \]

As has been cited by other authors and according to Eq.4, a larger concentration of paramagnetic centers lowers the $T_1$ value. Figure 5, shows that $T_1$ decreases when the weight percent of clay increases, suggesting an increase in the amount of $Fe^{3+}$ sites interacting with the polymer. The linear regression to the data, at $-10\ ^\circ C$, in Figure 5 is presented in Eq 5.
The combination of Eq 3 and Eq 4 would create an equation of the same form as the linear regression (Eq 5). However, the theory presented in Eq 4 was developed for a homogenous distribution of paramagnetic centers with each center having a spherically symmetric interaction with neighboring spins. For these composites, each paramagnetic center is embedded in the clay platelet. Those centers buried in the center of the aggregate will not influence the relaxation of the polymer’s spins and those at the edges of the aggregate will only be surrounded by polymer on one or two sides making their interaction with the polymer non-spherical. Therefore, as cited by other authors this model cannot be rigorously used to find an absolute concentration of paramagnetic centers; however, it does provide the correct functional dependence to explain our observations and allows us to ratio the changes occurring as more paramagnetic centers are exposed to the spins.

Figure 7 and Figure 8 show that the $T_1$ decreases with an increase in compressive strain suggesting an increase in the number of paramagnetic centers exposed to the polymer. This increase in number of exposed centers is likely the result of a deformation of the clay aggregates. As the aggregates break apart there is an increase in the interfacial area between the polymer and clay platelets. The decrease in $T_1$ for the Na$^+$ exchanged nanocomposites after 40% of strain was $\sim 0.30$ s, which from linear fit of Figure 5 (Eq 5), corresponds to a 226% increase in interfacial area. For the 30B exchanged nanocomposites, the decrease was $\sim 0.20$ s, corresponding to a 173% increase in interfacial area. Furthermore, experiments indicated that when the strain is released the $T_1$ does not change from its value at 40% strain. Therefore, the increase in interfacial area is irreversible. This suggests that it is possible to improve the dispersion of the clay by shearing the mixture when the clay is blended into the polyisoprene.

Improving the dispersion of clay increases the number of Fe$^{3+}$ sites in contact with the polymer and decreases the $T_1$ time constant. Figure 9 indicates that the Na$^+$ and 30B exchanged clay have a zero strain $T_1$ ($\sim 1.00$ s) higher than the zero strain $T_1$ values ($\sim 0.70$ s) of the 20A and 25A modified clay composites. The 20A and 25A modifications are nonpolar and more closely match the nonpolar structure of the polyisoprene, leading to more intercalation (Table 1). Better dispersion and the lower zero strain values of the $T_1$ time constants are consistent with more Fe$^{3+}$ exposure to the polyisoprene. This increased
exposure means fewer unexposed paramagnetic centers prior to compression. As a result, there is no
significant increase in interactions between the polymer and the clay when the composite is compressed.
Thus, as seen in Figure 9, there were no significant changes in the spin lattice relaxation time constants
with increased strain for the 20A and 25A modifications.

More interactions between the polymer and filler and better dispersion would be expected to
produce an improvement in modulus of the samples. Figure 9 shows clearly however, that the
compression modulus decreased meaningfully for the two samples containing the more compatible 20A
and 25A surfactants. The reason for this decrease lies in the anisotropic composite nature of the effective
filler particle when clay tactoids are present. There are substantial differences in the mechanical response
of clay-filler elastomers compared to more traditional carbon black filled compounds. In the latter,
favorable filler-polymer interactions lead to bound and occluded rubber which adds to the effective volume
filling capacity of the irreducible and non-deformable carbon black aggregates, thereby enhancing the
 modulus. Intercalated clay tactoids are anisotropic and deformable; the amount of readily sheared material
in the interlamellar galleries, dependent on surfactant modification, directly influences the soft shearing
modes of deformation of the anisotropic tactoids. Thus in the more compatible 20A and 25A blends, the
ease of the tactoid shearing overcompensates for any reinforcing effects of the filler and the modulus
decreases. It is also important to point out that better compatibility of surfactant and matrix polymer should
lead to an increased fraction of exfoliated clay sheets. As discussed in detail in a previous publication30,
these exfoliated sheets do not augment the modulus as effectively as a particle containing several clay
sheets. Reasons for this non-reinforcing property of clay fillers include the very low value of effective
volume fraction per unit weight of clay when an isolated surfactant-modified clay layer is considered. In
addition, there is a tendency for exfoliated clay sheets to adopt easily-deformed curved configurations in a
polymer matrix.

Continuation of this work focused on the use of magic angle spinning to resolve the three
chemically distinguishable protons on polyisoprene and independently monitor changes in their interactions
with the clay interface (Appendix 3). There were no differences between the interactions experienced by
all three types of protons. Furthermore, confirming our results from the static spectra, increases in
interfacial area were observed with an increase in compressive strain. Application of the magic angle spinning technique for compressed nanocomposites will be the focus of future publications.

Conclusion
Solid state NMR, through measurements of spin-lattice relaxation times, can be used to quantify the strain dependent evolution of interfacial area in clay-polyisoprene nanocomposites. Strain induced evolution of interfacial area is dependent on the surfactant employed and therefore the initial amount of intercalation by the polymer. In the clay-filled samples, soft modes of tactoid deformation compensated for any reinforcing effect of the filler. In this case, with the more highly intercalated tactoids, a statistically significant reduction in the modulus was observed.

Acknowledgement
The authors acknowledge funding from the US Air Force under Grant No. F49620-01-1-0447 without which this project would not be possible. In addition, the authors acknowledge the Center of Material Science (MIT-CMSE) for use of their microscopy and x-ray scattering facilities. A special thanks to Professor Jeff Abes for assistance with TEM.
References

21. Personal communication with Southern Clay Products representative.


Chapter 3

Strain Behavior of Cis 1,4-Polyisoprene-Laponite Clay Nanocomposites Monitored by Solid-State NMR

(To be submitted to Journal of Applied Polymer Science, G.M. Poliskie, K.K. Gleason)
Abstract

In order to illustrate the capacity of NMR to monitor compression induced changes in the morphology of nanocomposites, solid-state NMR results were directly contrasted to optical microscopy. Increases in the interfacial area of Laponite® clay in cis 1,4-polyisoprene composites were monitored during uniaxial compression. Interaction of the Co$^{2+}$ in the clay galleries with the polymer decreases the polymer's $^1$H spin-lattice relaxation time constant ($T_1$). The composite showed a decrease in $T_1$ time constant with increasing compressive strain. This behavior is consistent with an increase in interfacial area of the aggregate as it breaks apart. Increases in interfacial area of the aggregate were confirmed with optical micrographs.

Introduction

Many researchers have shown improvements in the mechanical properties of polymers with the addition of nanoclay fillers.$^{1-4}$ In such instances, there is a desire to link morphological changes in the composite with the increase in macroscopic strength. Due to the nanodimensions of the clay, the primary technique used to monitor these changes has been transmission electron microscopy (TEM). In particular, Kim, et.al. used TEM to analyze changes in the clay aggregates in a nylon-12 matrix prior to and post mechanical deformation.$^5$ Although TEM has the correct resolution to directly observe the clay platelets, the sample preparation is tedious and statistical sampling can be time consuming, as it requires numerous sections from multiple samples. Therefore, there is a desire to identify alternative characterization techniques.

A number of groups have used nuclear magnetic resonance (NMR) to characterize the molecular structure of polymer-clay composites and clay nanofillers. Studies by Zax, et. al. explored the topological constraints of polystyrene chains confined between two clay platelets.$^6$ In order to separately observe the polystyrene adjacent to the clay from that centered in the galleries, various segments of the composite were isotopically labeled. It was found that the polystyrene closest to the clay surface experienced slower motions than those in the bulk. Gates, et. al. have attempted to correlate changes in NMR parameters, such as spin-lattice relaxations and chemical shift, to the oxidation state of the iron in the clay.$^7$ In its highest oxidation state, Fe$^{3+}$, iron is paramagnetic and increases the relaxation of surrounding nuclei. Using these principles, VanderHart, et. al. have used the paramagnetic centers, Fe$^{3+}$, of natural occurring clay to identify the morphology of nylon-6 chains adjacent to the clay surface.$^8$ In that case, it was found that the
stability of the crystalline phase is dictated by the presence of the clay. These various morphologies were monitored using the spin-lattice relaxation, while the composite was spun at the magic angle. In those instances the magic angle spinning was used to resolve the resonances of nuclei in different crystalline phases. As will be discussed in further detail later, in addition to increasing spectral resolution, magic angle spinning also disrupts the spin diffusion between regions of different magnetic behavior. In this study, magic angle spinning was employed in order to independently monitor two regions of the composite: the polymer surrounding the clay versus the bulk polymer far removed from the clay.

If NMR were used to study strain induced morphological changes in the clay composites, a single experiment would yield quantitative and statistically representative data. In order to illustrate the capacity of NMR to quantitate changes in the shape of the clay aggregates, the NMR behavior was compared to optical measurements were the break-up of clay aggregates could be directly observed. In situ compression measurements were induced while observing the polyisoprene-Laponite® composite using NMR and optical microscopy. For NMR experiments, a novel compression device was constructed; while for optical microscopy, the polymer was compressed between two glass slides. Polyisoprene-Laponite® composites are a particularly useful system for optical microscopy; because, the polymer is translucent and the clay aggregates are micron sized. However, the observed correlation between the microscopy and NMR techniques, suggests the NMR could be independently used to quantitative changes in composites with smaller aggregates and opaque polymer matrices.

**NMR Background**

Previous work has highlighted the utility of static proton NMR to monitor the changes in interfacial area for polyisoprene-montmorillonite nanocomposites. The results from that study and this study are not directly comparable due to differences in both the location of the paramagnetic ions and the NMR techniques employed.

In order for NMR to be used to monitor changes in interfacial area, the clay must contain paramagnetic centers. Montmorillonite is a natural occurring clay with paramagnetic Fe\(^{3+}\) embedded in the clay structure. Conversely, Laponite® is a synthetic clay with no paramagnetic centers in its structure. Therefore, for this study the intergallery cation was exchanged with paramagnetic Co\(^{2+}\). The coupling of the paramagnetic ions with the protons on the polymer is inversely related the distance between them raised
to the sixth power. Thus, the difference in the placement of the paramagnetic center alters its strength of interaction with the surrounding polymer. In addition, when the inter-gallery ions are exchanged only the polyisoprene in the immediate vaccinate of the gallery will be exposed to paramagnetic centers. In comparison, when the paramagnetic center is embedded in the clay any chains in proximity to any side of a platelet will be affected by the paramagnetic center. Therefore, this technique may underestimate the total polymer-clay surface area but it is an equally accurate method for the determination of the changes in the surface area.

Employing magic angle spinning (MAS) while observing a compressed composite has certain advantages over static measurements. In analogy to previous NMR analysis of composites, the polyisoprene-Laponite® composites is anticipated to have two spatially distinct regions: those polymer chains close to the paramagnetic centers in the clay and those far removed from the clay. Each region of polymer has a characteristic magnetic behavior. When the composite is monitored by static spectra, spin diffusion occurs allowing the two regions to communicate and experience an averaged magnetic behavior. When monitored with MAS, spin diffusion is hindered reducing this communication. In the limit of very slow spin diffusion between regions, the individual components can be monitored independently and MAS can be employed to understand how a specific region of the composite responds to compressive strain.

The rate of change in the polarization (p) of the spins within the sample is dependent on two terms: spin diffusion (D) and direct coupling (C). The polarization is both a function of the distance between spins (r) and time (t) (Eq 1).

\[
\frac{\partial}{\partial t} p(r,t) = D \nabla^2 p(r,t) - C(p(r,t) - p_0) \sum_n |r - r_n|^{-6}
\]

For static experiments, it is expected that the spin diffusion and direct coupling would both contribute to changes in the polarization of the sample. For MAS, at speeds faster than the dipolar coupling constant, the dipolar coupling is averaged to zero over the cycle of a rotor period, hindering spin diffusion. Therefore, polarization of spins closest to the paramagnetic Co^{2+} will only be affected by direct coupling (Eq 2).
The polarization of the spins is related to the experimentally observed magnetization (M(t)) through integration of polarization over the sample volume (Eq 3).\(^{18}\)

\[
\text{Eq 3: } M_z(t) = \int p(r,t)d^3r
\]

This equation has been solved by numerous authors to determine the relationship between the magnetization (M(t)) as a function of time (t) (Eq 4).\(^{18,21}\)

\[
\text{Eq 4: } M(t) = \left(\frac{4}{3} \pi^{3/2} N_p C^{1/2} t^{1/2}\right) \text{ for } t < \frac{b^6}{C}
\]

In this case, the magnetization is a function of: the concentration of paramagnetic centers (N\(_p\)), the coupling constant (C) between the paramagnetic center and the proton and the time (t) elapsed after the magnetization is perturbed. This relationship suggests a plot of magnetization as a function of time should be linear when the delay time is less than the ratio of the sixth power of the spin diffusion barrier to the coupling constant. Typical values for \(b\) and \(C\) are 0.6 nm and \(1 \times 10^{-41}\) cm\(^6/s\),\(^ {21}\) respectively, so that a delay time less than 5 ms is required.

