THE EFFECTS OF CARBON BLACK REINFORCEMENT SYSTEMS ON CROSSLINKED SHAPE MEMORY ELASTOMERS

A Thesis

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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December, 2014
THE EFFECTS OF CARBON BLACK REINFORCEMENT SYSTEMS ON CROSSLINKED SHAPE MEMORY ELASTOMERS

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Thesis

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ABSTRACT

Shape memory polymers (SMPs) have been used for several decades with various transition mechanisms and microstructures. Traditional SMPs have used a block copolymer system to generate widely varying glass transition temperatures. When the polymer is heated above one block’s glass transition temperatures, the polymer can be deformed, cooled below the glass transition temperature, and the shape will then be locked into place. Further stimuli, typically heating, will cause the material to return to its original shape.

The present thesis attempts to make use of a second method of shape memory polymers. Prior work has shown that rubber can be made into a SMP when it is swollen with stearic acid, where the melt point of stearic acid, rather than a glass transition temperature, acts as the activation temperature. There are many advantages to this simple system including inexpensive materials, ease of handling stearic acid and rubber, and the wide use of rubber in industry. The first set of experiments aimed to determine a compound formulation that would allow the polymer to exhibit excellent shape memory behavior. A low state of cure enabled this and when tested on a DMA resulted in shape fixity of 62% with recovery in excess of 95%. Tensile and elongation testing helped in characterizing the physical and rheological properties of each compound. A solubility
A second set of experiments aimed to identify the effects of carbon black on the polymer’s shape memory behavior. While carbon black increased the modulus tremendously, it did not necessarily result in the expected monotonic increase in fixity. Fixity showed to have a sharp increase up to about 25 PHR carbon black but then plateaued with about 95% fixity. Recovery, however, showed a direct, negative relationship, steadily decreasing from about 100% to 93% as carbon black loading increased. The stress-strain curves identified a percolation point at which the tensile strength produced a minimum value at approximately 10 PHR carbon black. Finally, cross-link density also showed to relate directly with PHR carbon black loading, similar to the modulus, which increased proportionally with relative cross-link density, as calculated by the Flory-Rehner equation.
ACKNOWLEDGEMENTS

This thesis has been completed with the generous support of the Goodyear Tire & Rubber Co., without whom graduate school may not have been possible. My gratitude to Dr. Kevin Cavicchi, who offered to guide a part-time student with unending curiosity and inspiration. Most importantly, thank you to my family who have stuck with me through my pursuit for educational and scientific knowledge.
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CHAPTER I
INTRODUCTION TO SHAPE MEMORY POLYMERS

Shape memory polymers (SMPs) are a special class of materials that can recover shape when exposed to an external stimulus. The most common external stimulus used in the field of shape memory polymers is an activation temperature, sometimes referred to as a switching or transition temperature. The shape-memory behavior of polymers can be described by the process shown in figure 1.1, where a polymer is given its initial permanent shape (step 1), a deformation occurs that gives the polymer a temporary shape (step 2), an external stimulus is applied (step 3), which induces the polymer to return to its original permanent shape (step 4). Sometimes heat is a component of steps 2 and 3.

![Figure 1.1: Shape Memory Cycle](image-url)

1
Four categories of shape memory polymers have been identified by Liu, Qin, and Mather\(^1\): (1) covalently crosslinked glassy polymers, (2) covalently crosslinked semicrystalline elastomers, (3) physically crosslinked glassy polymers, and (4) physically crosslinked semicrystalline block copolymers. In the present study, a departure is made from the traditional definition of shape memory polymers given by Liu, et al., which will be described in a subsequent section.

Shape memory polymers have been used in many industrial applications, including textiles\(^2\), biomedical devices\(^3,4,5\), hydraulic systems\(^6\), and others. The first material commercially implemented for its shape memory properties was polynorbornene, produced by the Nippon Zeon Company\(^7\) of Tokyo, Japan.

Research in this field of study has for many years been centered on thermoplastic materials, such as specially designed block copolymers\(^8\). In this classic example of shape memory behavior, the glass transition temperature of the thermoplastic phase of the polymer is used as the locking mechanism. Heating the polymer above the glass transition temperature will allow the polymer to be bent and contorted to a desired second shape (step 2 in figure 1.1) where cooling the sample to beneath the glass transition temperature locks this shape into place. Reheating the sample above the glass transition temperature will allow the sample to recover back to the original shape (step 4 in figure 1.1) with nearly complete recovery. Since the first polymers with this capability were discovered, many more have been created that exhibit shape memory behavior under a substantially wider range of activation temperatures and strain-inducing mechanisms.
1.1 Statement of the Problem

Whereas materials of a thermoplastic nature have been used as SMPs for decades, polymers of an elastomeric rubbery nature have only recently been the focus of investigation. An inherent problem with this type of material is that the glass transition temperature of such rubbery materials is typically very low, in the case of polyisoprene (natural rubber, for instance) -57°C, which is often a temperature too low for shape memory applications. The benefits of this class of material, however, are quite numerous: they are very widely available, easily contorted and molded, retain an elastic component that can assist in shape recovery, and they are inexpensive, among other positive attributes. In contrast, despite these benefits, the elasticity of these materials can present difficulties as well, often contributing to poor shape fixity.

The understanding of how shape memory rubber (SMR) can be engineered is of critical importance for the application of shape memory rubber in industry. The focus of the present research was centered on how filler systems impact the shape memory, physical and rheological properties of SMRs, as well as the heat transfer characteristics of SMRs. Fillers and other additives have been used to modify the stiffness, hardness, elongation, and other properties of polyisoprene while also contributing to the rubber’s state of cure and affecting such rheological properties as creep and recovery. Furthermore, it was unclear if there was an impact of polymer-filler interactions on the shape memory behavior of SMRs. The present research utilized both reactive and unreactive filler systems to further understand their impact on shape memory.
A final aspect to this research was on how the rigid network, in this case crystalline stearic acid, reacted in situ with the filler systems employed. Because stearic acid has a melt point of about 69°C, it can be used in a wide range of industrial applications as a trigger material, used to crystallize within the polymer network to freeze the elastomer below the stearic acid melt point.

### 1.2 Historical Survey of Prior Work

There is very little research that has been completed in relation to shape memory rubber. The vast amount of research has historically been centered on classical shape memory polymers that employ two different chemical units as part of a block copolymer to reap the advantage of having two different glass transition temperatures, where one is used as the locking mechanism. Another branch of shape memory material that will not be investigated in this thesis is shape memory alloys. The present research, however, focused on rubber elastomers with very low glass transition temperatures that had been swollen with a fatty acid, specifically stearic acid, which then crystallized and acted as the locking mechanism. There is virtually no chemical bonding in this case.

The most common parameters describing shape memory materials are fixity, recovery, and activation temperature. Fixity is the ratio of the maximum strain upon applying a stress to the strain after cooling, when the stress is unloaded,

\[
R_f(N) = \frac{\varepsilon_u(N)}{\varepsilon_t}
\]  

(1)
where $R_f(N)$ is the fixity ratio in the $N$th cycle, $\varepsilon_u(N)$ is the unloaded temporary shape strain in the $N$th cycle, and $\varepsilon_l$ is the strain occurring during the maximum applied stress, $\sigma_m$, where $\varepsilon_l = \varepsilon(\sigma_m)$. In the present experiments, a heating cycle is used to equilibrate the sample and in this cycle a non-zero strain typically remains at the end. An additional term must be added to equation 1 to account for this additional strain. Thus, equation 1a is employed throughout the present thesis,

$$R_f(N) = \frac{\varepsilon_u(N) - \varepsilon_{exp}}{\varepsilon_l - \varepsilon_{exp}}$$  \hspace{1cm} (1a)

where $\varepsilon_{exp}$ is the strain after the first cycle. Recovery is defined as ratio of the strain of the sample after the deformed sample is reheated to the initial strain (or, put another way, the ratio of the length of the reheated sample to the original length of the sample prior to applying a stress),

$$R_t(N) = \frac{\varepsilon_l - \varepsilon_r(N)}{\varepsilon_l - \varepsilon_r(N - 1)}$$ \hspace{1cm} (2)

where $\varepsilon_r(N)$ is the recovery strain in the $N$th cycle and $\varepsilon_r(N - 1)$ is the recovery strain in the $(N - 1)$th cycle (for the first cycle, the recovery strain in the $(N - 1)$th cycle would be 0, reducing equation 2 to the ratio of the recovered distance and maximum strain in the first cycle).

In relation to the research surrounding this type of shape memory rubber and locking mechanism, Brostowitz, et al. discovered that rubber bands exhibit a remarkably resilient shape memory characteristic when swollen with stearic acid\textsuperscript{12}. In this technique,
rubber bands were identified to contain entirely cis-1,4-polyisoprene (PI) as the backbone polymer while filled with calcium carbonate to achieve various tensile, modulus, and elongation properties. Because stearic acid is readily soluble with cis-1,4-PI. It was further noted that as the filler content increased in the rubber bands, the amount of stearic acid swollen in the elastomer decreased. This became an important discovery for the present research, which aimed to identify how filler content affects the shape memory characteristics of PI.

Diani and Gall presented efforts to characterize the energy storage of cis-1,4-PI with very narrow polydispersity index (PDI) using molecular dynamics simulations\textsuperscript{13}. The scope of their work was contained to identifying and modelling the energy evolution experienced by the test elastomer, cis-1,4-PI. Initial modelling, conducted using an amorphous cell generation program, attempted to model rheological properties as well as van der Waals forces and Coulomb interactions. Basic properties of cis-1,4-PI were in good agreement with experimental data, notably the radius of gyration and characteristic ratio (where they successfully modelled \( \langle R^2 \rangle \sim 6\langle R_g^2 \rangle \)), showing the structure of the polyisoprene as random coils, and accurately predicting the density and expansion coefficients. Stress and strain relationships were synthesized with reasonable success. Finally, shape memory cycles were simulated using the Parrinello-Rahman barostat, a tool used for molecular simulations, showing success in modelling shape memory characteristics of cis-1,4-PI under uniaxial deformation at high temperature. However, large strain hydrostatic loadings in similarly high temperature conditions were more complicated to predict. The work completed by Diani and Gall did not investigate modelling of swollen or filled elastomers. Likewise, Golotina and Shardakov also
attempted simulating the shape memory effects of semi-crystalline polymers\textsuperscript{14}. Their approach accounted for constitutive equations characterizing thermomechanical behavior of the amorphous crystalline polymers as well as the kinetic equations derived from tensor analyses that described the intermolecular interaction evolution during shape memory cycles.