Although long range spin diffusion is interrupted with MAS, the large dipolar coupling constants are not completely averaged by MAS allowing some short range diffusion to remain, as would be the case for spins from the clay surface into the adjacent surrounding polymer can be estimated from the one dimensional diffusion equation (Eq 5).\(^ {11}\)

\[
\text{Eq 5: } X = (2Dt)^{1/2}
\]

To estimate the length scale that such short range diffusion would operate under MAS, the root mean squared distance (X) was computed using a diffusion time for the spins closest to the clay (\(T_1 = 30\) ms) and the diffusion constant (D). An approximation of the diffusion constant (0.005 nm\(^2\)/ms) was taken from the MAS narrowed linewidth.\(^ {20}\) A region of polymer (X) equal to \(\sim 1.1\) nm affected by the presence of the Co\(^{2+}\) in the clay galleries. This total region of \(\sim 1.1\) nm includes a barrier diffusion length of 0.6 nm in which the spins cannot be directly observed.
**Experimental**

Aldrich 97% cis 1,4-polyisoprene (Mw =790,000 g/mol, PDI=2.0) was used as received. Laponite® XLG grade synthetic clay was purchased from Southern Clay Products. The Na⁺ in the Laponite® galleries was exchanged with paramagnetic Co²⁺ by dissolving the clay in an aqueous supersaturated solution of cobaltous chloride. The exchange was monitored by wide angle x-ray diffraction. The basal spacing changed from 1.4 nm for Na⁺ to 1.1 nm for Co²⁺. Wide angle x-ray diffraction (WAXD) measurements were made on Riguku Ru300 x-ray generator with Cu Kα radiation. The operating voltage was 60 kV with a current of 300 mA. Spectra were taken in reflection mode from powder on glass slides.

All blends of polyisoprene and clay were solvent cast from a 1.1 wt% solution of polyisoprene in THF to which was added 0.15 wt% of the corresponding clay. After solvent evaporation, the clay made up 13 wt% of the polymer nanocomposite. All experiments and characterization were performed at room temperature.

Optical microscopy was performed on Olympus CX41 microscope with attached digital camera. The uncompressed polyisoprene-Laponite® composite had dimensions of 0.195"x0.195"x0.195" and was observed between two glass slides held at a fixed distance (0.195" ± 0.002"). The sample was compressed by decreasing the distance between the slides (0.117" ± 0.002") so that 40% strain was applied to the polymer. The reported circumference measurements are a statistical representation from three specimens from each sample and were made with Scion Image® software. The circumference is obtained from the number of pixels surrounding a circular object.

Environmental scanning electron microscopy (SEM) was performed on a Joel 2000FX instrument. Images were taken from a cryo-fractured surface as the polymer sat on a glass slide.

The device for in-situ NMR compression was constructed from a Teflon rod 0.15" in diameter and 1.00" in length. A Teflon spacer between the polymer and screw allowed for slip at one end of the specimen while the bottom of the Teflon device facilitated slip at the other. The specimen for these experiments had rectangular dimensions of 0.05" x 0.05" x 0.30". For all experiments, at 40% compressive strain, there was clearance between the polymer's circumference and the sides of the compression cell.
All NMR spectra were taken at room temperature with an Oxford 6.3 T magnet (with a 270 MHz $^1$H resonance frequency) using a Tecmag dual resonance pulse generator and receiver. Magic angle spinning (MAS) spectra were taken with a Chemagnetic 7.5mm probe with a 4μs π/2 pulse width and a spin speed of 2500 Hz. Spectra were acquired with a 10 μs dwell time and a 5 s recycle delay at room temperature and taken after a 10 minute wait for stress relaxation. Proton chemical shifts are reported to tetramethylsilane (0 ppm). Magnetization recovery curves were measured using an inversion recovery sequence ($\pi$-t -$\pi$/2-Acq). The magnetization of the spins ($M(t)$) was monitored as a function of delay time ($t$).

**Discussion**

Representative optical (1a) and SEM (1b) micrographs are presented in Figure 1. Both micrographs indicate the clay forms in micron sized clumps. Since a single platelet has a thickness of 1 nm and a radial length which varies between 25-75 nm, the clumps must be composed of many clay platelets. This suggests that, prior to deformation, there are unexposed Co$^{2+}$ centers in the aggregate which are not interacting with the protons on the polymer. It is important to establish the existence of these unexposed cobalt centers in order to interpret the NMR under deformation.

*Figure 1. Optical micrograph (1a) and SEM (1b) of the polyisoprene- Laponite® composite*
The image from the optical microscopy overstates the loading of clay since light is projected through the sample; while the SEM image provides a view of a single fracture plane through the polyisoprene-clay composite. Therefore, the SEM gives a more representative feel for the density of clay aggregates in the samples. However, optical microscopy, not SEM, was used for in situ measurements because the sample could be held at a constant strain while observed. This type of experiment more closely mimicked, and therefore allowed for a better comparison to, the deformation done in the NMR.

Figure 2 is a histogram of the number of particles in an area of 600 µm by 600 µm with a circumference in the range specified by each bin. Since the compression of the polymer causes it to expand laterally it would be expected that some of the particles would move outside of the area of the image decreasing the total number of particles observed. Therefore, the numbers were corrected for this change in the density of particles. In fact, the number of particles of all sizes increased when the polymer was compressed to 40% strain. This suggests the total number of particles observed increased. This could happen if the edge of the particles are oriented 90° to the plane of the sample and upon compression are rotated into the plane of observation making the particles observable in the compressed but not the uncompressed sample. Due to the repeatability between samples despite sample orientation there appears to be no preferred orientation of the clay in the composite. Therefore, these samples likely have a random orientation of clay platelets and this discussed orientation effect is minimal. Another possibility is the particle diameters below 15 µm increased in circumference upon compression, making them susceptible to analysis in the compressed sample but not in the uncompressed sample. Furthermore, the increase in the number of large particles observed supports the conclusion that the clay deforms with increased compressive strain. The change in circumference converts into an irreversible ~150% change in surface area.
Figure 2. Histogram of the number of particles for each bin of circumferences in the polyisoprene-Laponite® composite prior and post 40% compressive strain

The static proton spectrum of the composite was a single broad peak simulated with a Lorentzian lineshape. The full width half mass (FWHM) line width is a measure of the degree of dipolar coupling and was extracted from the simulation of the lineshape (FWHM ~ 1500 Hz). This broadening of the spectrum was removed by spinning at a speed higher than the linewidth. As observed in Figure 3, with MAS, using a spin speed of 2500 Hz, the three chemically distinguishable protons of cis 1,4-polyisoprene can be isolated at their isotropic chemical shifts (FWHM~ 50 Hz): $^2$H methyl (1.8 ppm), methylene (2.1 ppm) and methine (5.2 ppm). Therefore, the measured changes in magnetization were assigned to a particular type of proton.
Figure 3. Static and MAS $^1$H spectrum of the polyisoprene- Laponite® composite
The magnetization recovery plot in Figure 4 is the MAS magnetization associated with the three chemically distinguishable protons for the cis 1,4-polyisoprene-Laponite® composites. In this case, the behavior of all three protons is identical. In bulk cis 1,4-polyisoprene, differences in the mobility of the methyl group versus the main chain cause differences in the relaxation observed by carbon-13 NMR. Due to the stronger dipolar coupling of proton nuclei, it is believed that the strong intermolecular dipolar coupling, which cannot be completely averaged with MAS, causes this relaxation behavior to be identical despite differences in mobility. Therefore, proton NMR, while it gives superb sensitivity, it is not the ideal nucleus to observe when attempting to identify changes in the interchain mobility.

Figure 4. Magnetization recovery plot of the polyisoprene- Laponite® composite under 40% compressive strain
As discussed above, in addition to this improved resolution, the removal of dipolar broadening will alter the observed relaxation behavior of the nuclei and allow for independent observation of regions with different magnetization. Bloomberg, et. al.,\textsuperscript{14} found that when using MAS on a heterogeneous distribution of paramagnetic centers, the relaxation behavior is best described by a linear combination of two functions, each describing a different component of the system. In the case of a homogenous distribution of paramagnetic centers, where direct coupling dominates the relaxation, a single linear fit of $t^{1/2}$ is used \textsuperscript{15} ($R^2\sim0.92$). In homogenous materials, such as homopolymers, spin diffusion dominates, and the relaxation is described by a decaying exponential ($R^2\sim0.82$). The data in Figure 3 can best be described by a combination of a short time region which follows $t^{1/2}$ decay behavior, describing polymer adjacent to the clay, and a second region which follows an exponential decay behavior (Eq 6) at long times, describing polymer far removed from the clay ($R^2\sim0.99$).\textsuperscript{14}

$$M(t) = \left(\frac{4}{3} \pi^{3/2} N_p C^{1/2} t^{1/2}\right) + (1 - 2 \exp\left(-\frac{t}{T_1}\right))$$

As seen in Figure 4, at long times the magnetization of each of the chemically distinguishable protons can be described by an exponential decay. As suggested by other authors,\textsuperscript{24,25} this exponential effect is the behavior of the spins far removed from the paramagnetic centers and weakly influenced by their presence. As a function of strain, this long time behavior is identical to that of the homopolymer (Appendix 7). This behavior will be the focus of future publications. However, for now our focus will be on the polymer around the clay aggregates. Specifically, the data obtained in the linear region of the magnetization recovery curve, $t<5\text{ms}$, will be the focus of the rest of this discussion.

The normalized magnetization, for the short time delay, is plotted against the square root of time in Figure 5. The results presented are from the methylene resonance, but these slopes are representative of all three types of protons. An increase in the number of paramagnetic centers ($N_p$), interacting with proton’s spins on the polyisoprene, will increase the slope (Eq 4 & Eq 5). It has been observed by other authors,\textsuperscript{5,9} that clay clusters break apart upon macroscopic deformation. This deformation would increase the interactions between the protons and the paramagnetic centers due to the increase in interfacial area between the polymer and the clay aggregate. The slopes of the lines increase from $-0.15 \pm 0.02 \text{ s}^{-1}$ for 0%
strain up to \( -0.35 \pm 0.02 \text{ s}^{-1} \) for 40\% strain. Using Eq 4, the change in the slope corresponds to an irreversible increase in interfacial area of \( \sim 230\% \) after 40\% compressive strain.

*Figure 5.* Plot of normalized magnetization versus the square root of the delay time for the methylene resonance of polyisoprene- Laponite® composite as a function of compressive strain.

*graphs are vertically offset for clarity and comparison*
Day et al. have had success matching absolute paramagnetic concentrations measured with NMR to those measured with elemental analysis. In those instances, the interaction between the paramagnetic centers and the observed nucleus was spherically symmetric. The theory presented in Eq 4 was developed for a homogenous distribution of paramagnetic centers in which each center has a spherically symmetric interaction with its neighboring spins. For these composites, each paramagnetic center is embedded between the clay platelets. Those ions buried in the center of the aggregate will not influence the relaxation of the polymer’s spins and those at the edges of the aggregate will only be surrounded by polymer on one or two sides making their interaction with the polymer non-spherical. Therefore, as cited by VanderHart, et al., this model cannot be rigorously used to find an absolute concentration of paramagnetic centers; however, it does provide the correct functional dependence to explain our observations and allow us to ratio the changes occurring as more paramagnetic centers are exposed to spins.

The ~150% increase in surface area observed with optical microscopy is lower than the ~230% increase observed by NMR. Since NMR identifies changes in the bulk while microscopy identifies changes near the surface, it is not surprising that the increase in interfacial area observed by these two techniques is different. However, both techniques illustrate that the break-up of clay aggregates is a mode of deformation when these composites are compressed.

Conclusions

Through measurements of spin-lattice relaxation times, solid-state NMR can be used to quantify the strain dependent evolution of interfacial area in polyisoprene-clay composites. With the use of MAS, changes which occurred around the clay aggregates were isolated from the behavior of polymer far removed from the clay. The optical micrographs confirmed that the aggregates broke apart upon compressive strain. The quantitative changes observed with NMR represent changes occurring in the bulk while the optical micrographs represent changes near the surface.