Tiller, Heuwers, Katzenberg, Quitmann, et al. at the Technische Universität Dortmund (TU Dortmund) have also spent considerable effort examining the shape memory properties of cis-1,4-PI in the form of natural rubber to aide in the invention of cold energy storage systems\textsuperscript{15}. Tiller, et al. created lightly crosslinked cis-1,4-PI from natural latex with degree of crosslink density of approximately 0.4%. This material was able to store strains of up to 1000\% with high fixity at room temperature after the induced stress was released. A transient relaxation was noticed and the thermodynamic state of the material was deemed insufficiently robust. As they decreased the degree of crosslink density, the stored strains increased as well (for example, 0.2\% degree of crosslink density allowed induced strains of 1200\%), however fixity decreased. A 20°C stretching temperature was employed. They were able to improve the rheological stability by holding the samples for 60 seconds prior to releasing the stress. Upon increasing the temperature of the sample back to 26°C, the relaxation seen with lower degree of crosslink density occurred. DSC analysis showed the relaxation to have endothermic heat generation, which caused the sample to cool to 6°C. It was theorized that this superheating effect is a result of strain-induced crystallization forming crystals that stabilized in the elastomer and were able to be “frozen” in place. The activation temperature was shown to be strain dependent, coming as no surprise due to conservation
of energy and $dW = -dQ$, where $W$ is work and $Q$ is heat\textsuperscript{16}. Activation temperature was found to be approximately the melting temperature of the strain-induced crystals. Further research found that the activation temperature at which the crystals could be melted was dependent on internal stresses\textsuperscript{17} and could be modified after shape-memory programming had already taken place. To induce melting of the strain-induced crystals a transverse stress was applied with resulting data showing a linear dependency between the transverse stress and reduced activation temperatures (of up to 40\textdegree C). Alternatively, they also investigated the dependency of the activation temperature from an applied parallel stress\textsuperscript{18}. It was discovered that a parallel stress induced a strengthening of the strain-induced crystals and enabled the researchers to increase the activation temperature linearly, relative to the parallel strain increases. Further exploration into these materials resulted in a systematic investigation of the mechanical and thermodynamic properties of these new shape memory materials\textsuperscript{19}.

Lin, Ma, et al. have synthesized epoxidized natural rubber, crosslinking it with an oxa-Michael reaction, and measuring various shape-memory properties\textsuperscript{20}. Epoxidized natural rubber, while very similar to cis-1,4-PI, has many important differences, notably added epoxy groups where ordinary cis-1,4-PI would contain a double bond saturation (figures 1.2a and 1.2b).
The highly reactive epoxy group (in their research, the natural rubber was 50% epoxidized) was crosslinked using zinc diacrylate (ZDA) as a Michael reaction catalyst and crosslinking agent. Levels of ZDA were used varying from 5 to 60 parts per hundred rubber (PHR) to crosslink epoxidized natural rubber resulting in a variety of crosslink densities and glass transition temperatures. The glass transition temperatures were used as the activation temperatures of the elastomers. A silica filler was then compounded into the samples to observe its impact on shape memory and add a control mechanism to the shape memory of ZDA-crosslinked epoxidized natural rubber. The fixity and shape memory behavior of the unfilled samples showed to be highly dependent on the ZDA content of the compound and produced excellent results with high shape fixity and recovery nearing 100%. The silica was used to pinpoint the compounds’ mechanical properties via their stress-strain curves (stress at 100% strain ranged from 1.5 MPa to 21.1 MPa), and the compounds continued to portray excellent fixity and recovery, while also having a high degree of transparency.

The work of Weiss, Izzo, and Mandelbaum\textsuperscript{21} has shown that an elastomer, the zinc salt of sulfonated poly(ethylene-\text RA-propylene-\text RA-(5-ethylidene-2-norbornene)) (Zn-SEPDM), is a robust shape memory polymer when combined with a secondary material that acts as an \textit{in situ} locking phase. In this case, as with Brostowitz, a fatty acid was
used, zinc oleate, that provided sufficient support to overcome the stress induced by the
natural elastic response of the polymer. This phenomenon was shown by Dong and
Weiss to be a result of the dipolar interactions that the Zn-SEPDM and zinc oleate
formed with each other\textsuperscript{22}. Samples were prepared with variable zinc oleate
concentrations, with higher concentrations showing improved fixity. These relaxation
data was fitted to the Voigt model and the relaxation spectra generated. Over long
periods of time (in excess of 500 hours) the samples retained excellent fixity following a
short, but considerable, relaxation period. Recovery of the samples created a parabolic
response of zinc oleate concentration to recovery as a percentage of the original sample
size.
CHAPTER II

DEVELOPMENT OF AN ELASTOMERIC SHAPE MEMORY POLYMER

2.1 Introduction

The most popular and well-established method of generating shape memory polymers (SMPs) is by the synthesis of a block copolymer that exhibits multiphase characteristics such that one phase can act as the backbone network of the polymer while the other phase acts as a switching mechanism, usually by utilizing the glass transition temperature as an activation temperature to lock into place a temporarily programmed deformation of the material. This has been shown to be highly effective. A variety of polymers have been successfully proposed as block copolymers suitable for shape memory applications, notably polyurethane\textsuperscript{23}, styrene-\textit{b}-(ethylene-\textit{co}-butylene)-\textit{b}-styrene (SEBS) used with a filler system\textsuperscript{24} (due to the low glass transition temperature), poly (ethylene-co-vinyl acetate) (EVA)\textsuperscript{25}, and even biodegradable materials such as oligo [(\(\varepsilon\)-caprolactone)-\textit{co}-glycolide]-dimethacrylates (oCG-DMA), the star-shaped oligo [(\textit{rac}-lactide)-\textit{co}-glycolide] tetroles (oLG)\textsuperscript{26}, and poly[(l-lactide)-\textit{co}-(\(\varepsilon\)-caprolactone)\textsuperscript{27}, among many others. Since these polymers have two phases with separate glass transition temperatures, one of these phases can be crystallized while the other phase retains its own unique characteristics, allowing a shape to be programmed and locked into place. It has
been shown that the glass transition temperature of the locking phase can be modified in many ways, such as broadening or changing the glass transition temperature, to achieve a different activation temperature, the temperature at which the polymer will lock into the temporary shape.

There are many aspects of producing block copolymers that are attractive, but another subset of polymers, elastomeric rubber, has shown to be resilient and extremely cost-effective. These commodity elastomers, used in many products but most notably tires, tubing, and other applications that require elasticity with little temperature influence, are widely available and include cis-1,4-polyisoprene, polybutadiene, styrene-butadiene copolymer, and butyl rubbers. In response to this advantage some researchers have focused their efforts on a dual-phase system in which a rubber elastomer is swollen with molten fatty acid or fatty acid salt at an elevated temperature, which is then allowed to cool to a secondary temperature. As Brostowitz, et al. noted, when they swelled a sample of cis-1,4-PI-based rubber band with molten stearic acid, the crystals formed a “house of cards” structure that was able to resist the stress induced by the elastic rubber band. However it was suggested that other ingredients in the rubber bands did not influence the shape memory behavior of the samples due to corroborating data from similar testing of unfilled surgical tubing.

The present research exhibits the meticulous tasks in formulating a shape memory, crosslinked, rubber compound with adequate shape memory behavior to analyze the affects that filling the polymer with activated carbon black will have on fixity and recovery. Initial attempts at formulating a shape memory rubber focused on mimicking the formulation of the successful material found by Brostowitz, et al., a rubber band.
2.2 Materials and Experimental Methods

A formulation for a rubber band was initially used as seen in table 2.1\textsuperscript{30}. For reasons explained in the results and discussion section, the formulation in table 2.2 (a modified and simplified version of that found in table 2.1) was used in further experimentation.

Table 2.1: Rubber band formulation by Ciullo and Hewitt.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Parts Per Hundred Rubber (PHR)</th>
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<tbody>
<tr>
<td>cis-1,4-Polyisoprene</td>
<td>100.00</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>3.00</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>2.00</td>
</tr>
<tr>
<td>Diaryl-p-Phenylenediamines</td>
<td>1.00</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>10.00</td>
</tr>
<tr>
<td>4-Morpholinyl-2-Benzothiazole Disulfide</td>
<td>1.00</td>
</tr>
<tr>
<td>Tetramethylthiuram Disulfide</td>
<td>0.40</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Suppliers and raw material information is also provided. A major problem with using rubber bands is the lack of knowledge of the exact formulation used to create the elastomer.

Cis-1,4-PI, as a commodity, is actually 98.5% cis-1,4, with the remaining material 1% trans-1,4 and 0.5% 3,4-PI. For the purposes of this research it is assumed that polyisoprene is 100% cis-1,4-PI. Chemically speaking synthetic and natural polyisoprene
are virtually identical. But in an industrial setting these two materials perform quite differently, primarily in the green strength and tack, as relates to rubber processing. The reasons for this remain unknown and unpursued\textsuperscript{49}. Synthetic polyisoprene is produced in a continuous solution polymerization process that uses a Ziegler-Natta catalyst (titanium-aluminum). A literature value for the number average molecular weight for synthetic polyisoprene is about 375,000 grams/mol\textsuperscript{50}.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Trade Name</th>
<th>Supplier</th>
<th>Parts Per Hundred Rubber (PHR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-1,4-Polyisoprene</td>
<td>Natsyn 2200</td>
<td>Goodyear Tire &amp; Rubber Co.</td>
<td>100.00</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>Zoco 624</td>
<td>Zochem Inc.</td>
<td>1.00</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>VSTEARIN\textsuperscript{TM} SA29</td>
<td>Vantage Oleochemicals</td>
<td>1.00</td>
</tr>
<tr>
<td>4-Morpholinyl-2-Benzothiazole Disulfide</td>
<td>CureRite\textsuperscript{®} MBDS</td>
<td>Emerald Performance Matls.</td>
<td>0.33</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Rubbermakers Sulfur OT</td>
<td>Akrochem Corps.</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Compounds were mixed in a single pass using a 414 cm\textsuperscript{3} Thermo-Fisher Scientific Haake\textsuperscript{TM} Rheomix OS Lab Mixer using 55\% fill factor (228 cm\textsuperscript{3}), cam rotors heated to 55°C, mix chamber heated to 55°C, 4.14 MPa ram pressure, to a drop temperature of 108°C. Compounds were mixed in a “sandwich” style common to the trade, where half of the elastomer was inserted into the shaft, the fillers and additives added immediately after, and, finally, the remaining elastomer which completed the loading of the mixer. The cam rotors were set to 50 revolutions per minute (RPM). The
resulting rubber compounds were then milled on open-faced, non-temperature controlled mills for approximately 120 seconds, until each compound was suitably masticated for cutting into sheets for curing. Compounds were cured at 150°C for 80 minutes in a sheet compression mold.

Tensile testing was completed using dumbbells in the shape diagrammed below in figure 2.1.

![Dumbbell used in tensile testing.](image)

Each rubber sample had a thickness gauge of 2.2 mm along with the dimensions found in table 2.3.

<table>
<thead>
<tr>
<th>SEGMENT LABEL</th>
<th>LENGTH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25 mm</td>
</tr>
<tr>
<td>B</td>
<td>6 mm</td>
</tr>
<tr>
<td>C</td>
<td>115 mm</td>
</tr>
<tr>
<td>D</td>
<td>33 mm</td>
</tr>
<tr>
<td>$L_0$</td>
<td>25 mm</td>
</tr>
</tbody>
</table>

Tensile testing was completed using a standard Instron Universal Mechanical Testing Instrument with pull speed of 51 cm/minute to generate stress-strain characterizations.
To evaluate shape memory behavior, samples were subjected to dynamic mechanical analysis (DMA). DMA testing was completed using a TA Instruments Q800. The shape memory cycle is defined as the cycle used to heat the sample, deform it, and cool it (at this point, measure fixity), followed by a second heating and cooling cycle to measure recovery. These steps are outlined in table 2.4 in detail. The samples being tested were approximately 7.5 mm × 2.2 mm with a sample length of about 10 mm.

Table 2.4: Shape Memory Experimental Cycle.

<table>
<thead>
<tr>
<th>STEP NO.</th>
<th>DESCRIPTION</th>
<th>PARAMETERS</th>
<th>RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Temperature Increase</td>
<td>23°C - 75°C</td>
<td>10°C/min</td>
</tr>
<tr>
<td>2</td>
<td>Isothermal</td>
<td>75°C</td>
<td>10 mins</td>
</tr>
<tr>
<td>3</td>
<td>Temperature Decrease</td>
<td>75°C - 20°C</td>
<td>10°C/min</td>
</tr>
<tr>
<td>4</td>
<td>Isothermal</td>
<td>20°C</td>
<td>10 mins</td>
</tr>
<tr>
<td>5</td>
<td>Temperature Increase</td>
<td>20°C - 75°C</td>
<td>10°C/min</td>
</tr>
<tr>
<td>6</td>
<td>Isothermal</td>
<td>75°C</td>
<td>5 mins</td>
</tr>
<tr>
<td>7</td>
<td>Stress Increase</td>
<td>0 MPa - 0.10 MPa</td>
<td>0.10MPa/min</td>
</tr>
<tr>
<td>8</td>
<td>Temperature Decrease</td>
<td>75°C - 20°C</td>
<td>10°C/min</td>
</tr>
<tr>
<td>9</td>
<td>Isothermal</td>
<td>20°C</td>
<td>5 mins</td>
</tr>
<tr>
<td>10</td>
<td>Stress Decrease</td>
<td>0.10 MPa – 0 MPa</td>
<td>Immediate</td>
</tr>
<tr>
<td>11</td>
<td>Isothermal</td>
<td>20°C</td>
<td>5 mins</td>
</tr>
<tr>
<td>12</td>
<td>Temperature Increase</td>
<td>20°C - 75°C</td>
<td>10°C/min</td>
</tr>
<tr>
<td>13</td>
<td>Isothermal</td>
<td>75°C</td>
<td>10 mins</td>
</tr>
<tr>
<td>14</td>
<td>Temperature Decrease</td>
<td>75° - 20°C</td>
<td>10°C/min</td>
</tr>
<tr>
<td>15</td>
<td>Isothermal</td>
<td>20°C</td>
<td>10 mins</td>
</tr>
</tbody>
</table>

Alternatively, a 3-dimensional plot of the shape memory cycle is shown in figure 2.2. This is the actual shape memory cycle that was used in DMA experimentation in chapters 2 and 3.
Cure and vulcanization characteristics were taken on a moving die rheometer (MDR), which is an adaptation of the Alpha Technologies rubber process analyzer (RPA). Samples were prepared using constant cylindrical volume, with weight of 5 grams. Oriented polyester film from 3M was used on each side of the sample to keep from sticking to the serrated discs while maintaining a no-slip boundary. Cure rates were evaluated at 150°C for 120 minutes.

Crosslink density information was collected using low-field nuclear magnetic resonance (LF-NMR) using the Carr-Purcell-Meiboom-Gill sequence and CONTIN
algorithm (CPMG-CONTIN) at 400 MHz. Samples were run on a Bruker Minispec Benchtop NMR instrument (Low Field NMR). The samples were packed into 10-mm NMR tubes, with Carr-Purcell-Meiboom-Gill (CPMG) data acquisition at 70°C and 120°C. The CPMG-CONTIN (inverse LaPlace transform) LF-NMR method was used. Relaxation time distributions \(T_r\), \(T_{m1}\), and additional other \(T_m\) populations) are measured. \(T_r\) is designated the rigid time constant, sensitive to network crosslinks, polymer filler interactions, and network entanglements. \(T_{m1}\) is designated the first mobile time constant, sensitive to a lesser extent to crosslinks, and dangling chain ends. XLD-r, proportional to the network cross-link density, is \(1/T_r\). The uncertainty in the XLD-r is \(~0.50\).

The ambiguity surrounding the formulation of the rubber bands used in Brostowitz, et al. presents challenges at drawing conclusions as to how the additives, fillers, cure system, and other ingredients (of which some are likely unidentified) affect the shape memory characteristics of the rubber bands. The formulation in this research was stripped to its barest ingredients needed to make a cross-linked elastomer so that the shape memory effects of these ingredients could be easily discernable.

2.3 Basics of the Vulcanization Reaction and State of Cure

Vulcanization is the chemical reaction of crosslinking rubber first discovered by Charles Goodyear and patented by the same in 1839\(^31\), and again with refinements in 1844\(^32\). During vulcanization, the rubber elastomer undergoes rheological and chemical change, the explanations of which are contentious even to this day\(^33\). There were many theories describing the chemical reaction or reactions responsible for crosslinking rubber,
such as, but not exclusive of, the Thiozone Theory\textsuperscript{34}, Ostromislensky’s Theory\textsuperscript{35}, Thiocyanic Acid Theory\textsuperscript{36}, Amine Sulfides Theory\textsuperscript{37}, Polysulfide Theory\textsuperscript{38}, Disulfide Theory\textsuperscript{39}, Theory of Feuchter\textsuperscript{40}, and the Physicochemistry Theory\textsuperscript{41}. Further advancements in the understanding of vulcanization have taken place over the years and it is generally accepted that the reaction mechanism herein presented is an accurate representation of the chemical process underwent in vulcanization.

The reaction was diagramed succinctly by Kumar and Nijasure\textsuperscript{42}, beginning with a breakdown of the sulfenamide curing agent, usually added with sulfur, to expedite vulcanization. The cyclic eight-atom free sulfur will simultaneously break down into $S_x$ units (where $x$ is typically 3-5) where these smaller sulfur chains chemically link the broken down sulfenamide, as in figure 2.3, steps 1a and 1b.
Figure 2.3: Schematic of vulcanization reaction with cis-1,4-polyisoprene.
The sulfur chains then link two benzothiazole groups together (step 2), which creates a readily active sulfur linkage, which is then able to attack a hydrogen atom on the exposed backbone of the cis-1,4-PI chain (step 3). The benzothiazole group then detaches, leaving a radical sulfur ending (with $S_x$, where the end sulfur is the radical), which readily attacks a second cis-1,4-PI chain, creating a sulfur crosslink (step 4). The benzothiazole that detached can then be recycled, as the proton attached to the nitrogen shifts to the sulfur radical, stabilizing the molecule.

It is well known that the class of accelerator that is used can greatly impact the cured physical and rheological properties of the rubber compound in question. Moore, et al. describe how sulfur can be used alone as a crosslinking agent (under high enough temperature, typically above 140°C) where about forty to fifty atoms of sulfur are needed to form a single crosslink. It is shown that, with the introduction of the benzothiazole class of accelerators, just a single molecule of accelerator is sufficient to form a crosslink. The structure of 4-morpholinyl-2-benzothiazole disulfide (MBDS), the curative used in the present research, can be seen in figure 2.4.

![Chemical structure for MBDS.](attachment:image.png)

Figure 2.4: Chemical structure for MBDS.

The chemistry of MBDS is not well documented, however baseline research has been completed that compares this curing accelerator to other common accelerators at the time it was first used in the vulcanization reaction, and in general it obeys a similar pathway.
to that portrayed in figure 5. Initially validated for its effectiveness in 1963, how MBDS reacted in the vulcanization reactions was not investigated until 1989 by Craine and Raban\textsuperscript{46}, who discussed the chemistry in the context of general sulfenamide acceleration, and the great benefit to this molecule is the ready dissociation of the benzothiazole agent from the morpholine group, leaving a very reactive and exposed radical sulfur able to initiate the crosslinking reaction.

When the accelerator and sulfur are depleted, or more generally when the vulcanization reaction has reached its desired end, the compound is said to have reached its maximum state of cure. The state of cure, as mentioned previously, was measured using a moving die rheometer (MDR). In this method\textsuperscript{47}, a sample of rubber is placed in the MDR test cavity, which is sealed, where the temperature is maintained at a desired temperature of interest. The rubber samples are held at constant volume so that the entirety of the chamber is filled. The chamber consists of two parallel, serrated plates which are rotationally oscillated, exerting a shear strain on the sample. Using the simple equation for torque, equation 3, the torque can be calculated from measured quantities.

\[
\tau = ||\mathbf{r}|| \cdot ||\mathbf{F}|| \sin \theta
\]  

(3)

where \(\tau\) is the torque in dN·m, \(\mathbf{r}\) is the displacement vector, \(\mathbf{F}\) is the force vector, and \(\theta\) is the rotational angle. When a curve is generated, it will appear as in figure 7.
In a cure curve, there are several times (x-axis) of interest. These times correspond to the indicated lines in figure 2.5. Line (a) represents the maximum torque and (d) the minimum torque, where the difference, the delta torque, is an important indication of the modulus of the compound. The time associated with line (b) indicates the time to 90% of the full state of cure (T90), generally accepted to be the time closest to the full state of cure. Line (c) indicates the time to 25% of the full state of cure (T25), an important indicator for processing of a compound. The slight undulation early in the curve is a result of the initial breakdown of the rubber compound prior to cure activation. In some occasions the curve indicated by line (e) may result. This is a result of a curative system prone to “marching modulus,” which is a condition where the modulus of the compound will continue to increase with time at the elevated temperature. In other occasions, another condition will occur, indicated by line (f), showing a drop in torque after reaching
the maximum state of cure. In this case, reversion is occurring, where the cured network is beginning to break down with prolonged exposure to the elevated temperature. While there are isolated situations where either of these results is an engineered goal, in general both conditions are undesirable due to the compound’s cured state being unstable.