The correlation between NMR and optical microscopy indicates, with certainty, that NMR relaxation measurements can be used to quantify differences in interfacial area of nanocomposites. With this being established, the techniques developed in this paper could be applied to analyze strain induced changes in interfacial area for samples which are not optically clear or samples in which the particle dimensions make microscopy techniques difficult.
Acknowledgement

The authors acknowledge funding from the US Air Force under Grant No. F49620-01-1-0447. This work also made use of MRSEC Shared Facilities supported by the National Science Foundation under Award Number DMR-9400334.
References:


10. Personal communication with Southern Clay Products representative.


Chapter 4

Plastic Crystalline Behavior of Ethyl Substituted Polyhedral Oligomeric SilSesquioxane (POSS)

(To be submitted to Inorganic Chemistry, G.M. Poliskie, T.S. Haddad, R.L. Blanski, K.K. Gleason)
Abstract

This study describes the synthesis and molecular mobility of both partially deuterated and fully protonated ethyl polyhedral oligomeric silsesquioxane (POSS) crystals. Phase transitions were identified with differential scanning calorimetry at \( \sim 258 \) K and \( \sim 253 \) K for partially deuterated and fully protonated ethyl POSS, respectively. A change in entropy of \( \sim 20.2 \pm 5 \text{ J mol}^{-1} \text{K}^{-1} \) was observed for both transitions. Abrupt changes in the spin lattice relaxation and linewidth were detected with solid state proton nuclear magnetic resonance (NMR) spectroscopy, at the same temperatures detected with calorimetry. This NMR behavior suggests a transition in molecular motions of both ethyl derivatives. For deuterated ethyl POSS, the motions become increasingly anisotropic after the temperature is lowered past its transition point. Both derivatives exhibit an increase in the correlation time (\( \sim 30 \pm 2 \text{ ns to } \sim 530 \pm 15 \text{ ns} \)) and activation energy (\( \sim 16 \pm 2 \text{ kJ/mol to } \sim 20 \pm 2 \text{ kJ/mol} \)) for molecular tumbling at temperatures past their respective transitions.

Introduction

Polyhedral oligomeric silsesquioxane (POSS) is a fused cage of cyclic siloxanes used as a nanofiller in composite research. Synthetic work has strived to functionalize the substituents on POSS molecules in order to increase its compatibility with an organic polymer matrix. However, both free POSS molecules and POSS tethered to polymer chains form localized crystalline POSS domains in the polymer matrix. As a step toward decoupling the molecular motions of the polymer from that of the POSS, solely the molecular motions of POSS crystallites were the focus of this work.

The POSS molecule has two principle modes of rotation which includes: the rotation of the individual organic substituents edge of the cage and tumbling of the POSS cage about an axis of symmetry. In particular, rapid molecular tumbling of molecules ordered in a three dimensional crystalline array is termed plastic crystalline behavior. Plastic crystals exhibit rapid molecular reorientation at high temperatures which slows to a rigid limit when cooled below a transition temperature, resulting in a small reduction in entropy (3-20 J mol\(^{-1}\)K\(^{-1}\)). Three-dimensional crystallographic reordering, using x-ray diffraction (XRD) and differential scanning calorimetry (DSC) can often be linked to changes in the molecular motions monitored by nuclear magnetic resonance (NMR). All three techniques have been employed to fully characterize the crystallographic, energetic and molecular motions of the plastic...
crystalline adamantine. Nordman and Schmitkon found adamantane went through a crystallographic phase transformation at 209 K between a high temperature cubic phase and the low temperature tetragonal phase. Furthermore, the cubic a-axis was found to have rotated 9° with respect to the c-axis of the low temperature tetragonal phase. Calorimetry performed by Chaung and Westrum confirmed a first order phase transition at 209 K with a change in entropy of 3.4 Jmol⁻¹K⁻¹. Finally, spectroscopists, Resing and McCall, et. al., characterized the molecular motions of these phases and found adamantane molecules underwent isotropic reorientations around the C₆ axis at room temperature. The transition to hindered molecular rotation is marked by discontinuities at 209 K in the solid state proton spin lattice relaxation time constant and spectral linewidths. In addition, cubane is another plastic crystal which has not been as fully characterized as adamantane using these same techniques. Cubane is polymorphic and characterized by two high temperature phase transitions at: 394K and 405K. Like adamantane it is known to undergo rapid isotropic tumbling in its highest temperature phase. Due to the similarity in the molecular architecture of cubane and POSS and the possibility that POSS undergoes isotropic molecular tumbling, it may be of interest to monitor POSS molecules as a function of temperature.

Previous work by Larsson and coworkers, has used x-ray diffraction to monitor crystallographic phase transitions in crystals of POSS containing various fully protonated organic substituents. Larsson notes a crystallographic phase transition of n-propyl POSS at 272 K from a close pack hexagonal unit cell in the high temperature phase to triclinic unit cell in the low temperature phase. Other substituents including methyl, ethyl, i-propyl, and n-butyl were also studied using the Klofer method; however, no transition was observed for these derivatives, down to the lowest experimentally accessible temperature of 243 K. Differential scanning calorimetry by Kopesky, et. al. identified a transition at 330 K for i-butyl functionalized POSS; however, no detailed entropic information about the phase transitions of POSS molecules has been reported. There has been no solid-state nuclear magnetic resonance spectroscopy reported on the characteristic molecular motions of these phase transitions.

In the interest of characterizing the molecular motions as a function of temperature in POSS crystallites, this paper will describe calorimetry and various solid-state NMR experiments on crystals of ethyl substituted POSS. Despite Larsson's conclusions, we have identified a phase transition in fully protonated ethyl POSS (253 K) suggesting there may be a limit to the sensitivity of the Klofer method.
when the temperature is only dropped a few degrees below the transition point. Furthermore, ethyl substituted POSS was chosen for this study because it could be isotopically labeled from a commercially available vinyl derivative (Figure 1). A comparison between fully protonated and partially deuterated ethyl POSS illustrates how changes in chemical labeling change transition properties. In addition, deuterium NMR was used to analyze the partially deuterated derivative and provided a sensitive measure of the change in symmetry of molecular motions occurring during the phase transitions. These NMR results were confirmed with differential scanning calorimetry.

Figure 1. Molecular structure of ethyl POSS

A. Partially Deuterated Ethyl POSS

R= CHD-CH\textsubscript{1.14}D\textsubscript{1.86}

B. Fully Protonated Ethyl POSS

R= CH\textsubscript{2}-CH\textsubscript{3}

Experimental

Synthesis of Octaethylsilsesquioxane, (CH\textsubscript{3}CH\textsubscript{2})\textsubscript{8}(Si\textsubscript{8}O\textsubscript{12}). In a glass-lined 200 mL PARR pressure reactor, 10.0 grams (15.8 mmole) of octavinylsilsesquioxane, (CH\textsubscript{3}=CH\textsubscript{2})(Si\textsubscript{8}O\textsubscript{12}), was dissolved in 60 mL of dry toluene. After adding 50 mg of 10% palladium on carbon heterogeneous catalyst, the reaction vessel was sealed, pressurized to 500 psi with 99.99% hydrogen gas, heated to 70 °C and stirred for 16 hours. The hydrogenated product was isolated by filtering the solution through celite, reducing the solvent volume and cooling the solution to -20 °C to induce crystallization. Three crops of crystals were obtained in this way,
then combined together and sublimed at 150 °C under dynamic vacuum (10^{-2} torr) to give 9.10 grams of product (14.0 mmole, 89 % yield). A single product is evidenced by $^1$H, $^{13}$C and $^{29}$Si NMR spectroscopy. $^1$H NMR (relative to internal CHCl$_3$ at 7.26 ppm): 1.00 ppm (CH$_3$, triplet, $^3$$J_{H-H}$ = 8.0 Hz), 0.61 ppm (CH$_2$, quartet, $^3$$J_{H-H}$ = 8.0 Hz). $^{13}$C NMR (relative to internal CDCl$_3$ at 77.0 ppm): 6.51 ppm (CH$_3$), 4.08 ppm (CH$_2$, $^{29}$Si satellites $^1$$J_{Si-C} = 109$ Hz). $^{29}$Si NMR (relative to external SiMe$_4$ at 0.0 ppm): -65.5 ppm ($^{13}$C satellites $^1$$J_{Si-C} = 109$ Hz).

**Synthesis of deuterated-Octaethylsilsesquioxane.** The same hydrogenation procedure was followed except that 98% deuterium gas was used instead of hydrogen. 10 grams of octavinylsilsesquioxane was converted into 9.3 grams of partially deuterated octaethylsilsesquioxane. The product is a complex mixture of not just (CH$_2$DCHD)$_4$(Si$_4$O$_{12}$), but contains numerous products arising from catalyst induced scrambling of the deuterium. The $^1$H NMR spectrum shows an integral ratio of the methyl group to the methylene group of 1.14:1.00; the idealized product with the addition of one deuterium to each carbon would have an expected ratio of 2:1. In the $^{13}$C spectrum, peaks corresponding to CH$_3$CH$_2$Si groups are easily identified, and a DEPT 135 sequence $^{13}$C NMR spectrum demonstrates that the methyl groups can be CH$_3$, CH$_3$D or CHD$_2$ and the methylene groups can be CH$_2$ or CHD. Evidence for perdeuterated methyl or methylene groups was not observed. $^1$H NMR (relative to internal CHCl$_3$ at 7.26 ppm): 0.98 ppm (methyl, broad multiplet), 0.60 ppm (methylenes, broad multiplet). $^{13}$C NMR (relative to internal CDCl$_3$ at 77.0 ppm): 6.52, 6.42, 6.34, 6.24, 6.15, 6.05, 5.95, 5.87, 5.77, 5.67, 5.58, 5.48, 5.39, 5.20 ppm (d$_n$-CH$_3$), 4.08, 3.98, 3.87, 3.80, 3.77, 3.72, 3.62, 3.52, 3.44, 3.34, 3.23 ppm (d$_n$-CH$_2$). $^{29}$Si NMR (relative to external SiMe$_4$ at 0.0 ppm): -65.4 ppm (broad multiplet).

As identified in the synthesis procedure, the 3:2 ratio for the methyl to the methylene resonances, from the solution $^1$H NMR, indicated the desired fully protonated ethyl derivative was synthesized. For this reason, this product will be referred to as fully protonated ethyl POSS. Unfortunately, the deuteration of the ethyl POSS resulted in a complicated mixture of products (Figure 1). The desired deuterated ethyl product had an expected ratio of 2:1 for the methyl to methylene from solution $^1$H NMR resonances. However, the ratio for the synthesized product was 1.14:1. The palladium catalyst has been known to create C-H activation$^{18,19}$ and the deuterium gas was more than 98% pure suggesting more that on average each ethyl substituent had more than three deuterium isotopes. Despite this scrambling of isotopic products, the
deuterated ethyl POSS product contained residual protons from the vinyl precursor allowing for a direct comparison of the two POSS derivatives using solid-state $^1$H NMR. Therefore, the deuterated product will be referred to as partially deuterated POSS.

**Differential Scanning Calorimetry**

Dynamic scanning calorimetry (DSC) was performed on a Q1000 TA instrument. Each sample was run in an aluminum pan with a step scan of two loops between 183 K and 273 K. The ramp rate was 5 K/minute. Data was analyzed using Universal Analysis software.

**NMR Spectroscopy**

Deuterium solid state NMR spectra were taken with a Wang 7 T magnet (with a 45 MHz $^2$H resonance frequency) using a Tecmag single resonance pulse generator and receiver. Static deuterium ($^2$H) experiments were performed on a home built probe with a 2.5 µs $\pi/2$ pulse width. Deuterium spectra were acquired with a solid echo sequence ($\pi/2$-x-$\pi/2$-Acq) and a fixed delay time (t) of 21 µs.

Proton solid state NMR spectra were taken with an Oxford 6.3 T magnet (with a 270 MHz $^1$H resonance frequency) using a Tecmag dual resonance pulse generator and receiver. Static proton ($^1$H) experiments were performed on a home built probe with a 2µs $\pi/2$ pulse width. Proton spectra were acquired with a 10 µs dwell time and a 5 s recycle delay.

Simulations of line shapes for the static proton spectra were performed with a single peak using GRAMS® software. Simulated peaks were Gaussian with the full width half mass (FWHM) line widths extracted from the simulation.

Spin-lattice relaxations for the proton experiments were measured using an inversion recovery sequence ($\pi$-x-$\pi/2$-Acq). A single least square exponential was fit to the peak intensity (M) versus delay time (t), resulting in a two parameter fit yielding: the equilibrium peak intensity ($M_o$) and the spin-lattice relaxation time constant ($T_1$) (Eq 1).^{20}

$$Eq \ 1: \ M(t)=M_o(1-2\exp(-t/T_1))$$

This single exponential was used for the POSS data with an $R^2$ value of ≥ 0.99.

From the plot of ln$T_1$ versus the inverse of temperature, the activation energies were calculated from the slope of the line (Eq 2) multiplied by the molar gas constant.^{20} The slopes were taken from the most linear region of the data which created an $R^2$ value > 0.98.
Eq 2: \[ \ln T_i = -\frac{E_a}{RT} \]

**Results and Discussion**

**I. Differential Scanning Calorimetry (DSC)**

The cooling and heating curves for both partially deuterated (2a) and fully protonated ethyl (2b) POSS are presented in Figure 2. For partially deuterated ethyl POSS, an endotherm and exotherm occur at 257 ± 2 K and 251 ± 2 K, respectively. For fully protonated ethyl POSS, the endotherm and exotherm occur at 254 ± 2 K and 247 ± 2 K, respectively. From the DSC scans, the change in enthalpy of the phase transition is taken from the integral of heat capacity versus temperature. Likewise, the change in entropy is estimated by dividing the enthalpy by the phase transition temperature.\(^{21}\) The change in enthalpy and change in of the partially deuterated POSS entropy were within error of each other for both the endotherm (5470 ± 700 J mol\(^{-1}\), 21.8 ± 2 J mol\(^{-1}\) K\(^{-1}\)) and the exotherm transitions (4580 ± 700 J mol\(^{-1}\), 17.8 ± 5 J mol\(^{-1}\) K\(^{-1}\)) (Table 1). The change in enthalpy (5000 ± 700 J mol\(^{-1}\)) and change in entropy (20.2 ± 5 J mol\(^{-1}\) K\(^{-1}\)) were identical for both phase changes of the fully protonated POSS.

*Figure 2. Differential scanning calorimetry measurements of partially deuterated and fully protonated ethyl POSS*
Table 1: Characteristics of the phase transition and phase behavior of ethyl substituted POSS extracted from DSC

<table>
<thead>
<tr>
<th>Substituent*</th>
<th>Transition Temperature (K) (± 2 K)</th>
<th>ΔH (J mol⁻¹) (± 500 J mol⁻¹)</th>
<th>ΔS (J mol⁻¹ K⁻¹) (± 2 J mol⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHDCH₂D</td>
<td>Texo = 257</td>
<td>4580</td>
<td>17.8</td>
</tr>
<tr>
<td></td>
<td>Tendo = 251</td>
<td>5470</td>
<td>21.8</td>
</tr>
<tr>
<td>CH₂CH₃</td>
<td>Texo = 254</td>
<td>5000</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>Tendo = 247</td>
<td>5000</td>
<td>20.2</td>
</tr>
</tbody>
</table>

* H stands for ¹H and D stands for ²H isotope

Solid-solid phase transitions are commonly marked by energetic transitions identified with calorimetry. ²⁻²⁴ Typical values for plastic crystalline solids are a change in enthalpy of ~ 3000-6000 J mol⁻¹ and a change in entropy of ~ 10-20 J mol⁻¹ K⁻¹, respectively. ²¹⁻²⁴ For instance previous, work by Jozkow, et. al. found a first order solid-solid phase transition for plastically crystalline pyridinium (C₅H₁₀NH)BiCl₄ identified by an endotherm at 119 K and an exotherm at 114 K. They found the change in entropy was 7.4 J mol⁻¹ K⁻¹, for both the observed endotherm and exotherm. ²²

Our results indicate that POSS undergoes a similar solid-solid phase transition with values comparable to other plastically crystalline solids. The thermal hysteresis in the heating and cooling transitions suggests the transition is first order.

II. Deuterium NMR Analysis

The static ²H NMR spectra, of the deuterated ethyl POSS at 298 K, 248 K and 243 K are shown in Figure 3. At room temperature the splitting is 6 Hz and increases to 40 Hz at 248 K. There was no change in the splitting of 40 Hz at 248 K down to our lowest experimentally accessible temperature of 203 K.
At a single orientation, the quadrupolar splitting ($\Delta v$) depends on the quadrupolar coupling constant ($e e Q / h \sim 200 \text{kHz}$ for C-D) and the angle ($\theta$) between the principal electronic field gradient, oriented along the C-D bond, and the magnetic field (Eq 3). 

$$\text{Eq 3. } \Delta v = \frac{3}{2} \left( \frac{e e Q}{h} \right) \langle 3 \cos^2 \theta - 1 \rangle / 2$$

Averaging the angle ($\theta$) over all the C-D bonds in the molecule gives the order parameter (Eq 4). 

$$\text{Eq 4. } P_2 \left( \cos \theta \right) = \langle 3 \cos^2 \theta - 1 \rangle / 2$$
The splitting occurs when $P_2(\cos(\theta))$ is nonzero, corresponding to a situation where the electronic field gradient at the nucleus is not completely averaged to zero by molecular motions. Therefore, the order parameter is a quantitative measure of the degree of orientation in the sample.

Furthermore, the symmetry of the motions is dictated by molecular symmetry. For highly symmetric plastically crystalline compounds, such as adamantane ($T_d$), a combination of rotations about the $C_n$ axis is enough to produce a symmetric isotropic $^2\text{H}$ lineshape at room temperature. However, derivatives of adamantane, with a lower molecular symmetry, exhibit splitting in deuterium spectra at room temperature.

For our partially deuterated POSS, splitting is observed at all three temperatures with the magnitude of the splitting corresponding to a change in order parameter of the C-D bond. Figure 3 indicates an abrupt increase in the splitting from 6 Hz at 298 K to 40 Hz at 248 K. Thus, the increase in splitting (Eq 3) corresponds to greater than five-fold increase in the order parameter from $26 \times 10^{-3}$ at 298 K to $133 \times 10^{-3}$ at 243 K. As the temperature decreases fewer rotational states of POSS molecules are energetically accessible, leading to an increase in the order parameter (Eq 4). Therefore, the larger splitting (40 kHz) at lower temperatures indicates the molecules become more ordered and motions become increasingly anisotropic. This abrupt transition in the order parameter is consistent with a first order phase transition.

If the ethyl POSS were fully deuterated it would have a higher order of symmetry ($O_h$) than adamantane and therefore would be expected to have an isotropic deuterium lineshape at room temperature. However, the deuterium insertion reaction instead created a mixture of partially deuterated products of lower symmetry (Figure 1). This mixture of products, and therefore the lower molecular symmetries, most likely caused an asymmetry (6 kHz) in the lineshape due to anisotropic reorientations of the molecules at 298 K.

III. Proton NMR Analysis

In order to analyze the motions of both types of POSS molecules, proton NMR spectra were acquired as a function of temperature. In all cases, the proton spectrum was broad and featureless; however, the width of the spectrum varied. A representative set of static proton spectra for partially deuterated and fully protonated ethyl POSS are presented in Figure 4 at three temperatures of 298, 248 and 243 K.
As seen in Figure 5, the linewidth increased with a decrease in temperature for both POSS derivatives. However, the partially deuterated POSS has a consistently smaller linewidth compared to the fully protonated POSS. A discontinuity occurs at $258 \pm 2$ K for the partially deuterated ethyl POSS and $253 \pm 2$ K for the fully protonated ethyl POSS.

Figure 5. Solid-state $^1H$ linewidth as a function of temperature for fully protonated and partially deuterated ethyl substituted POSS
Changes in linewidth of proton spectra have previously been used to mark the phase transition of a number of plastically crystalline solids. Gutowsky and Pake found an abrupt increase in the static proton linewidth of 1,1,1-trichloroethane as it passed through a phase transition temperature at 134 K. They theorized that the proton spectrum linewidth is dependent on the frequency and type of motion of the molecule, which in turn is a function of temperature and an energy barrier for motion. Thus, they derived the following equation to relate the experimental linewidth to the underlying thermodynamic parameters (Eq 4).

\[
\delta v^2 = V^2 + U^2 - V^2 \tan^{-1} \left( \frac{\alpha \delta v}{\nu_i} \right)
\]

The linewidth (\(\delta v\)) is related to the linewidth for a rigid lattice (U), the linewidth after completion of a narrowing motion (V), a constant to correct for any inadequencies in the lineshape analysis (\(\alpha\)), and the reorientation frequency (\(\nu_i = (2\pi \tau_i)^{-1}\)). Therefore, the experimental linewidth (\(\delta v\)) describes the transition between the motions of the rigid lattice (U) and motionally narrowing motions (V), limited by the thermal energy and molecular symmetry. In terms of 1,1,1-trichloroethane, Gutowsky and Pake suggested the change in linewidth would describe a transition between rigid molecules and a hindered rotation of the methyl group. In order to link the experimental linewidth to the thermodynamic parameters, Bloomberg, Pound and Purcell (BPP) theory, was used to relate the correlation time (\(\tau_i\)) to the activation energy barrier for the two different modes of motion experienced in each crystallographic phase (Eq 5).

\[
\tau_i = \tau_o \exp \left( -\frac{E_a}{RT} \right)
\]

This assumption of Arrhenius behavior suggests that the correlation time (\(\tau_i\)) is dependent on a characteristic correlation time (\(\tau_o\)), activation energy (\(E_a\)), temperature (T) and the molar gas constant (R). Gutowsky and Pake’s theory gives an order of magnitude approximation for the characteristics of molecular motions, specifically activation energies and correlation times. Therefore, these parameters are rarely extracted from lineshape analyses; however, this formulation provides a theoretical framework for qualitative observations. Specifically, the above equations (Eqs 4 and 5) indicate the linewidth is proportional to the correlation time and different correlation times would describe the molecular motions on each side of the phase transition. Thus, an increase in linewidth is consistent with an increase in the
correlation time for molecular tumbling as the molecules become increasingly rigid when the temperature is lowered.27

Using this theory, Andrew and Eades described the increase in static proton linewidth for benzene at 100 K, as a decrease in molecular tumbling about its C₆ axis of symmetry (τᵣ).28 Andrew and Eades also commented on the efficiency of proton NMR to measure the differences between intramolecular and intermolecular dipolar communication of protons by comparing the linewidths of 1,3,5-partially deuterated and fully protonated benzene. The strong dipolar couplings allow for all the protons on the crystal lattice to communicate with each other prior to relaxation. Both intramolecular communication, between protons on the same substituent, and intermolecular communication, between protons on different molecules, influence the proton relaxations and linewidths. In plastic crystals, when the molecules undergo isotropic tumbling the intermolecular interactions dominate the relaxation and when the molecule becomes more rigid the intramolecular interactions dominate. Therefore, proton NMR is a behavior averaged by both intramolecular and intermolecular communication, where the observation is skewed depending on the degree of mobility in the crystal. The differences in linewidth between the two benzene derivatives gave a quantitative determination of the amount of intramolecular communication disrupted by the presence of the deuterium atoms. Qualitatively, they found that deuterated benzene had a consistently smaller linewidth than fully protonated benzene due to the decreased intramolecular dipolar interactions caused by the presence of the intermittent deuterium isotope.28

Gutowsky and Pake’s theory gives the correct functional dependence to describe the ethyl POSS data represented in Figure 4. Because of Eq 4 and 5, the experimental linewidth for the POSS crystals was graphed as a function of temperature. The abrupt transition observed at 258 K for deuterated ethyl POSS and 253 K for fully protonated ethyl POSS, indicate that different molecular motions, at the kilohertz frequency, dictate the linewidth prior to and after the transition. Furthermore, the increase in linewidth at low temperatures suggests molecular motions are hindered and are described by a longer correlation time past the transition point.

It should be noted that while ¹H NMR allows for a direct comparison between the two POSS derivatives, it is not the ideal choice for studying the molecular motions of phase transitions due to the extensive dipolar communication between protons. If the ethyl POSS product had been cleanly deuterated
the same quantitative analysis used by Andrew and Eades could have been performed on the POSS samples. However, our data provides the same qualitative observation that was observed for benzene. In Figure 4 and Figure 5, we observed a consistently smaller linewidth for the partially deuterated ethyl POSS. This difference between the ethyl derivatives implies the intermittent deuterium isotope decreases intracommunication between protons. Therefore, the fully protonated ethyl POSS is measurably influenced by intramolecular interactions.

These changes in molecular motions can be further characterized with the proton $T_1$ spin-lattice relaxation time constant, which is a sensitive measure of molecular reorientations occurring at the Larmor frequency, 270 MHz. Figures 6 and 7 are the Arrhenius plots of the ln $T_1$ versus the inverse of temperature for the POSS molecules. For the fully protonated POSS there is a discontinuity in the graph at 253 K and for the partially deuterated POSS at 258 K. For both POSS molecules the activation energy for the low temperature region is higher than that of the high temperature region.