2.4 Results and Discussion

Initial studies attempted to develop a formulation that would exhibit shape memory behavior when swollen with stearic acid. Knowing that rubber bands had successfully been used for this purpose, a rubber band formulation, as outlined in table 2.2, was mixed and tested. When the sample was inserted into molten stearic acid, purple liquid leached out of the compound. This material was believed to be diaryl-p-phenylenediamines, a common anti-oxidant used to provide shelf life to rubber bands. Since the rubber used in the present research did not require weathering protection and since diaryl-p-phenylenediamines are not impactful to the compound’s physical properties at low levels (less than 5 PHR), the formulation used herein was limited to only those materials needed to crosslink the rubber. The materials in this formulation were cis-1,4-PI (synthetic), zinc oxide and stearic acid (in appropriate amounts these two additives work together to activate the vulcanization reaction, however in slow curing situations, they are not a required material for crosslinking to occur, as in figure 5), and MBDS. With 100 PHR cis-1,4-PI, 1 PHR of each of the other four materials was also added. The cure curve for this compound, indicated in figure 7, indicates that at very long cure times (in excess of about 55 minutes), a slight reversion begins to take place.
Figure 2.6: Cure curve for compound with 100PHR cis-1,4-PI and 1 PHR each of stearic acid, zinc oxide, sulfur, and MBDS.

The initial breakdown of the rubber in the first few minutes is the predictable breakdown that always happens, as mentioned in the previous section. A delta torque of about 4.75 dN·m is seen, but the reversion exhibited between 50 and 120 minutes is quite undesirable. This could be an indication of excessive cure in the formulation. More notable were the shape memory results shown in figure 2.7a while the stress and temperature cycles described in table 2.4 can be seen in figure 2.7b.
(a) Shape memory results for 100 PHR cis-1,4-PI and 1 PHR each of stearic acid, zinc oxide, sulfur, and MBDS.

(b) Stress and temperature cycles used in DMA testing.

Figure 2.7: Shape memory cycle and results for standard compound.
In this case, the fixity was extremely low, as was the total strain by the induced 0.1 MPa stress. Using equations 1a and 2, the fixity was 34.5% with a maximum strain of 17.8%. Compared to Brostowitz’s results using the standard office rubber band, where maximum strain of 66% was found\textsuperscript{12}, this shows very low strain. In addition, during the isothermal stage lasting for 10 minutes starting at the 65th minute, there is no creep seen, only a slight extension of the strain, attributable to linear thermal expansion.

It is important to note that slightly crosslinked rubber and rubber that is heavily crosslinked have shown to not have substantially different coefficients of thermal expansion. As Mason notes, given constant molecular weight of the elastomer of approximately 250,000 g/mol, and crosslink density ranging from 1.05 to $10^{19}$ crosslinks/gram, the coefficients of linear expansion only differed, in the viscoelastic range, from 7.0 to $7.3 \times 10^{-4} \, ({}^\circ\text{C}^{-1})$\textsuperscript{51}. Uncrosslinked polyisoprene shows a similar value within the range of the crosslinked polyisoprene, of $7.05 \times 10^{-4} \, ({}^\circ\text{C}^{-1})$\textsuperscript{52}. Thus, it is expected to see slight expansions upon heating, as in exhibited between both 5 and 15 minutes as well as 70 to 75 minutes.

Nevertheless, the shape memory behavior of this sample was shown to be insufficient for examination, as evidenced by the extremely low initial strain and fixity levels. In response, a further series of compounds were mixed, as displayed in table 5. As polyisoprene is known to exhibit excellent shape memory properties when in an appropriate state of cure, changes to the cure system were compounded into these seven samples.
Table 2.5: Sample formulations used in cure variation analysis.

<table>
<thead>
<tr>
<th>Compound No.:</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
<th>#7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cis-1,4-PI</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>0.66</td>
<td>1.00</td>
</tr>
<tr>
<td>MBDS</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>0.66</td>
<td>0.25</td>
<td>0.33</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.00</td>
<td>0.75</td>
<td>0.50</td>
<td>0.25</td>
<td>0.00</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td><strong>Total PHR:</strong></td>
<td><strong>104.00</strong></td>
<td><strong>103.75</strong></td>
<td><strong>103.50</strong></td>
<td><strong>103.25</strong></td>
<td><strong>103.00</strong></td>
<td><strong>102.91</strong></td>
<td><strong>102.58</strong></td>
</tr>
<tr>
<td><strong>Specific Gravity:</strong></td>
<td><strong>0.920</strong></td>
<td><strong>0.919</strong></td>
<td><strong>0.918</strong></td>
<td><strong>0.917</strong></td>
<td><strong>0.915</strong></td>
<td><strong>0.915</strong></td>
<td><strong>0.914</strong></td>
</tr>
</tbody>
</table>

Using Compound 1 as the same control from the previous experiment, compounds 2 – 5 systematically reduced the amount of sulfur by 0.25 steps to 0 PHR and then, using 0.25 PHR sulfur as a basis for comparison (compound 4), the MBDS was reduced by 1/3 PHR each in compounds 6 and 7. Each of these compounds was used to generate stress-strain curves, rheometer cure curves, and DMA shape memory behaviors.

The curemeter curves for compounds 1 – 5 showed interesting results from the standpoint of reversion and time to maximum torque (or maximum state of cure).
From figure 2.8, as sulfur loading is reduced, the reversion characteristics are also reduced. Likewise, the delta torque decreases, indicative of lower values of modulus, both shear and 300% modulus (as an example from the stress-strain curve). It was postulated in the introduction from literature that cis-1,4-PI will crosslink in the presence of only MBDS at elevated temperatures, given enough time. With no sulfur, this compound failed to reach a maximum state of cure in the 120 minute test time. While it may eventually reach a suitable state of cure, given a substantially longer time at 150°C, in practice and in industry this would be of little value. The compound with the best
balance of cure rate and reversion resistance is the compound with 0.25 phr sulfur and 1 phr MBDS.

With this result, two further compounds, numbers 6 and 7, were tested and compared to compounds 1 and 5 to analyze the effects of a reduction in MBDS as the primary cure accelerator.

Figure 2.9: MDR Curve for MBDS variation in cure study. Curves are identified by their compound number indexed in table 2.5.

It should come as no surprise that a decrease in MBDS resulted in lower torque and indicatively lower elastic modulus values, as seen in table 2.6.
Table 2.6: Cure properties for compounds 1 – 7.

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>Delta Torque (dN·m)</th>
<th>Max Torque (dN·m)</th>
<th>Stress at 300% Strain (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.25</td>
<td>5.93</td>
<td>1.19</td>
</tr>
<tr>
<td>2</td>
<td>4.07</td>
<td>5.71</td>
<td>1.13</td>
</tr>
<tr>
<td>3</td>
<td>3.95</td>
<td>5.62</td>
<td>1.18</td>
</tr>
<tr>
<td>4</td>
<td>3.52</td>
<td>5.16</td>
<td>1.01</td>
</tr>
<tr>
<td>5</td>
<td>2.05</td>
<td>3.66</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>2.87</td>
<td>4.50</td>
<td>0.80</td>
</tr>
<tr>
<td>7</td>
<td>1.78</td>
<td>3.43</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Samples 1 – 3 did not show appreciably different stress at 300% strain values with decreasing sulfur, however with low sulfur and small amounts of accelerator, the drop in elastic modulus was apparent. The stress strain curves for compounds 1 – 4 can be found in figure 2.10 and compounds 1, 4, 6, and 7 in figure 2.11. Sample 5 was cured but did not reach a sufficient state of cure for tensile testing after 120 minutes at 150°C.

Figure 2.10: Stress-Strain curves for sulfur adjusted compounds.
Once again it is noted that adjustments in sulfur levels down to 0.25 PHR had minimal effect on the stress-strain properties, about a 25% reduction of the stress at 500% strain, while reducing the MBDS accelerator had quite a dramatic effect, reducing the stress at 500% strain from about 1.5 MPa to 0.8 MPa, nearly 50%. This may be attributed to the fact that the compounds with higher amounts of sulfur were oversaturated with sulfur atoms given the high amount of sulfur-donating accelerator also included. But when the accelerator is reduced using a minimal amount of sulfur, just 0.25 PHR, it has a substantial higher impact on the cured physical properties, in particular the stress-strain curves.

All of these compounds, 1-4, 6, and 7 (reiterating that compound 5 did not reach a suitable state of cure for further testing) were subjected to DMA deformation analysis,
the curves of temperature and deformation for the control (compound 1) can be seen in figure 2.13. This testing was completed after swelling the polymer for 30 minutes in a bath of molten stearic acid at 75°C. Shape memory properties for compound 1 can be seen in figure 2.12.

![Figure 2.12: Shape Memory results for compound 1.](image)

Similar to the compound in the initial rounds of experimentation, initial strain under 0.10 MPa of stress was quite low, maximizing at approximately 19.5%, with shape fixity, as calculated by equation 1a, of just 18.8% but with nearly complete recovery, using as a starting and ending point the strain of the sample after and accounting for thermal expansion and contraction with variation in temperature.

DMA results for compounds 1 – 4, 6 and 7 can be seen together in Appendix B, where cure differences are taken into account as explained in table 2.5. Shape memory
characteristics of the sulfur adjustments have been isolated in figure 2.13a and MBDS adjustments are isolated in figure 2.13b.

(a) Sulfur variation effects on shape memory (compounds 1 – 4).

(b) MBDS variation effects on shape memory (compounds 1, 4, 6, 7).

Figure 2.13: Material variation effects on shape memory properties.
As portrayed by figure 2.13, it is evident that decreasing the state of cure increases the ability to fix a stress-induced deformation and increases the maximum deformation. At its best, compound 7 exhibited shape fixity of 62%.

After swelling, using the Flory-Rehner equation, the molecular weight between crosslinks can be determined,

\[
\ln(1 - \phi_e) + \phi_e + \chi \phi_e^2 = \frac{v_e \tilde{V}_1}{N_{av} V_0} \left( \frac{\phi_e}{2} - \phi_e^{1/3} \right) \quad (4)
\]

where \(\phi_e\) is the volume fraction of rubber at equilibrium of swelling \((V_0/V)\), \(\chi\) is the interaction parameter of polymer solvent, \(v_e\) is the number of effective strands, \(N_{av}\) is Avogadro’s constant, \(\tilde{V}_1\) is the molar volume of solvent (where stearic acid is known to be a dimer), and \(V_0\) is the molar volume of polymer. Since \(v_e\) is unknown, it is easy to replace it using the relationship in equation 5,

\[
\frac{v_e}{V_0} = \frac{\rho N_{av}}{M_x} \left( 1 - \frac{2M_x}{M} \right) \quad (5)
\]

Where \(\rho\) is the swollen compound density, \(M_x\) is the average molecular weight between crosslinks, and \(M\) is the molecular weight of the elastomeric monomer prior to vulcanization. Replacing \(v_e/V_0\) in equation 4 and using equation 6 for the interaction parameter,

\[
\chi = \frac{\tilde{V}_1}{RT} (\delta_1 - \delta_2)^2 \quad (6)
\]
where $\delta_1$ and $\delta_2$ are the solubility parameters for polyisoprene and stearic acid, respectively, $R$ is the universal gas constant, and $T$ is the absolute temperature, one can solve for the average molecular weight between crosslinks (equation 7).

$$M_x = \rho \left[ \frac{\ln(1 - \phi_e) + \phi_e + \left( \frac{V}{RT} (\delta_1 - \delta_2)^2 \right) \phi_e^2}{\left( \frac{\phi_e}{2} - \phi_e^{1/3} \right) \bar{V}_1} + \frac{2\rho}{M} \right]^{-1} \tag{7}$$

Applying equation 7 for each of the compounds 1-4, 6, and 7, a clear picture emerges. Using Hansen Solubility Parameters\textsuperscript{53} to calculate $\chi$, where stearic acid has $\delta_1 = 17.52 \text{ MPa}^{1/2}$ and polyisoprene has $\delta_2 = 17.55 \text{ MPa}^{1/2}$, the Flory-Huggins interaction parameter is calculated as 0.0003 at 75°C. $\phi_e$ can be calculated as $V_0/V$ and the average molecular weight between crosslinks for each polymer is listed in table 2.7. Along with the molecular weights between crosslinks can be seen the low field NMR results for each compound.

<table>
<thead>
<tr>
<th>Compound ID:</th>
<th>$M_x$ (g/mol)</th>
<th>$T_{m1}$ (ms)</th>
<th>$T_r$ (ms)</th>
<th>XLD-r (1/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 1</td>
<td>31.8</td>
<td>26.4</td>
<td>1.16</td>
<td>0.864</td>
</tr>
<tr>
<td>Compound 2</td>
<td>31.8</td>
<td>26.4</td>
<td>1.15</td>
<td>0.869</td>
</tr>
<tr>
<td>Compound 3</td>
<td>31.9</td>
<td>27.8</td>
<td>1.23</td>
<td>0.814</td>
</tr>
<tr>
<td>Compound 4</td>
<td>32.0</td>
<td>29.3</td>
<td>1.39</td>
<td>0.722</td>
</tr>
<tr>
<td>Compound 6</td>
<td>32.0</td>
<td>29.4</td>
<td>1.65</td>
<td>0.607</td>
</tr>
<tr>
<td>Compound 7</td>
<td>32.1</td>
<td>25.3</td>
<td>2.05</td>
<td>0.487</td>
</tr>
</tbody>
</table>

NMR data suggests that compounds 1 and 2 have similar crosslink densities, while the remaining compounds decrease in crosslink density progressively. This is corroborated
in the elongation and fixity of compounds 1 and 2, which can be seen with a complete set of shape memory data along with the other compounds in table 2.8.

Table 2.8: LF-NMR Data and Shape Memory Properties of all Compounds.

<table>
<thead>
<tr>
<th>Compound ID:</th>
<th>XLD-r (1/s)</th>
<th>(\varepsilon_r(0))</th>
<th>(\varepsilon_l)</th>
<th>(\varepsilon_u(0))</th>
<th>(\varepsilon_r(1))</th>
<th>(R_t(N))</th>
<th>(R_f(N))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound 1</td>
<td>0.864</td>
<td>6.3%</td>
<td>19.5%</td>
<td>9.9%</td>
<td>7.1%</td>
<td>94%</td>
<td>27%</td>
</tr>
<tr>
<td>Compound 2</td>
<td>0.869</td>
<td>1.9%</td>
<td>13.3%</td>
<td>4.2%</td>
<td>2.7%</td>
<td>93%</td>
<td>20%</td>
</tr>
<tr>
<td>Compound 3</td>
<td>0.814</td>
<td>1.5%</td>
<td>12.3%</td>
<td>3.7%</td>
<td>2.5%</td>
<td>91%</td>
<td>20%</td>
</tr>
<tr>
<td>Compound 4</td>
<td>0.722</td>
<td>3.3%</td>
<td>18.6%</td>
<td>7.9%</td>
<td>4.8%</td>
<td>90%</td>
<td>30%</td>
</tr>
<tr>
<td>Compound 6</td>
<td>0.607</td>
<td>4.1%</td>
<td>25.0%</td>
<td>11.7%</td>
<td>5.7%</td>
<td>93%</td>
<td>36%</td>
</tr>
<tr>
<td>Compound 7</td>
<td>0.487</td>
<td>15.5%</td>
<td>54.9%</td>
<td>40.0%</td>
<td>18.3%</td>
<td>93%</td>
<td>62%</td>
</tr>
</tbody>
</table>

All compounds had excellent recovery, however fixity increased with decreasing elastic modulus, as indicated by crosslink density. Figure 2.14 shows the relationship between crosslink density, as measured by XLD-r, and fixity, \(R_f(N)\).

![Crosslink Density vs. Fixity](image)

Figure 2.14: Fixity as a function of crosslink density.
As crosslink density decreases the fixity increases. On the other hand, there is a notable decrease in fixity as the elastic modulus increases. It is evident that there is not necessarily a direct relationship with modulus and fixity; that is, elastic modulus without any context for interpretation. Figure 2.15 shows this correlation.

![Figure 2.15: Fixity as a function of stress at 300% strain.](image)

Despite the general trend seen in figure 2.15, it is difficult to draw a generalized conclusion that there is a relationship between elastic modulus and fixity. This may be understandable due to the differing effects that sulfur variation and MBDS variation had on the stress at 300% strain. Thus, it is important to understand and quantify the effects of elasticity rather than tensile or strength and measure the balance in forces of rubber elasticity against the stability of the stearic acid crystal structure. This would be a fascinating study for future work, however in the present study, the necessity rested in
developing an elastomeric rubber that has a suitable amount of fixity to determine the
effects of carbon black on this fixity property. It appears that the most suitable amount of
fixity is attained with the lowest crosslink density, corresponding to compound 7.

Using the Flory-Rehner equation, equation 4, a term for the relative cross link
density can be established.

\[
\frac{v_e}{V_0} = \frac{\ln(1 - \phi_e) + \phi_e + \chi \phi_e^2}{\left(\frac{\phi_e}{2} - \phi_e^{1/3}\right) \tilde{V}_1}
\]  

(8)

Charting this value against the relative crosslink density calculated from the NMR
experiments resulted in figure 2.16.

Figure 2.16: NMR cross link density (XLD-r) as a function of
relative crosslink density (\(v_e/V_0\)).
There seemed to be a direct relationship between the two measures of crosslink density, affirming the trend seen in DMA testing that the lower the crosslink density, the more pronounced the shape memory properties. While the $R^2$ value for the crosslink density relationship is statistically significant, at 0.78, showing a good relationship, it does hint at the sensitivity of the test method.

To achieve a measurable degree of shape memory behavior, compound 7 appeared to provide the best properties. All compounds in the described experiments were soaked for 30 minutes to achieve uniformity in the allowance of the molten stearic acid to swell the sample rubbers. It is known that increased filler content decreases the amount of stearic acid that can diffuse into the system (all other properties being equal). A final swelling experiment was completed to determine the correct amount of time required to swell compound 7 and achieve equilibrium (maximum concentration). Samples of compound 7 were swelled for 5 minutes to 60 minutes in five minute increments and then tested to the shape memory cycle on the DMA.

Figure 2.17 plots fixity ($R_f$) and maximum elongation ($\varepsilon_f$) against time allowed to swell in stearic acid.
Figure 2.17: Fixity and maximum elongation as a function of swell time.

From this solubility information, equilibrium takes place after approximately 45 minutes of swelling in stearic acid. The maximum elongation showed to be at its maximum after 45 minutes of soaking. Prior experiments, with samples soaked for 30 minutes, may not have reached equilibrium, however since all samples were soaked for the same time, this variable was held constant. Confidence in those results was further instilled with the direct relationship seen between XLD-r take from NMR peak analysis and the calculated relative crosslink density from the Flory-Rehner equation (equation 8).
2.5 Conclusion

Results from shape memory experimentation show that compound 7, with minimum sulfur (0.25 PHR) and MBDS (0.33 PHR), swelled with molten stearic acid for 45 minutes, consists of the optimum ingredients to perform further shape memory testing on filled elastomers. The primary mechanisms of shape memory in this system appear convincingly to be fixity from the crystallization of cooled stearic acid with recovery generated from the melting of the stearic acid and the elasticity of the rubber, originating from the stored entropy of the rubbery system.