*Figure 6. Solid-state $^1$H spin-lattice relaxation time constants ($T_1$) as a function of temperature for fully protonated ethyl substituted POSS*
Using the dipolar part of the spectral density formula, the $T_1$ time constant is on the Larmor frequency for the $^1$H isotope ($\omega = 270$ MHz) and the correlation time ($\tau_i$) for molecular motion.\(^8\)

Eq 6: \(1/T_1 = C\frac{\tau_i}{(\tau_i^2 + 1)} + 4\tau_i/(4\tau_i^2 + 1)}\)

Applying Bloomberg, Pound, and Purcell theory, inserting Eq 5 into Eq 6, suggests a plot of $T_1$ versus the inverse of temperature will have a minimum.\(^8,27\) This theory is only applicable to materials in which a single correlation time ($\tau_i$) dictates the spin-lattice relaxation for the entire experimental temperature range. This is often not the case for solids in which a phase transition occurs in the temperature range causing different motions to dominate the relaxation in each phase.

It has been well documented for numerous solids that, when a phase transition occurs over the experimental temperature range a minimum will not be observed.\(^8,12,21\) Instead, as the molecular motions
decrease with a decrease in temperature, there is a discontinuity in the graph at the transition temperature. For example, Resing, et. al. found that the $T_1$ time constants from static proton NMR of adamantane has a discontinuity in the graph at 209 K where the crystallographic phase transition occurs. At temperatures above the transition, it is suggested that adamantane rotates freely about a C$_6$ axis of symmetry, described by a short correlation time and after the transition this motion is energetically less accessible, described by a longer correlation time.$^{8,13}$

The discontinuities, observed in Figure 4 and 5, indicate that different molecular motions of POSS dictate the relaxation of the nuclear spins prior to and after the phase transition. In addition, that transition to rigid mobility occurs at a higher temperature ($258 \pm 2$ K) for the partially deuterated sample compared to the fully protonated sample ($253 \pm 2$ K). Due to the scrambling of deuterated products it is difficult to conclude whether the increase in the transition temperature is the result of the heavier isotope or the identified asymmetry of the molecular structures. It is plausible that the increased mass of the deuterium labels increases the moment of inertia for the molecules decreasing the molecular tumbling in the high temperature phase. This decreased mobility would require less thermal energy to be removed in order for the molecules to become completely rigid. It is equally likely that due to the scrambling of the deuterated products, on average, the asymmetry in the POSS molecules excludes certain modes of motion; therefore, decreasing the mobility in the high temperature phase and increasing the temperature at which the molecule becomes completely rigid.

The characteristic correlation time and the activation energy for the molecular motions can be determined assuming BPP theory. When the temperature was decreased from 298 to 243 K, the characteristic correlation time ($\tau_o$) increased from $28 \pm 2$ ns to $530 \pm 15$ ns and from $32 \pm 2$ ns to $520 \pm 15$ ns, for the partially deuterated and fully protonated POSS, respectively (Table 2). For both the fully protonated and partially deuterated ethyl POSS, the activation energy for molecular tumbling is lower at temperatures above the transition ($E_a \sim 16 \pm 2$ kJ/mol) than below ($E_a \sim 20 \pm 2$ kJ/mol) (Table 2).
Table 2: Characteristics of the phase transition and phase behavior of ethyl substituted POSS from NMR

<table>
<thead>
<tr>
<th>Substituent*</th>
<th>Transition Temperature in NMR (K) (± 2 K)</th>
<th>$E_a$ (kJ/mol) Phase I (high temperature) (± 2.0 kJ/mol)</th>
<th>$E_a$ (kJ/mol) Phase II (low temperature) (± 2.0 kJ/mol)</th>
<th>$\tau_v$ Phase I (25 °C) (ns) (Ti) (±2 ns)</th>
<th>$\tau_v$ Phase II (-30 °C) (ns) (Ti) (±15 ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHDCH$_2$D</td>
<td>258</td>
<td>15.0</td>
<td>18.3</td>
<td>28 (Ti ~ 5s)</td>
<td>530 (Ti ~ 2s)</td>
</tr>
<tr>
<td>CH$_2$CH$_3$</td>
<td>253</td>
<td>15.6</td>
<td>20.0</td>
<td>32 (Ti ~ 3s)</td>
<td>520 (Ti ~ 2s)</td>
</tr>
</tbody>
</table>

* H stands for $^1$H and D stands for $^2$H isotope

Simulations of the molecular motions of POSS performed by Capaldi, et. al. determined the correlation time for isotropic molecular tumbling of a single cyclopentyl POSS molecule in a vacuum. The time scale with this random, isotropic tumbling of the POSS molecule around its $C_n$ axis of symmetry was 5 ns. The isotropic rotation of the cyclopentyl groups had a correlation time of 120 ps. In addition, the activation energy, found for adamantane, where NMR has been shown to be sensitive to changes in the ability of the molecule to tumble around their $C_6$ axis, was ~ 22 kJ/mol.

Therefore, the activation energy and correlation times extracted from the spin-lattice relaxation data for our ethyl POSS, as presented in Table 2, are consistent with a more restricted tumbling of the POSS molecule around its $C_n$ axis of symmetry. However the difference in the transition temperature suggests a difference in the degree of molecular mobility in the high temperature phase of each derivative. Therefore, the similarity in the correlation times and activation energies between the two derivatives is unexpected. It is possible that for both POSS derivatives the dipolar coupling allows the intermolecular interactions of the protons to dominate the relaxations on both sides of the transition temperature. This intermolecular communication between POSS molecules on the lattice may mask the differences in the intramolecular interactions caused by molecular tumbling. In fact, the dipolar communication could cause an average behavior of the intermolecular and intramolecular interactions to be observed. Therefore, despite the fact that the values of the activation energy and correlation times mimic $C_n$ rotations caution needs to be taken when interpreting these experiments.

Despite the ambiguity in the interpretation of the absolute value of the correlation time and activation energy, it can be stated that both POSS molecules undergo a phase transition marked by abrupt changes in molecular motions. Furthermore, this overall increase in activation energy and correlation times
with decreased temperature is consistent with restricted molecular mobility in the low temperature phase due to a lower thermal energy.

**Conclusions**

Phase transitions occur in ethyl POSS molecules and have been identified using calorimetry and various NMR experiments. The transition points observed with calorimetry are identical to those observed with NMR. The behavior observed with calorimetry and NMR are typical to those of plastic crystals. The temperature of the phase transition was tuned by isotopically labeling the substituents on the POSS molecule. At higher temperatures, the molecular reorientations are rapid and for deuterated POSS slightly anisotropic. After the transition, and at lower temperatures, the molecular reorientations are slower and for deuterated POSS increasingly anisotropic.

**Acknowledgement**

The authors acknowledge funding from the US Air Force under Grant No. F49620-01-1-0447.
References


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Chapter 5

Strain Induced Changes in Cis 1,4-Polyisoprene Monitored by Solid State NMR
Abstract

Using magic angle spinning proton NMR, the spin lattice relaxation ($T_1$) time constants of monodisperse cis 1,4-polyisoprene were monitored as a function of in situ compression. With a novel compression device, the monodisperse 710,000 g/mol sample was compressed up to 40% strain. After 40% strain, there was a 26 ± 8%, 19 ± 9% and 27 ± 9% increase in the spin lattice relaxation time constants for the methyl, methylene and methine resonances, respectively. Furthermore, with the use of proton NMR, acquisition is sufficiently rapid that the spectra could be acquired during the stress relaxation. As a function of time, there were no observed changes in the spin lattice relaxation time constants, illustrating the behavior could not be described by the macroscopic stress relaxation. We hypothesize that the decrease in the spin lattice relaxation time constant may be the result of chain fragmentation under mechanical strain.

Introduction

Due to the widespread use of elastomers in products such as tires and adhesives,¹ the mechanisms involved in mechanical behavior have been of interest for decades. Specifically, the stress relaxation properties of polyisoprene have been investigated since the late 1940's.²-⁶ Doi and Edwards explained the macroscopic exponential decay of stress as chains slipping out of physical entanglements.⁷ However, Mooney and coworkers suggest the stress relaxation in a vacuum can often be described by a two term equation which describes a transient relaxation caused by the rupture of secondary bonds and a second term to describe the exponential decay caused by the molecular level chain rupture and slippage.⁸

This was followed by NMR studies focused on molecular motions monitored as a function of crosslink density and in situ tensile deformation.⁹⁻¹¹ For a variety of polymers, molecular motions induced by mechanical deformation have been investigated.¹²⁻¹⁶ Various NMR techniques have been used to probe these molecular motions as a function of strain, with the premise that understanding deformation at the molecular level will aid in formulating polymers with desired mechanical properties. For instance, Von Meerwall and coworkers discovered large changes in the low frequency spin-spin relaxations of tensile strained polyisoprene using static proton NMR.⁹ However, it was not until large amounts of tensile strain that the polymer chains became microscopically aligned increasing the dipolar interaction and spin-spin relaxation.
These are the first experiments to utilize the higher frequency spin lattice relaxation measurements in order to explore the molecular mechanisms occurring during in situ compression and magic angle spinning. Additional information is achieved by removing the majority of the strong dipolar couplings, using magic angle spinning, and observing the behavior of each chemically distinguishable resonance. The magic angle spinning (MAS) spin lattice relaxation time constant behavior of polydisperse polyisoprene has proven to be complicated (Appendix 7). Therefore, these in situ compression techniques are best illustrated with a monodisperse sample which has proven to have a simpler behavior. Furthermore, this work extends the use of NMR to expose the time dependence of the molecular motions induced by compression. Proton spectra can be taken much faster in comparison to other nuclei, which results in an ability to observe the spin lattice relaxation behavior at various points during the macroscopic stress relaxation. Therefore, we were able to determine if there was a direct correlation between high frequency molecular relaxation and macroscopic global polymer relaxation. Finally, we hypothesize that the trends observed in the spin lattice relaxation time constants, as a function of compressive strain and time, are consistent with chain scission during stress relaxation.

**Experimental**

Monodisperse (PDI=1.02) 97% cis 1,4-polyisoprene was purchased from Polymer Source Standards (M<sub>N</sub>= 710,000) and used without further purification. This materials will be referred to as 710k.

The mechanical data were acquired with an Instron Model 4201 operated in compression mode at room temperature. The specimens were rectangular with dimensions: 0.2 in. x 0.2 in. x 0.4 in. The polymer specimen is sandwiched on the top and bottom by Teflon inserts, allowing for equal slip on both sides during compression. A 1 kN compression load cell was used for all tests. The stress relaxation in the polymer was measured as a function of time, at a constant strain of 40%.

All NMR spectra were taken with an Oxford 6.3 T magnet (with a 270 MHz ¹H resonance frequency) using a Tecmag dual resonance pulse generator and receiver. The magic angle spinning (MAS) spectra were taken with a Chemagnetics 7.5mm probe at a sample spin speed of 2500 Hz. A compression device was fabricated to enable in-situ NMR measurements of specimens under constant strain. The compression device for the MAS spectra was constructed from a Teflon rod 0.15 in. in diameter and 1.00 in. in length. The specimen for these experiments had rectangular dimensions: 0.05 in. x 0.05 in. x 0.30 in.. A Teflon spacer between the polymer and screw allowed for slip at one end of the specimen while the
bottom of the Teflon device created slip at the other. For all experiments, there was clearance between the polymer’s circumference and the sides of the compression cell. After a 10 minute wait for mechanical equilibrium after compression, spectra were acquired with a 4 μs π/2 pulse width, a 10 μs dwell time and a 5 s recycle delay, unless otherwise specified. The spectra were referenced to tetramethylsilane (0 ppm). Strains at 0, 20, 40% were investigated.

Spin-lattice relaxations were measured using an inversion recovery sequence (π-t-π/2-Acq). A single least square exponential was fit to the peak intensity (M) versus delay time (t), resulting in a two parameter fit yielding: the equilibrium peak intensity (M₀) and the spin-lattice relaxation time constant (T₁) (Eq 1).¹⁷

\[
M(t) = M_0 (1 - 2 \exp(-t/T_1))
\]

This single exponential fit was used for the monodisperse polyisoprene and gave an $R^2$ value ≥ 0.99.

**Discussion**

Figure 1 is the macroscopic stress relaxation curve. The stress has decayed to a plateau 10 minutes after the stress was first induced.

*Figure 1. Stress relaxation curve of 710k cis 1,4-polyisoprene at 40% strain*
As observed in Figure 2, with MAS, using a spin speed of 2500 Hz, the three chemically distinct protons of cis 1,4-polyisoprene can be resolved (FWHM ~ 50 Hz): methyl (1.8 ppm), methylene (2.1 ppm) and methine (5.2 ppm). Therefore, individual T₁ time constants could be determined for the three chemically distinguishable protons.

*Figure 2. MAS $^1$H spectrum of monodispersed 710k cis 1,4-polyisoprene*

The high natural abundance of protons requires fewer scans in order to acquire the spin lattice relaxation data. Therefore, the spin lattice relaxation time constants could be taken during various stage of the macroscopic stress relaxation. Figure 3 is the spin lattice relaxation times for each resonance as a function of time at 40% strain. There is an initial drop of in T₁ of the resonance from 412 to 304 ± 25 ms.
for the methyl, from 344 to 280 ± 25 ms for the methylene, and from 360 to 258 ms for the methine resonance. In all three cases, the decreases are larger than the uncertainty in the measurement (± 25 ms).