With recovery values ranging from 90% – 100%, the crosslink density, adjusted through curative and sulfur levels, was the primary contributor to changing fixity levels. It is also noteworthy that the time each sample was soaked in stearic acid had an enormous effect on the shape memory behavior of that rubber. The rubber bands used in Brostowitz were soaked for 30 minutes, however it is speculated that due to a much tighter crosslink network and higher crosslink density, the maximum elongation and ultimately the fixity are much lower with the present samples than with the rubber band samples used in previous work around shape memory rubber. Furthermore, future work may center around the complicated task of analyzing the chemistry involved in the MBDS-zinc oxide-sulfur-stearic acid vulcanization reaction and its chemical effect on shape memory. The vulcanization reaction of particular sulfonamides is not particularly well understood and, thus, a more thorough understanding of the chemical reactions and intermediates could also provide additional insight into how best to control the shape memory fixity and recovery mechanisms of shape memory rubber.
CHAPTER III
IMPACT OF A CARBON BLACK FILLER SYSTEM ON AN ELASTOMERIC
SHAPE MEMORY POLYMER

3.1 Introduction

Rubber tires have been produced since the late nineteenth century, relying upon the principals of Charles Goodyear’s vulcanization process to turn a soft polymer into an elastic tire suitable for transportation\textsuperscript{31}. Many polymers have been used for tire production, including, but not limited to, natural rubber (cis-1,4-polyisoprene) and synthetic cis-1,4-polyisoprene (cis-1,4-PI), polybutadiene (PBD), butyl, halogenated butyl, chlorinated butyl, styrene-butadiene random and block copolymers (SBR), and others of a wide range of microstructure\textsuperscript{55}. SBRs can be made by emulsion and solution polymerization processes, both of which offer unique physical properties, further enhanced by functionalizing the backbone of the polymer or, in recent industrial development, incorporating in-chain functionalization\textsuperscript{56}. Polymers can also be oil-extended, where a plasticizing agent, commonly a petroleum-derived oil but in some cases plant or mineral-derived, is incorporated into the elastomer prior to the finishing process in the polymer production plant.

To systematically adjust the rheological properties of rubber compounds, filler systems are commonly employed. These filler systems act to reinforce the soft
elastomeric compound as well as provide various tractive properties for use on roadways. More specifically to the tire rubber industry, it improves properties such as abrasion resistance (analogous to tread wear) and tensile strength. Carbon blacks are most often described by their American Society for Testing and Materials (ASTM) designation. The most common grades of carbon blacks can be seen with their ASTM nomenclature in table 3.1.

Table 3.1: Carbon blacks as designated by ASTM standard D1765-14.

<table>
<thead>
<tr>
<th>ASTM Classification</th>
<th>OAN No. (cm³/100 g)</th>
<th>NSA (m²/g)</th>
<th>Pour Density (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N110</td>
<td>96-98</td>
<td>124-130</td>
<td>335-353</td>
</tr>
<tr>
<td>N220</td>
<td>96-100</td>
<td>112-115</td>
<td>337-361</td>
</tr>
<tr>
<td>N330</td>
<td>85-89</td>
<td>76-80</td>
<td>370-393</td>
</tr>
<tr>
<td>N347</td>
<td>97-101</td>
<td>85-86</td>
<td>324-345</td>
</tr>
<tr>
<td>N375</td>
<td>95-98</td>
<td>91-95</td>
<td>345-350</td>
</tr>
<tr>
<td>N550</td>
<td>83-87</td>
<td>39-41</td>
<td>353-369</td>
</tr>
<tr>
<td>N650</td>
<td>81-86</td>
<td>33-38</td>
<td>358-377</td>
</tr>
<tr>
<td>N772</td>
<td>58-60</td>
<td>31-32</td>
<td>507-530</td>
</tr>
<tr>
<td>N990</td>
<td>36-37</td>
<td>7-9</td>
<td>642-653</td>
</tr>
</tbody>
</table>

Oil absorption number (OAN) is a measure of how readily a carbon black will absorb a liquid, which provides an insight into the structure of the carbon black (a description of what the structure, particle size, and surface area are as it pertains to carbon black is explained in a subsequent paragraph). As specified by International Organization for Standardization (ISO) protocol 4656:2007, the carbon black sample of defined mass (dried 125°C for 1 hour, then stored in a desiccant at room temperature until testing) is placed (in a compressed or uncompressed state) under constant mixing by rotating rotors as a standard oil, particularly dibutyl phthalate or a paraffin oil, is mixed
into the carbon black. The apparatus, called an absorptometer, measures the torque in the rotors as a burette delivers the chosen oil into the mixing chamber. When the rotors reach the torque limit switch, the procedure is completed and the volume of oil in the same is recorded and reported, after normalizing the results, as volume of oil per 100 g of carbon black.

Nitrogen surface area (NSA) is the method used to measure internal and external surface area of a sample of carbon black. To measure NSA a sample of carbon black is prepared in the same way as in the OAN test procedure. A Dewar of liquid nitrogen is filled and allowed to reach temperature equilibrium. The pressure of the Dewar, \( P_0 \), is then measured two or three times over an hour to determine that equilibrium has occurred. The free space of the sample cell is then determined, usually by a simple calculation using the density of carbon black as 1.9 g/cm\(^3\). Depending on \( P_0 \), five data points of the amount of nitrogen adsorbed are taken between \( P/P_0 = 0.1 \) to 0.3, where \( P \) is the variable test pressure and the volume of nitrogen adsorbed, \( V_a \), is calculated from equation 9.

\[
V_a = \frac{Volume \ of \ Nitrogen \ for \ each \ dosing \ sample \ mass}{g} \quad (9)
\]

The resulting measurements are then used to create a Brunauer-Emmett-Teller (B.E.T.) plot, which uses the BET Equation,

\[
\frac{P}{V_a(P_0 - P)} = \frac{1}{V_mC} + \frac{C - 1}{V_mC} \times \frac{P}{P_0} \quad (10)
\]
where \( P \) remains the test pressure and \( P_o \) the reference saturation pressure of the nitrogen, \( V_m \) is the volume of nitrogen per gram that covers one monomolecular layer, and \( C \) is the B.E.T. constant. The B.E.T. plot is then made charting \( P/P_o \) on the x-axis and \( P/[V_o(P_o - P)] \) on the y-axis. From equation 10 it is readily seen that the surface area can now be calculated as

\[
S.A. = V_m \times A_{N_2}
\]

where \( A_{N_2} \) is the area occupied by 1 cm\(^3\) of nitrogen and equals Avagadro’s number multiplied by the area of a nitrogen molecule in square meters divided by the number of cubic centimeters of occupied by one mole of gas at standard temperature and pressure (STP), and \( V_m \) is the inverse of the sum of the Y-intercept of the B.E.T. plot and the slope of the straight line of the B.E.T. plot (\( P/P_o \) in the range of 0.05 to 0.3 is in the linear region of a B.E.T. curve).

Finally, pour density, the final column in table 3.1, is the amount of carbon black that it takes to fill a 1000 cm\(^3\) container. In this simple experiment, carbon black is poured into a container of this specified size until it forms a cone above the rim of the container. It is then levelled with a spatula and the mass is recorded. This mass is the pour density\(^{62}\).

The relationship between fillers, notably carbon black and silica, and the rheological properties of rubber compounds continues to be vigorously researched, with much recent experimentation centering upon constitutive modeling of filled elastomeric systems\(^{63-67}\), measuring and constitutively modeling viscoelastic responses to stimuli\(^{68-70}\).
and modeling of the network (carbon black and carbon chain backbone) interactions in filled vulcanized systems\textsuperscript{71-72}. It is this final area that is most challenging.

Characterizations of the interaction between carbon black and the vulcanized polymer backbone are not well understood at this time, however it has been concluded that carbon black does have a significant effect on the activation energy of the vulcanization reaction as well as the modulus and other rheological properties. Because the carbon black acts as a secondary structural skeleton in addition to the carbon chain of the elastomer, slight changes in the colloidal properties of the carbon black have a tremendous impact on the compound at large\textsuperscript{73}. Shifts in the properties mentioned in table 3.1 alter the physical properties of the compounds that contain them. The OAN is indicative of the structure of a carbon black. Structure is analogous to how the carbon black particles react to one another electrostatically in a branched or linear fashion. Those particles with a higher OAN tend to have a higher propensity to form clusters of high structure. This idea of structure is visualized in figure 3.1.

(a) Low Structure Carbon Black  
(b) High Structure Carbon Black

Figure 3.1: Carbon Black Structure.
When a compound has a part for part replacement of a low structure carbon black with a high structure carbon black, this will cause the storage modulus to increase as well as the tangent delta\textsuperscript{75} (in addition to inferior dispersion\textsuperscript{74}). The same trend has consistently been found with increasing surface area and decreasing particle size. As the surface area increases, the interactions with the polymer chain backbone are presented the opportunity to increase, but the mathematical modeling of these interactions is still an enigma to scientific researchers. If carbon black is envisaged as a sphere, the particle size is simply a measure of the diameter, and as the particle size decreases, the free space of the rubber compound decreases and the modulus (via the carbon black reinforcing network) increases.

The activation energy is an extremely important characteristic of a vulcanized rubber compound. The activation energy is the energy required to initiate the vulcanization reaction. It can be thought of as the energy needed to reach a threshold where the cross-linking of rubber backbone chains will occur. The mathematical relationship is important in looking at the effect of carbon black on compounds and is simple to derive. Elaborating on figure 2.5, it is necessary to define several parameters, as seen in figure 3.2.
In figure 3.2 $t$ is a given time in the cure reaction where $t_{min}$ is the time at the minimum state of cure and $t_{max}$ is the time at the maximum state of cure. $\Gamma$ is the torque at a given time where $\Gamma_{min}$ is the minimum torque (corresponding to $t_{min}$ and the minimum state of cure) and $\Gamma_{max}$ is the maximum torque (likewise corresponding to $t_{max}$ and the maximum state of cure). Figure 3.2 is also useful to describe the consumption of accelerator, where $a$ is the total concentration of accelerator, $x$ is the total amount of reacted accelerator, and the remaining unreacted accelerator is expressed as $(a - x)$. State of cure ($SOC$) is defined as the amount of reacted accelerator to the total amount of concentration available, $SOC = x/a$, such that $0 \leq SOC \leq 1$. Using basic reaction kinetics and the principal that the rate of reaction is proportional to the concentration of reaction, a simple kinetic equation is derived,
\[
\frac{dx}{dt} = k(a - x)^n
\]  
(12)

where \( x \) is the amount of reaction accelerator at time \( t \), \( a \) is the initial concentration available, \( k \) is the rate constant as a function of temperature, \( t \) is time, and \( n \) is the order of reaction, assumed here to be 1. Recall that the state of cure is the ratio \( SOC = x/a \) and solving for \( x \), inserting into equation 12 and simplifying the expression results in

\[
\frac{d[SOC]}{dt} = k(1 - SOC) \rightarrow \ln(1 - SOC) = \int_{t_{min}}^{t} kd\tau \quad (13a)
\]

where \( k = K_0 e^{E_A/RT} \)  
(13b)

where \( \tau \) is a time constant, \( K_0 \) is the kinetic rate constant (inclusive of \( k \), the local rate constant), \( E_A \) is the activation energy, \( R \) is the universal gas constant, and \( T \) is the absolute temperature. Equations 13a simply says that the logarithm of the amount of uncross-linked rubber is equal to an Arrhenius-defined rate expression as a function of \( \tau \). This rate constant adheres to the familiar expression noted in equation 13b\textsuperscript{76}. This is profound because it allows for easy analysis of simple rheometer curves to evaluate the activation energy. The question of what the Arrhenius pre-exponential factor can be valued at is of little consequence because it is lumped into the overall rate constant, which is evaluated graphically. As the temperature increases in the reaction there are more and more collisions, occurring with increasing energy. Thus the heat of reaction is also increasing and the enthalpy change becomes greater and greater. Evaluating the integral in equation 13a results in
\[
\ln(1 - SOC) = -K_o(t - t_o)e^{-\frac{E_A}{RT}} = -k(t - t_o)
\] 

(14)

We can find the SOC from the curves, as seen in figure 3.2, by dividing the torque at time \(t\) from the difference of the maximum and minimum torques, which is then graphed as a function of time. The slope of the effective portion of the resulting graph (corresponding to the steepest region of the MDR curve) allows a calculation of \(k\). Rearranging terms in equation 14,

\[
\ln \left( \frac{k}{K_o} \right) = -\frac{E_A}{R} \cdot \frac{1}{T}
\]

(15)

which includes the activation energy in terms of constants and parameters that are known.

When several rate constants are calculating at different temperatures, a graph of \(\ln(k)\) with respect to \(1/T\) can be created, where the resulting slope represents the desired quantity, activation energy, divided by the universal gas constant.

The present study examines the variation of carbon black loading with shape fixity. As shown in chapter 2, with increases in swell time, until an optimum concentration is reached of stearic acid, the shape memory properties, namely fixity, are not at their optimum. It is hypothesized that as the level of carbon black increase, the shape fixity will also attain a higher percentage. Furthermore, because of the expected increase in modulus as the loading of carbon black increases, it would not be unexpected if the elongation decreased directly with increased levels of carbon black. Finally, an
examination of the effects of carbon black on the activation energy, and the quantification of that relationship, was examined.

3.2 Materials and Experimental Methods

The formulations used in this series of experiments can be seen in table 3.2. Variations in carbon black loading range from 0 PHR to 60 PHR and the remainder of each formulation is identical to the resulting compound identified as optimal in chapter 2.

Table 3.2: Formulations used for carbon black variation.

<table>
<thead>
<tr>
<th>Ingredient (PHR)</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
<th>#7</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-1,4-Polyisoprene</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>N330 Carbon Black</td>
<td>0.00</td>
<td>10.00</td>
<td>20.00</td>
<td>30.00</td>
<td>40.00</td>
<td>50.00</td>
<td>60.00</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>4-Morpholinyl-2-Benzothiazole Disulfide</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
<td>0.33</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The carbon black utilized in this study is N330 produced by Sid Richardson Carbon and Energy Company. It has OAN of about 102 ± 5 cm$^3$/100 g with iodine adsorption number (similar to nitrogen adsorption number as explained in the previous section) of about 82 ± 5 mg/g. All other materials shared the same supplier and technical specifications as those in chapter 2.
Compounds were mixed in a single pass using a 414 cm$^3$ Thermo-Fisher Scientific Haake$^\text{TM}$ Rheomix OS Lab Mixer using 55% fill factor (228 cm$^3$), cam rotors heated to 95°C, mix chamber heated to 95°C, 4.14 MPa ram pressure, to a drop temperature of 160°C. Compounds were mixed in a “sandwich” style common to the trade, where half of the elastomer was inserted into the shaft, the fillers and additives added immediately after, and, finally, the remaining elastomer which completed the loading of the mixer. The cam rotors were set to 50 revolutions per minute (RPM). The resulting rubber compounds were then milled on open-faced, non-temperature controlled mills for approximately 120 seconds, until each compound was suitably masticated for cutting into sheets for curing.

Tensile testing was completed using dumbbells in the shape diagrammed in figure 2.1. Each sample had a thickness gauge of 2.2 mm along with the dimensions found in table 2.3. Tensile testing was completed using a standard Instron Universal Mechanical Testing Instrument with pull speed of 51 cm/minute to generate stress-strain characterizations. Compounds were cured at 150°C for 80 minutes in a sheet compression mold.

To evaluate shape memory behavior, two methods were employed. Samples continued to be subjected to dynamic mechanical analysis (DMA). DMA testing was completed using a TA Instruments Q800. The shape memory cycle is defined as the cycle used to heat the sample, deform it, and cool it (at this point, measure fixity), followed by a second heating and cooling cycle to measure recovery. These steps are outlined in table 2.4 in detail and were not duplicated in this section. The samples being tested were approximately 7.5 mm × 2.2 mm with a sample length of about 10 mm.
A second method of shape memory analysis was also used. Carbon black-filled samples that were unswollen were subjected to a manual form of shape memory testing that mimicked the testing on the DMA. In this method, a sample is fastened between two binding clips, one of which is suspended from a rod. Using a similar cycle to that shown in table 2.4, shape memory measurements were recorded using a digital caliper. The shape memory cycle began with the suspension of the sample from the rod for 10 minutes to allow gravity to equilibrate the initial length, which was measured as the distance between the two binder clips. The sample was then submerged into a bath of water heated to 75°C for 5 minutes, after which a 0.1 MPa stress was applied by hanging a weight from the bottom binder clip. This stress was calculated using the very simple equation, \( \sigma = F/A \) where \( F = ma \). Acceleration, \( a \), is taken as gravity while \( m \) is the mass of the weight and \( A \) is the cross sectional area of the test sample. The cross sectional area was also measured using a digital caliper. After 10 minutes, the sample was removed from the bath and the length measured. After the sample cooled, another length measurement was taken, after which the weight was removed. A subsequent 10 minute relaxation period was used after which a fixity length was measured. The sample was then resubmerged into the heated bath for 10 minutes and withdrawn where a recovery length was measured.

Cure and vulcanization characteristics were measured on a moving die rheometer (MDR), which is an adaptation of the Alpha Technologies rubber process analyzer (RPA). Samples were prepared using constant cylindrical volume, with weight of 5 grams. Oriented polyester film from 3M was used on each side of the sample to keep from sticking to the serrated discs while maintaining a no-slip boundary. Cure rates were
evaluated at 150°C for 120 minutes. To examine the activation energy variation with carbon black loading, cure measurements were taken at 150°C, 160°C, 170°C, and 180°C. Although the sample is specified by mass, the approximate dimensions of the disc were 4.1 cm diameter by 0.15 cm height.

Swelling of samples was completed using the same method for each piece of rubber, despite differences in filler content. Each sample was soaked for 60 minutes in a bath of molten stearic acid held at 75°C. Once the 60 minute period had elapsed, the samples were withdrawn from the stearic acid bath and placed in a cool 25°C bath of distilled water for cooling and hardening of the crystalline stearic acid, used for further testing procedures.

### 3.3 Results and Discussion

Initial tensile properties show a clear correlation between PHR carbon black and elongation. As shown in figures 3.3 and 3.4, the relationship shows both viscoelastic and non-viscoelastic characteristics.
Figure 3.3: Stress at 400% strain as a function of carbon black loading.

Figure 3.4: Stress at all elongation ratios as a function of carbon black loading.
Examining figure 3.3, the region from 0 to 20 PHR carbon black shows interesting non-linearity that is indicative of the rubber materials exhibiting viscoelastic elongation behavior. This is expected since the lower carbon black loadings allow the viscoelastic nature of the cis-1,4-PI to dominate the response to the induced stress. However, as the carbon black loadings increase the behavior becomes more linear. In this case, predominantly linear behavior would be expected, potentially indicative of increased shape fixity. However, when one looks at figure 3.4 there are interesting undulations at 15 and at 40 PHR that become more pronounced with increased elongation ratio. Based on Einstein’s theory on viscosity, extended to the modulus of filled rubbers, this undulation is likely due to experimental error.

Examining a theoretical prediction of modulus, as seen in figures 3.5a and 3.5b, compared to the experimental data (figure 3.3), several notions emerge. Figure 3.5a shows experimental data compared to the Einstein equation\(^\text{78}\), Guth-Gold equation\(^\text{79}\), and Smallwood equation\(^\text{80}\), as described below.

\[
E = E_o(1 + 2.5\phi) \quad (16)
\]

Equation 16 is the Einstein equation, where \(E\) is the modulus of the filled system, \(E_o\) is the modulus of the unfilled elastomer system, and \(\phi\) is the volume fraction of filler.

\[
E = E_o(1 + 2.5\phi + 14.1\phi^2) \quad (17)
\]
Equation 17 is the Guth-Gold equation, as refined by these scientists to apply the Einstein equation to highly filled elastomers. The final relationship that will be used to compare models of modulus for filled elastomers is the Smallwood equation.

\[
E = E_o(1 + 0.67f \phi + 1.62f^2 \phi^2)
\]  

(18)

where \( f \) is a geometric factor that accounts for the asymmetric nature of carbon black as it aggregates into colloidal domains and is primarily based on the ratio of the particle’s length to its width. In practice, scientists such as Mullins and Tobin\(^81\) have used \( f \) as a fitting parameter, which is what was completed for the present data. The shape factor, \( f \), was best determined to be 3.0. In figure 3.5a stress-strain data for 10 PHR carbon black is shown against the Einstein, Guth-Gold, and Smallwood equations. In this chart, showing data for low carbon black volume fraction (10 PHR, \( \phi = 4.7\% \)), all three equations show good fit to the data at low elongations, however at high strain (greater than 200\%) the theoretical modulus deviates substantially from the data. In figure 3.5b, showing the three theoretical models and experimental results for the 50 PHR carbon black sample,
Figure 3.5: Experimental stress-strain data for two loadings of carbon black compared to Einstein, Guth-Gold, and Smallwood theoretical equations.

(a) 10 PHR carbon black sample.

(b) 50 PHR carbon black sample.
At lower strains and lower loadings all three equations show good agreement with experimental data but as strain levels and carbon black volume fraction increases, the equations begin to deviate substantially. Even with the geometric scaling factor incorporated into equation 18, additional terms would be necessary to better fit the data to very high elongations. This was also noted by Kilian, Schenk, and Wolff who proposed a theory based on the Van der Waals network model as applied to vulcanized rubber. The resulting equation from their work can be shown to be an amalgamated description of macroscopic properties with microscopic forces. It is written as

\[
E = E_o D(\lambda_r) \left[ \frac{1}{1 - \frac{D(\lambda_r)}{D_m}} - aD(\lambda_r) \right]
\]  

(19)

where \(E_o\) is the modulus of the unfilled sample and \(D, \lambda_r, \text{ and } D_m\) are described as

\[
D = \lambda_r - \lambda_r^{-2}
\]  

(20a)

\[
\lambda_r = \frac{\lambda - \left(\frac{v}{\lambda}\right)^{1/3}}{1 - \left(\frac{v}{\lambda}\right)^{1/3}}
\]  

(20b)

\[
D_m = \left(\frac{M}{M_s}\right) - \left(\frac{M}{M_s}\right)^{-2}
\]  

(20c)

where \(\lambda\) is the ratio of elongation to initial length, \(v\) is the ratio of filler particle volume to the total volume of the system, \(M\) is the molecular weight of the elastomeric chain, and \(M_s\) is the molecular weight of a single Kuhn segment. By this accounting for additional
elasticity from vulcanization as well as inter-chain forces, such as Van der Waals, this approach would present an interesting topic of approach for future investigators and will be discussed further in chapter 4.

Chartering tensile strength as a function of carbon black loading, figure 3.6 shows that the compound degrades up to 10 PHR and then builds strength linearly until reaching a maximum at 60 PHR, the highest loading tested.

10 PHR appears to be a percolation threshold, below which the filler simply acts as flaws since it cannot build a network at those low loadings. As the compound builds the network, from the minimum threshold loading, it continues to build strength into a stronger and stronger network. Further evaluation of the stresses at 300% strain as a function of carbon black shows a similar effect, seen in figure 3.7, however up to the
percolation point the stress at 300% strain has little effect, since the reinforcement is held within the vulcanized network.

![Figure 3.7: Stress at 300% strain as a function of carbon black loading.](image)

It is relevant to analyze the logarithmic plot of stress versus elongation, shown in figure 3.8.
Figure 3.8: Stress-strain curves for carbon black filled samples.

(a) Stress-strain curves for filled samples.

(b) Logarithmic plot of the stress strain curves for filled samples.
It is likewise notable that this chart exhibits classical rheological properties associate with filled polymers. From \( \ln(\gamma) \), where \( \gamma \) is strain ratio, of about 2.3 to 4.5, all of the samples exhibit extremely linear behavior with little viscoelastic impact. But from \( \ln(\gamma) \) of about 4.5 and beyond, depending on the filler loading, the onset of the viscoelastic behavior is quite pronounced. The higher the filler content of the compound, the earlier the viscoelastic behavior was exhibited. Because of the lack of a filler reinforcing phase in the control, there is an extremely pronounced shift toward viscoelasticity due to the overwhelming impact of the vulcanized elastomer.

Examining a plot showing relative cross-link density, calculated from the Flory-Rehner equation, as a function of carbon black PHR also shows interesting characteristics.

![Figure 3.9: Relative cross-link density as a function of carbon black loading.](image-url)
Many experiments have shown carbon black loading to steadily increase and then plateau, such as Baeta, Zattera, et al.\textsuperscript{83} who showed an exponential relationship between filler loading and cross-link density. Figure 3.9 shows this relationship as well. All samples were soaked for 60 minutes, however small variations in the higher loaded samples can be attributed to the fact that increased filler content will require increased soaking time. It was believed that 60 minutes would be sufficient for complete saturation of the stearic acid and the data in figure 3.9 shows this assumption largely accurate. As the carbon black loading increased higher than 50 PHR there seemed to be little impact on the XLD reported. With a given cure system this observation is likely due to the diminished impact that carbon black has on diminishing the effect of the accelerator due to interference.

Of most importance to the present thesis, the shape memory characteristics for each sample were also examined. Figure 3.10 shows the unfilled sample and the sample containing 10 PHR carbon black.
Figure 3.10: Shape memory cycle for 0 PHR and 10 PHR carbon black samples.

It is obvious from the data that the elongation increased after 10 PHR carbon black was added to the unfilled compound. In addition, fixity was also increased while the recovery remained near 100% and virtually unchanged from the control. The remaining shape memory curves can be seen in figure 3.11.
Figure 3.11: Shape memory cycle for rubber filled with 0 – 60 PHR carbon black.

It is most evident that the relationship between carbon black loading and maximum elongation is not linear or progressive even though the elongation data from tensile testing showed a monotonic trend. One possible explanation manifests itself in a generic set of vulcanizate property curves. Carbon black is a reinforcing material, however at very high loadings, typically in excess of 70 – 80 PHR, the reinforcing nature of the filler system inhibits the strength of the material and will reduce the effectiveness of the vulcanized reinforcement. This is easily seen in figure 3.12, showing various physical property trends as a function of carbon black loading.\textsuperscript{84}
In particular, it is important to examine the tensile strength curve (purple) in which the percolation point is assumed to have already been breached. Notice how it peaks and then decreases. The same trend can be seen in figure 3.13, taken from the shape memory results as ultimate elongation as a function of filler for all stearic acid-swelled samples.
It is believed that the data point taken at 30 PHR shows higher deviation due to instrumentation error. In general, this follows the same trend as seen in the tensile strength curve in figure 3.12. As previously explained, the filler network reaches a saturation point where it begins to inhibit the vulcanization reaction, even as hardness and hysteresis continues to increase, as seen in the trends of figure 3.8.

The shape memory behaviors are striking as well. Shape fixity as a function of carbon black loading is shown in figure 3.14. As in figure 3.13 the data associated with 30 PHR shows a trend not similar to the whole.
As carbon black loadings increased, the shape fixity has also increased, although there is very little discernible difference between 20 PHR and 60 PHR after a steady incline from 0 PHR to 20 PHR. A small amount of filler, not less than 20 PHR carbon black, is necessary for this system to retain greater than 93% shape fixity. Upon observation of the samples after testing in the DMA, there was a visible brittleness to the two samples with 50 and 60 PHR carbon black. The initial explanation for this is that the carbon black in these higher loadings is likely so high as to inhibit the strain-induced crystallization the cis-1,4-PI exhibits, but this is difficult to analyze because of the strain-induced crystallization differences between natural and synthetic polyisoprene. Toki, Che, Rong,
et al. showed how unvulcanized natural and synthetic polyisoprenes had extremely different stress-strain curves and, as a result, a dramatic difference in strain-induced crystallization onset\textsuperscript{85}. However vulcanized natural and synthetic polyisoprenes showed quite a different story, with the stress-strain characteristics only different at strains above 300\%. Since the DMA used to generate the present data did not exceed 160\% strain, it is then possible to treat the present data as if the synthetic cis-1,4-PI used reacted the same way and the carbon black in extremely high loadings impeded the compound from exhibiting its proper strain-induced crystallization characteristics.

A direct relationship was identified when comparing recovery to amount of carbon black in the sample. Figure 3.15 shows this trend and the stark relationship between PHR carbon black and recovery.

![Figure 3.15: Shape memory recovery as a function of carbon black level.](image-url)
The direct relationship between recovery and carbon black loading compared to the non-monotonic relationship of tensile strength and carbon black loading suggests that the recovery is more a function of the carbon black resulting in a “harder” compound, rather than the state of the sulfur cross-linking network. With increased carbon black also will come increased hysteresis, which is easily verified by finding the ratio of the storage and loss moduli. Hysteretic energy loss from increased carbon black content would explain poorer recovery with higher filled compounds. On the other hand, the fixity seems to be more erratic, possibly due to the elastic nature of the vulcanized network and the balance of free energy derived from the elasticity of the compound compared to the filler network. It was also observed that there was a slight relaxation of all compounds after the strain was held, evidenced by the dip in the overall strain percent after the 0.10 MPa stress was applied at about 42 minutes. As seen in the previous chapter, thermal expansion and contraction was noted for all samples when the temperature of the compound would increase and decrease, respectively, at no stress. However, the carbon black loadings did affect the magnitude of the expansion. Figure 3.16 shows this comparison and it exhibits a parabolic relationship, with a minimum between 10 and 30 PHR.
For similar reasons to those already explained for the effects on tensile strength, the amount of thermal expansion depends on the balance of filler network as long as the network is able to form a support system beyond a critical concentration. Once again, it is likely that the 30 PHR data point is in slight error, thus normalizing the plot in 3.16 with the tensile strength trend shown in figure 3.6.

It finally became necessary to investigate the impact of the filler network on the shape memory properties of unswollen materials. Using the second shape memory method described in section 3.2 shape memory properties were examined for compounds with 30 PHR and 60 PHR carbon black. Fixity and recovery for these two compounds are shown in figure 3.17.
Figure 3.17: Fixity and recovery for unswollen, filled samples.

The high degree of recovery for both samples indicates an extremely strong elastic force able to overcome the “fixed” network of the carbon black in both loadings. But even more surprising is the ability for the filled, but unswollen compounds to utilize the carbon black network to exhibit fixity at 53% and 85% for the 30 PHR and 60 PHR samples, respectively. This contrasts with swollen sample fixity of 94% and 95% for 30 and 60 PHR, respectively. One might expect that a reduction in reinforcement, through elimination of the stearic acid crystalline network, would result in reduced fixity, as shown here. This data presents an interesting means of comparing the contribution to fixity from the carbon black and stearic acid networks independently, and from the unexpectedly high degree of fixity shown by the present unswollen samples, it appears that the contributions to fixity from the carbon black network are quite high. Recovery
remains high, in excess of 90%, and since the carbon black network did not inhibit the recovery of the swollen samples, it would not be expected in this circumstance either.

The shape memory characteristics displayed by the carbon black-filled samples were unexpected. It is suggested that this may be in part a result of the low strains seen in these experiments, which did not exceed 30%. 18% and 27% maximum strain was seen on the 30 PHR and 60 PHR filled samples, respectively. At these low strains, little break down of the carbon black network would be expected, thus retaining some of its reinforcing properties. Had strains exceeded 50%, 100%, or even 300% the results may have been different.

As a final examination into the effects of filler systems on shape memory, it was explained in the introduction to chapter 3 that the conductivity of carbon black