Figure 3. Spin lattice relaxation ($T_1$) time constants as a function of duration of compressive strain for 710k cis 1,4-polyisoprene at 40% strain

![Graph showing $T_1$ time constants](image)

The first $T_1$ relaxation experiment is completed 6 minutes after strain is induced. After 6 minutes, the stress has decayed from 0.05 MPa to 0.002 MPa consistent with a 96% decrease of the total stress. Therefore, there is a large amount of macroscopic stress decay occurring during the first experiment (6 minutes) and little during the second (12 minutes). However, there is no further decline in the $T_1$ time constants or a change after the strain has been removed. Using another nucleus such as carbon-13, a typical experiment would take approximately no less than 10 minutes. Therefore, proton spectra are ideally suited to studying the molecular mobility during the macromolecular polymer stress decay.
Figures 4 to 6 are the magnetization recovery curves as a function of compressive strain on monodisperse 710k polyisoprene after a 10 minute wait for stress relaxation of the methyl, methylene and methine resonances, respectively.

Figure 4. MAS magnetization recovery curve for the methyl (a) resonance of compressed 710k cis 1,4-polyisoprene after a 10 minute wait for mechanical equilibrium

\[
\ln\left(\frac{M(t)}{M(0)}\right) = -\frac{t}{T_1}
\]

\(T_1 = 412 \pm 25\) ms

\(T_1 = 370 \pm 25\) ms

\(T_1 = 303 \pm 25\) ms
Figure 5. MAS magnetization recovery curve for the methylene (b) resonance of compressed 710k polyisoprene after a 10 minute wait for mechanical equilibrium.

\[ T_1 = 344 \pm 25 \text{ ms} \]
\[ T_1 = 303 \pm 25 \text{ ms} \]
\[ T_1 = 278 \pm 25 \text{ ms} \]
The $T_1$ time constants of all resonances decrease continuously from 0% to 40% strain. The changes were from 412 to 303 ms, from 344 to 278 ms and from 360 to 256 ms for the methyl, methylene and methine resonances, respectively, with a typical error of ±25 ms. The spin lattice relaxation of the methylene resonance was within experimental error of the methine. However, the methyl resonances are slightly longer than the other two resonances. Protons relax through a dipolar mechanism, which is a through space interaction between protons. Due to their high abundance and close proximity, the relaxation rates of each proton is significantly influenced by other surrounding protons. Therefore, it is often difficult to
identify individual behaviors of each chemically distinguishable proton.\textsuperscript{17} Since the methylene and methine resonances are within error of one another it is likely that the dipolar communication between the moieties lead to the same relaxation rate. The methyl group is known to rotate so quickly that it inefficiently couples with surrounding nuclei resulting in a longer relaxation than other protons.\textsuperscript{18} Therefore, the longer relaxation for the methyl group most likely is the result of a faster rotation in comparison to the other protons.

There are numerous conditions which can change the observed spin lattice relaxation time constant that can be categorized as changes in either chain mobility or the surrounding chain environment. Most commonly, changes in spin lattice relaxations are associated with changes in the mobility of the chemical moieties. For this study, polyisoprene's relaxations are in the $\omega \tau << 1$ region of the spectral density curve since the measured $T_2$ was less than $T_1$.\textsuperscript{17} This means that a shorter $T_1$ time constant implies a faster correlation time for molecular motion, at the Larmor frequency (270 MHz) time scale. The spin lattice relaxation can be caused by dipolar mechanism mitigated by motional averaging of the chains ($T_{1\text{dipolar}}$), or by the presence of other faster relaxation modes in the protons environment ($T_{1\text{center}}$) (Eq 2).

\textbf{Eq 2:} \[ \frac{1}{T_{\text{observed}}} = \frac{1}{T_{1\text{center}}} + \frac{1}{T_{1\text{dipolar}}} \]

Therefore, there are a variety of explanations for the observed decrease in the spin lattice relaxation time constants with an increase in strain. They include a situation in which there are no fast relaxing centers and the observed $T_1$ decreases simply because of faster segmental mobility. Or it could be a situation where there is an additive contribution that includes fast relaxing centers from more mobile chain ends or the formation of dangling bond paramagnetic centers.

Argon and coworkers simulated the deformation mechanics of glassy solids, such as copper and zirconium alloys.\textsuperscript{20} Small strains on the solid create plastic flow leading to local dilation of the atoms. Furthermore, this dilation is followed by a local incremental increase in the maximum shear strain. Given a constant volume there are local regions of inelastic dilation due to an increased flow concentration creating a shear activity in the range of 0.5-0.1 for a macroscopic external strain of $5 \times 10^4$.\textsuperscript{20} Therefore, plastic flow caused by strain results in localized dilation which increases the mobility of the atoms. Furthermore, they found that once strain was released plastic flow ceased and the dilation was removed. For an elastomer, the plastic flow can result in the mobility of the internuclear vector associated with the individual repeat
The compressive strain disturbs the chains from their equilibrium configuration, causing the polymer to flow and resulting in localized increase in dilation and shear strain.

Under this mechanism, the decrease in the spin lattice relaxation time constant results from the plastic flow of the polymer chains increasing their molecular mobility. This is consistent with the observations in Figure 4 to 6. Furthermore, presumably the larger the macroscopic strain the larger the local shear activity and dilation creating a larger mobility and lower spin lattice relaxation time constant. However, the large differences in the spin lattice relaxation observed in Figures 4 to 6, are unparalleled in comparison to observation of other in situ compression experiments. In addition, one would expect the spin lattice relaxation time constant to return to its original value after the mechanical strain has been removed. As seen in Figure 3, the spin lattice relaxation time constant does not change after the strain is removed.

Nakaoki and coworkers, using methyl terminated monodisperse polyethylene (M_N=1138 g/mol), were able to distinguish the relaxation of the end groups from the internal repeat units of the polymer. Using MAS carbon-13 NMR, they found a faster spin lattice relaxation of methyl terminated end caps (T_1=1.6 s) compared to the internal repeat units of the chain (T_1=32 s). This suggests that NMR spin lattice relaxation times may decrease if a sufficient concentration of highly mobile chain ends are present in order to decrease the expected value from that of the more immobile repeat units.

Therefore, it is possible that these faster motions of the chain ends act as centers for relaxation for the chain segments. In the presence of rapidly rotating chain ends, the observed spin lattice relaxation should be an additive effect of the motionally averaged dipolar (T_{dipolar}) and the chain ends contribution (T_{center}) (Eq 2). The observed spin lattice relaxation time constant would decrease only if the chain ends came into closer proximity to the segments causing an increased communication between the two moieties. However, the chain ends are likely randomly distributed throughout the polymer. Upon compression the chain ends should maintain their same spatial distribution with surrounding segments. Therefore, the spin lattice relaxation is not likely to change due to the chain ends.

Chain rupture due to deformation has been experimentally and theoretically investigated for a variety of semicrystalline and rubbery polymers. Theoretically, chain rupture is likely to occur when the chain has been fully extended from its Gaussian configuration to its extended end-to-end length. For
elastomers chemical crosslinks limit the extensibility of the chain to dimensions less than the theoretical end-to-end distance. Case and coworkers found that the extensibility of an elastomer is inversely related to the crosslink density and degree of functionality of the crosslinks. These results have been verified by Mead and coworkers who found that peroxide crosslinked polyisoprene and polybutadiene were susceptible to chain scission at high tensile strains (100%). Using electron spin resonance, it was determined that the allylic radical decays rapidly to a peroxy radical due to recombination with atmospheric oxygen, when the polymer is held above 25°C.

Using this mechanism, the T1 time constants would decrease due to chain rupture with increasing compressive strain. As the chains ruptures, the dangling bonds act as paramagnetic centers for more efficient spin lattice relaxation of the protons on the polymer. The expected amount of chain rupture can be determined by finding the expected concentration of paramagnetic chain ends.

The paramagnetic contribution for a system with spin diffusion has been worked out by others, who have found an inverse dependence of the spin lattice relaxation time constant with the concentration of paramagnetic centers. This implies that as the polymer is exposed to more paramagnetic centers the spin lattice relaxation time constant would decrease. From Figures 4 to 6, with a 40% compressive strain, there is a 26 ± 8%, 19 ± 9% and 27 ± 9% decrease in the T1 of the methyl, methylene and methine resonances, respectively. In the presence of paramagnetic centers the observed spin lattice relaxation should be an additive effect of the motionally averaged dipolar (T1_dipolar) and paramagnetic contributions (T1_para = T1_center) (Eq 2). The changes observed in Figures 4 to 6 for the T1 time constant are more reasonable for what would be expected from the formation of paramagnetic centers. It is expected there would be no preferred interaction of each chemically distinguishable proton with the paramagnetic centers. Therefore, as seen in Figures 4 to 6, each proton responds to the strain with a decrease in T1 time constants. Furthermore, if the chains ruptured we would expect there would be no reversible change in the T1 after releasing the load. As seen in Figure 3 there was no change in the T1 time constant when strain was released, or as a function of time. Even if the radicals on the chain ends terminated, it is plausible that the decreased molecular weight of the polyisoprene could cause a decrease in the observed spin lattice relaxation time constant since molecular mobility of the shorter chains is greater and there is an increased concentration of chain ends.
Although the formation of paramagnetic centers is qualitatively consistent with the observed trends, additional experiments need to be undertaken in order to fully validate this mechanism. Principally, fracture mechanics is most commonly explored using electron spin resonance (ESR) in order to identify and quantify the presence of free radicals. The unique compression device used in these NMR experiments could be easily modified to be used in ESR measurements.

Conclusion

These are the first experiments to be reported on the high frequency motions occurring during stress relaxation. Magic angle spinning allowed us to reduce the effect of dipolar coupling and observe each proton on the cis 1,4-polyisoprene backbone. There was a decrease in the $T_1$ time constants with an increase in compressive strain for each resonance. There was no change in the proton spin lattice relaxation time constants as a function of time suggesting the change in relaxation was caused by an irreversible mechanism. We hypothesize that these faster relaxations are most likely the result of chain rupture which creates paramagnetic centers. This explanation creates an irreversible change in the observed mobility, as evidenced in the spin lattice relaxation time constant once the load is released.
References:


Chapter 6

Summary and Future Work
Conclusions

Proton NMR

Although a variety of nuclei are available for nuclear magnetic resonance (NMR), the techniques developed in this thesis have centered on the use of proton NMR. Protons have the highest abundance and largest gyromagnetic ratio (99.98%, 2.67x10^8 T·s⁻¹) in comparison to other natural occurring nuclei, such as carbon-13 (1.11%, 4.1x10⁷ T·s⁻¹) and deuterium (0.02%, 6.73x10⁷ T·s⁻¹).¹² There are three relevant consequences to the size of these parameters. First, the magnetization (M) for a nucleus is proportional to the abundance (a) and the gyromagnetic ratio (γ) squared (Eq 1).¹

\[ M = a \gamma^2 \]

Spectra are a summation of magnetization from a number of individual scans of the sample. Therefore, the higher abundance and gyromagnetic ratio of protons translates into spectra which require fewer scans to obtain a high signal to noise. Specifically, as shown in Table 1 the proton spectrum takes the least amount of time (less than a minute) since a fewer number of scans are required.

<table>
<thead>
<tr>
<th>Type of Nucleus</th>
<th>Typical Time for a 1-Dimensional Spectrum (minutes)</th>
<th>Typical Number of Scans Used for a 1-Dimensional Spectrum (at least 10:1 signal:noise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton</td>
<td>Less than 1</td>
<td>4</td>
</tr>
<tr>
<td>Deuterium ( [\text{CD}_2\text{CD} = \text{CCD}_2\text{CD}_2]_n )</td>
<td>10</td>
<td>32</td>
</tr>
<tr>
<td>Carbon</td>
<td>10</td>
<td>32</td>
</tr>
</tbody>
</table>

This property is particularly useful for monitoring the motions of stress relaxation of composites where the largest changes in macroscopic mechanical behavior occur within the first five minutes after applying a strain. Therefore, the techniques developed in this thesis can be applied to polymers in order to quickly capture compression induced changes in polymer mobility as a function of time. Second, the higher natural abundance means these techniques could be used on commercially available polymers without further modification. In this case, synthetic cis 1,4-polyisoprene was used to illustrate the capabilities of these techniques. Third, dipolar coupling (C), and therefore the observed linewidth (Δν), is a measure of the amount of communication between protons in the sample (Eq 2).¹

\[ C = 0.67\gamma^3 r^3 = \Delta \nu \]
The dipolar coupling constant ($\mathcal{C}$) is dependent on: the gyromagnetic ratio of the proton ($\gamma$), Plank's constant ($h$) and the distance ($r$) between interacting protons. Due to their high abundance, the distance ($r^{-3}$) between communicating protons is relatively short causing an increase in the coupling constant. Therefore, the high abundance causes extensive dipolar coupling between all the protons in the sample. In addition, since the gyromagnetic ratio squared is proportional to the dipolar coupling constant, the higher gyromagnetic ratio for protons increases their strength of their interaction (Eq 2). Due to this dipolar communication, the observed behavior is an average over an extensive number of protons. For the homopolymer, the area over which behavior is averaged can be found using a three dimensional diffusion equation (Eq 3).

\[ Eq \ 3: \ X = 6Dt \]

In which case, the spherical radius of interaction of a proton ($X$) is dependent on the spin-lattice relaxation ($T_1$) and the diffusion constant ($D$), extracted from the static linewidth. For a nanocomposite, the distance for communication between protons is best described by the one-dimensional diffusion equation (Eq 4). *

\[ Eq \ 4: \ X = 2Dt \]

Different linewidths and diffusion lengths are observed with static and MAS NMR techniques. Therefore, static and MAS techniques were contrasted in order to determine how this communication hinders analysis and how it can be minimized in order to allow for independent observation of the magnetically distinct regions of the polymer composites.

**Static Proton NMR**

The static linewidths are the largest observed in solid state NMR analysis. In this work, typical values were ~3000 Hz and ~20000 Hz for polyisoprene-clay composites and POSS, respectively. According to Eq 2, the larger linewidths, relative to MAS, indicate a larger amount of dipolar coupling.

For the nanocomposites, decreases in the spin lattice relaxation time constants were the result of increases in the polymer's interaction with the paramagnetic centers in the clay. Specifically, as

* In this case the decreased dimensionality takes into account that protons near the clay surface will not be entirely surrounded by protons from the polymer.
compressive strain was increased the clay aggregate sheared apart increasing the polymer’s contact with the natural occurring paramagnetic iron in the clay structure. The breadth of the peak prevented the spin lattice relaxation time constants from being assigned to a particular moiety. For the nanocomposites, each proton had a distance of interaction of 3.1 nm (Eq 4). Therefore, due to this extensive communication between protons, changes in the spin lattice relaxation time constants described a change in the average proton behavior in the composite.

Finally, abrupt changes in the static proton spin-lattice relaxation time constants marked a change in the molecular mobility caused by phase changes in POSS crystals. However, intramolecular interactions, between protons on the same molecule, and intermolecular interactions, between protons on adjacent molecules, both dictated the relaxation. Using Eq 3, the spherical radius of interaction for an average proton was 26.3 nm and 27.7 nm for fully protonated and partially deuterated POSS, respectively. Therefore, due to the extensive dipolar coupling, the effect of these two mechanisms was averaged when observed with static proton NMR.

**Magic Angle Spinning (MAS) Proton NMR**

Although static in situ NMR compression measurements have been previously reported, these are the first to be done while acquiring spectra under MAS. In order to remove some of the ambiguity caused by the extensive dipolar coupling, the in situ compression device was modified to fit in a ceramic MAS rotor. By spinning at a frequency larger than the static linewidth at the magic angle (θ=54.74°) the dipolar coupling is averaged to zero during the cycle of a rotor period. As a result, the resonances were resolved to the isotropic chemical shifts causing typical linewidths of ~50 Hz, for both the polyisoprene and polyisoprene-clay composites.

Using MAS, the observed resonances of polyisoprene were further refined to the chemical shifts of the three chemically distinguishable protons: the methyl, methylene and methine. This allowed for individual spin-lattice relaxation time constants for each distinguishable proton to be monitored, independently. Each distinguishable proton was equally sensitive changes in compressive strain. Using Eq 3, the changes in linewidth translates into a 0.7 nm spherical radius of interaction for each proton. This identical behavior of each proton suggests that all the dipolar communication was not completely disrupted.
with MAS. The distance between protons on the same repeat unit are likely to be less than 0.7 nm apart leading to communication and identical spin lattice relaxation time constants for the methylene and methine resonances.

Similar to the homopolymer, the nanocomposite spectra could be resolved to the isotropic chemical shifts of the chemically distinguishable protons. However, there were no observed differences in the behavior of each moiety with compressive strain. Using Eq 4, the changes in linewidth translates into a 1.1 nm distance of interaction. Therefore, MAS could be used to independently monitor polymer close to the clay surface and polymer far removed from the clay aggregate. Furthermore, it was found that only the polymer within 1.1 nm of the clay surface responded to the changes in interfacial area of the aggregate.

The static POSS experiments illustrate the limitations of the MAS technique. The linewidths for these spectra were between 16000-20000 Hz depending on the labeling of the ethyl substituent. The maximum spin speed for the Chemagnetic’s 7.5 mm probe is 6000 Hz. Therefore, it was not possible to spin outside the static linewidth to fully resolve these spectra. In effect, these MAS techniques are only useful for polymers which have a static linewidth less than 6000 Hz. This limits the possible materials to those with high intrinsic mobility, such as elastomers.

Observations of the Materials: Polyisoprene, Clay-Polyisoprene Nanocomposites, POSS Crystals

Magic angle spinning proton NMR was used to measure the strain dependent spin lattice relaxation behavior of cis 1,4-polyisoprene. The spin lattice relaxation time constants continually decreased with an increase in compressive strain. Furthermore, the use of proton NMR allowed us to monitor the spin lattice relaxation at various points during the macroscopic stress relaxation. We found that the spin lattice relaxation time constants did not changes as a function of time or when the load was released from the sample. Therefore, we conclude that this irreversible deformation is consistent with the possibility of strain induced chain rupture.

Using these NMR techniques, increases in polymer-clay interfacial area were observed with increased clay dispersion and increased compressive strain. As the chemistry of the surfactant matched that of the homopolymer, there was an increase in the polymer-clay interfacial area identified by a decrease in the spin lattice relaxation time constant. In terms of the observed mechanical behavior, the spin lattice
relaxation time constants decreased as the polymer-clay interfacial area increased due to the shearing of clay aggregates. Most composites showed at least a doubling of interfacial area after 40% compressive strain. For polyisoprene-laponite composites, the changes in interfacial area were verified with optical microscopy. As opposed to microscopy techniques, NMR allows for observations of the bulk behavior without the need for statistical sampling.

Finally, phase transitions were identified and the changes in molecular mobility were characterized, with static proton and deuterium NMR, for fully protonated (253 K) and partially deuterated (258 K) ethyl POSS. A change in isotropic labeling resulted in an increase in the transition temperature. Both derivatives experience fast molecular tumbling at high temperatures and slow molecular tumbling past their respective transitions. Specifically, past their respective transitions there is an increase in correlation time and activation energy for molecular tumbling observed with solid state NMR. Calorimetry and powder diffraction were used to corroborate a first order solid-solid phase transition occur for both derivatives of ethyl POSS. Further work on materials with a clean addition of the deuterium isotope would aid in further characterizing the motions and changes in the transition point.

**Future Work**

Further improvements in minimizing dipolar coupling could lead to refinement of some of the conclusions made on the materials used in this thesis. One of the advantages of the designed MAS compression device is that the isotropic chemical shift of the chemically distinguishable resonances of other nuclei can be observed while the polymer is compressed. The carbon-13 nucleus could be an enlightening alternative to proton NMR. Carbon-13 is less abundant and therefore would require more scans to obtain a comparable signal-to-noise to these proton spectra. However, the decreased natural abundance also decreases dipolar coupling perhaps allowing for a more detailed analysis of the changes in mobility. In the case of polyisoprene, other authors have identified differences in the mobility of chemically distinguishable carbons using MAS solid state NMR. For instance, Schaefer found that the methyl carbon ($T_1 = 52$ ms) has a shorter relaxation than the alkene carbons ($T_1 = 95$ ms). Likewise, there may be differences in the response of each chemically distinguishable carbon to changes in compressive strain.
We have found in the context of this work, that magic angle spinning allows for isolated observation of different regions of a polymer composite while under mechanical deformation. Therefore, these techniques could be applied to other composites in order to identify changes in molecular level mobility at the interface. One attractive alternative is epoxidized polyisoprene blended with monodispersed silica beads. Cataldo found improved mechanical strength of epoxidized polyisoprene when the polymer was blended with untreated silica. He hypothesized this improvement in macroscopic mechanical properties was the result of the polymer hydrogen bonding with the silica surface. Using the MAS technique, the polyisoprene adjacent to the surface could be monitored separately from the bulk. The strength of the hypothesized hydrogen bonding could be identified using variable temperature NMR. At higher temperatures the spin lattice relaxation should decrease due to a decrease in hydrogen bonding as a result of increased molecular mobility. Similarly under compressive strain, the interactions of the interface may decrease as the mobility of the polymer increases.

Traditional fillers, such as glass fibers and carbon black, are often crosslinked to the matrix. Increases in mechanical behavior is the result of the energy dissipation caused by breaking the covalent bonds between the interface of the polymer and inorganic filler. Likewise it is anticipated that if polyisoprene were covalently bonded to the clay surface there would be an improvement in the mechanical modulus. This work has indicated that shearing of clay aggregates is a mechanism of deformation at relatively low amount of compressive strain in samples which are not covalently bonded to the matrix. These developed techniques could be used to determine if the same mechanism occurs in a polymer system where the polymer chains are directly bonded to the composite or if the same mechanism occurs at a higher level of strain. The changes in mechanism can then be related to any observed changes in the macroscopic mechanical properties. Based on the work of traditional fillers it is anticipated that halting the shearing mechanism may result in improved mechanical strength.

The composites studied in this thesis was considered to be randomly oriented. According to Mohr's circle, the largest amount of shearing should occur for the clay aggregates which are oriented at a 45° angle to the principle axis of deformation. The orientation of the clay aggregates could be controlled by spin casting multiple layers and allowing them to fuse into a contiguous sample. After spin casting the clay aggregates would be aligned parallel with the surface of the spin coater. The aggregates can be
oriented at a 45° angle to the compression axis by orienting and cutting the sample at that angle. Using the NMR techniques developed in this thesis, the compression of this sample would give the maximum amount of shearing expected for a given amount of strain. When compared with the randomly oriented solvent cast samples, it would be possible to quantitate the percentage of clay aggregates oriented at a 45° angle.

Finally, in this work the composites showed a constant increase in surface area with increasing compressive strain. However, there is likely an upper compressive strain limit upon which the aggregate will no longer shear apart. In order to determine that limit the compression device could be redesigned as two Teflon plates. Nylon screws at the edges decreases the spacing between the plates thereby increasing the compressive strain. These experiments would only be done under static conditions but there would be no radial confinement on the amount of strain that could be applied to the sample. Under these experimental conditions this maximum shear limit could be determined.

References


Appendices
Appendix 1: Description, Diagram and Photograph of the MAS Compression Device

API-1:
Description:
The MAS device for in-situ NMR compression was constructed from a Teflon rod 0.15" in diameter and 1.00" in length. A Teflon spacer between the polymer and screw allowed for slip at one end of the specimen while the bottom of the Teflon device facilitated slip at the other. The specimen for these experiments had rectangular dimensions of 0.05" x 0.05" x 0.30". For all experiments, at 40% compressive strain, there was clearance between the polymer's circumference and the sides of the compression cell.

Diagram:

Photograph:
Appendix 2: Representative Stress Relaxation Experiments for 13 wt% Na⁺ exchanged MMT-cis 1,4-polyisoprene nanocomposites

AP2-1: Stress relaxation of 13 wt% Na⁺ exchanged MMT clay and cis 1,4-polyisoprene nanocomposites with a continuous and step strain loading

Acquisition of NMR spectra begins here after 10 minutes

- stepped strain
- continuous strain

![Graph showing stress relaxation over time with marked strain levels and NMR acquisition time]
Appendix 3: Representative MAS $^1$H Compression Studies of MMT-Polyisoprene Samples

AP3-1: Plot of normalized magnetization versus the square root of the delay time for the methylene resonance of 25A modified MMT-polyisoprene composite as a function of compressive strain.

AP3-2: Bar graph of the coefficient (slope) for the protons of the 25A modified MMT-polyisoprene composite.
AP3-3: Plot of normalized magnetization versus the square root of the delay time for the methylene resonance of 30B modified MMT-polyisoprene composite as a function of compressive strain.

AP3-4: Bar graph of the coefficient (slope) for the protons of the 30B modified MMT-polyisoprene composite.

Change in Interfacial Area: ~220%
Appendix 4: Representative Solution Spectra of Protonated Ethyl POSS (Spectra Supplied by Haddad Group)

AP4-1: $^{13}$C Solution Spectrum of Protonated Ethyl POSS

13C NMR of sublimed E8718 (Viny18718 + Hydrogen) in CDCl3

- 6.511
- 4.621
- 4.080
- 3.536
29Si NMR of Protonated Ethyl POSS
Appendix 5: Representative Solution Spectra of Deuterated Ethyl POSS (Spectra Supplied by Haddad Group)

AP5-1: \(^{13}C\) Solution Spectrum of Deuterated Ethyl POSS in Toluene at 70°C, recorded on a 1H NMR in CDCl3.

V1878 + D2 (600 ps)
Note integrals indicate H/D exchange occurred.

$1^H$ and $D^2 + D$ (500 psi) in Toluene at 70°C overnight. $^1H$ NMR in CDCl$_3$. Residual toluene present.
VT85 + D2 (600 psi) in Toluene at 70 C overnight. 29Si NMR in CDCl3.
Appendix 6: X-ray Data of Ethyl Substituted Polyhedral Oligomeric Silsesquioxane (POSS)

Experimental: Wide angle x-ray diffraction (WAXD) measurements were made on a SMART APEX x-ray generator with Mo Kα radiation. The operating voltage was 50 kV with a current of 35 mA. Spectra were taken from powder, placed in a borosilicate capillary (I.D. = 0.05 mm, O.D. = 0.50 mm), mounted in the beam path.

AP6-1: WAXD Spectra at Various Temperatures for Fully Protonated Ethyl POSS

![Graph showing WAXD Spectra at various temperatures](image-url)
Results: The shifts in the positions of the peaks in the above spectra illustrates that a crystallographic phase transition occurs. However, the Mo source causes the reflections at low angles to overlap making a unit cell determination for each phase unreliable with this data.
Appendix 7: Representative MAS $^1$H Compression Studies Polydisperse Polyisoprene

**Experimental:**

Polydisperse (PDI=3.40, $M_w=938,000$ g/mol, $M_N=276,000$ g/mol) 97% cis 1,4-polyisoprene was purchased from Aldrich.

The mechanical data were acquired with an Instron Model 4201 operated in compression mode at room temperature. The specimens were rectangular with dimensions: 0.2 in. x 0.2 in. x 0.4 in. Both the top and bottom of the polymer specimen had a Teflon-polymer interface allowing for equal slip on both sides. A 5 kN compression load cell was used for all tests. The stress relaxation in the polymer was measured, meaning a strain of 40% was placed on the polymer sample and the stress was monitored as a function of time.

All NMR spectra were taken with an Oxford 6.3 T magnet (with a 270 MHz $^1$H resonance frequency) using a Tecmag dual resonance pulse generator and receiver. Static $^1$H experiments were performed on a home built probe with a 2 $\mu$s $\pi/2$ pulse width. The magic angle spinning (MAS) spectra were taken with a Chemagnetic 7.5 mm probe with a 4 $\mu$s $\pi/2$ pulse width and a spin speed of 2500 Hz. Spectra were acquired with a 10 $\mu$s dwell time and a 5 s recycle delay and taken after a 10 minute wait for mechanical equilibrium.

The compression device, used for static spectra, was a Teflon rod 0.25 in. in diameter and 1.00 in. in length. The polymer was placed in a threaded hole 0.18 in. in diameter and compression was induced by successive turns of a nylon screw. The polymer specimens were rectangular with the dimensions: 0.09 in. x 0.09 in. x 0.30 in. The device for MAS spectra was constructed from a Teflon rod 0.15 in. in diameter and 1.00 in. in length. The specimen for these experiments had rectangular dimensions: 0.05 in. x 0.05 in. x 0.30 in. A Teflon spacer between the polymer and screw allowed for slip at one end of the specimen while the bottom of the Teflon device created slip at the other. For all experiments, there was always clearance between the polymer's circumference and the sides of the compression cell.

Spin-lattice relaxations were measured using an inversion recovery sequence ($\pi$-t -$\pi/2$-Acq). A single least square exponential was fitted to the peak intensity (M) versus delay time (t), resulting in a two parameter fit yielding: the equilibrium peak intensity ($M_o$) and the spin-lattice relaxation time constant ($T_1$) (Eq 1).

\[
\text{Eq 1: } M(t)=M_o(1-2\exp(-t/T_1))
\]

This single exponential fit was used for the monodispersed polyisoprene and the static spectra of the polydispersed polyisoprene with an $R^2$ value $\geq 0.99$. A two exponential fit was appropriate for the MAS spectra of the polydispersed polyisoprene. In this case, the data was fit to four parameters (Eq 2): equilibrium peak intensity ($M_o$), spin-lattice relaxation time constants ($T_{1S}, T_{1L}$), and proportion of spins experiencing each relaxation ($F_L, (1-F_L)$).

\[
\text{Eq 2: } M(t)=(1-F_L)M_o(1-2\exp(-t/T_{1S}))+F_LM_o(1-2\exp(-t/T_{1L}))
\]
Results:

AP7-1. Static and MAS $^1$H spectrum of polydisperse cis 1,4-polyisoprene

Figure AP7-1 is the proton ($^1$H) spectrum of polydispersed cis 1,4-polyisoprene under static and MAS conditions. In the static spectrum, the methine resonances can be differentiated from the overlapping resonances of the methyl and methylene protons. Under MAS conditions the three chemically distinguishable protons can be isolated at their isotropic chemical shifts: $^2$methyl (1.8 ppm), methylene (2.1 ppm) and methine (5.2 ppm). As seen in Figure 1, prior to magic angle spinning there was enough molecular mobility to resolve the methine resonance from the overlapping methyl and methylene resonance. Therefore, individual $T_1$ time constants could be assigned to the methine resonance and the combined methyl and methylene resonance. The static spectrum was further narrowed to the isotropic chemical shift values upon spinning at the magic angle. Therefore, with MAS, individual $T_1$ time constants could be assigned to the three chemically distinguishable protons: the methyl (a), methylene (b) and methine (c).
AP7-2. Magnetization recovery plot of polydisperse cis 1,4-polyisoprene measured statically and under MAS conditions

For the polydispersed sample (AP7-2), a single time constant ($T_1 \approx 390$ ms) fits the data under static conditions. Under MAS conditions, the magnetization recovery is best fit to two time constants: a short ($T_{1S} \approx 30$ ms) and long ($T_{1L} \approx 380$ ms) relaxation. This behavior was representative of each of the three chemically distinguishable protons.
AP7-3. $T_1$ time constants for the methylene resonance under static and MAS conditions measured with increasing compressive strain.
From Figure (A7-4), the $T_1$ time constants, measured under static conditions, decreased with an increase in compressive strain. In addition, the fraction of the long component ($F_L$), measured in the MAS experiment, decreases with an increase in strain. However, within experimental error, the long ($T_{1L}$) and short ($T_{1S}$) spin lattice relaxation time constants remain constant with strain.

AP7-4. Percentage of long component ($F_L$) under MAS conditions measured with increasing compressive strain for the methyl, methylene and methine protons.

As illustrated in Figure A7-4, for all three chemically distinguishable protons, the fraction of long component ($F_L$) decreases with increasing strain. Furthermore, there is no significant difference in the behavior of each of these three distinguishable protons.
AP7-5. Stress Relaxation at 40% strain

The mechanical data for the stress relaxation of the polydispersed cis 1,4-polyisoprene is represented in Figure AP7-5. The highest level of stress is reached instantaneously with an exponential decay plateauing to a finite value after 20 minutes.
Conclusion:

Both the static and MAS spin lattice relaxation time constants decreased with an increase in compressive strain. Furthermore, the MAS relaxation allows for the observation of two distinct relaxation mechanisms not observed in the static spectra due to strong dipolar coupling. Unlike the monodisperse cis 1,4-polyisoprene there are two spin lattice relaxation time constants observed in this polydisperse sample. In addition, the fraction of the long component included in the observed spin lattice relaxation time constant recovers to a value similar to that prior to the introduction of strain.

The long relaxation component is within error of that obtained for the monodisperse sample \(T_{1L} \sim 380 \, \text{ms}, T_{1\text{Monodisperse}} \sim 340 \, \text{ms}, \text{AP7-2}\). As far as the assignment of the lower spin lattice relaxation time constant \(T_{1S} \sim 30 \, \text{ms}\), there was no indication of impurities in the dynamic scanning calorimetry or gel permeation chromatography to suggest a molecular identity for that substance. Therefore, further work would need to elucidate the identity of the fast relaxing component.

Due to the yellow coloration of the cis 1,4-polyisoprene and the fact that the equilibrium stress level is larger (0.005 MPa, AP7-5) than that of the monodisperse sample (0.001 MPa), it is suspected that the sample may be lightly crosslinked. According to Figures AP7-2,3,4 the behavior of all three protons is within experimental error in this sample. The free radical mechanism for crosslinking of cis 1,4-polyisoprene has been determined by a number of researchers.\(^3\) It has been shown that the crosslinks form from attack of the double bond and often impede the mobility of the adjacent methyl group.\(^5\)
in mobility would make this group more susceptible to dipolar communication with surrounding protons causing an identical relaxation to be observed for each proton. Therefore, this identical behavior of all three distinguishable protons is a spectroscopic conformation that there may be crosslinks in this sample. This may be a source for the different spin lattice relaxation behavior for polydisperse versus the monodisperse samples.

Provided the polydisperse sample is crosslinked, it would be more susceptible to chain rupture than the monodisperse sample. It is plausible that like the monodisperse sample the polydisperse sample undergoes chain rupture during compressive strain causing an increasing in the spins which relax through a faster mechanism due to the increased concentration of paramagnetic centers. This could be why this material never fully recovers to its initial values after the load is removed; however, some crosslinks remain intact allowing for partial recovery of the initial spin lattice relaxation behavior.

References:


Appendix 8: Representative MAS $^1$H Spin Lattice Relaxation Behavior of Monodisperse Polyisoprene

Experimental:

Various monodisperse 97% cis 1,4-polyisoprene (PDI=1.02, $M_N=710,000$, 56,000, 3,620 and 1,400 g/mol) were purchased from Polymer Source Standards and used without further purification. These will be referred to as 710k, 56k, 3.6k and 1.4k, respectively.

All NMR spectra were taken with an Oxford 6.3 T magnet (270 MHz $^1$H resonance frequency) using a Tecmag dual resonance pulse generator and receiver. The magic angle spinning (MAS) spectra were taken with a Chemagnetics 3.2 mm probe with a $2 \mu$s $\pi/2$ pulse width at a spin speed of 2500 Hz.

To obtain spin-lattice relaxation parameters an inversion recovery sequence ($\pi-\pi/2$-Acq) was used. A single least squares exponential was fitted to the peak intensity (M) versus delay time (t) according to Eq. 1, resulting in a two parameter fit yielding: the equilibrium peak intensity ($M_0$) and the spin-lattice relaxation time constant ($T_1$).

$$M(t) = M_0(1-2\exp(-t/T_1))$$

This single exponential fit was used for the monodispersed polyisoprene and the static spectra of the polydisperse polyisoprene with an $R^2$ value $\geq 0.99$.

Results:

AP-1. Spin lattice relaxation time constants as a function of an inversus number average molecular weight for monodisperse polyisoprene for MAS Proton Spectra
As seen in Figure AP8-1, there is a slightly linear increase for each of the protons with the number average molecular weight, 1,400 g/mol to 56,000 g/mol. The $T_1$ increased from 340-390 ± 15 ms, 280-350 ± 15 ms, and 300-360 ± 15 ms for the methyl, methylene and methine resonances, respectively. At high molecular weights, above 56,000 g/mol, the same spin lattice relaxation time constant was obtained (410 ± 15 ms methyl, 350 ± 15 ms methylene and 360 ± 15 ms methine). For all molecular weights the methylene resonance has the fastest $T_1$ time constant followed by the methine and the methyl.

Conclusion:

As seen in Figure AP8-1, the $T_1$ time constants of the methylene and methine resonances are within error of each other. Therefore, the molecular mobility of each moiety is probably comparable allowing for efficient coupling and homogenization of the spin behavior. The methyl resonance is significantly longer. It is improbably that the methyl group is rotating slower than the methine or methylene. Instead, as seen in other experiments, it is more likely that the methyl is rotating so quickly that it inefficiently couples to other protons therefore taking a longer time to relax.

Finally, at low molecular weight (1,400 mol/g to 56,000 g/mol) the $T_1$ time constant seems to be sensitive to the concentration of chain ends. It is likely that the lack of topological constraints on the chain ends allow them to rotate faster and are therefore experience a faster nuclear relaxation. In comparison, the segmental motions are likely longer and are described with a longer nuclear relaxation. At low molecular weights, high concentration of chain ends, enough chain ends are present to decrease the overall observed $T_1$ time constant. At high molecular weights, low concentration of chain ends, it is hypothesized that the internal segments dominate the relaxation and therefore the same $T_1$ time constant is obtained irrespective of molecular weight.

References: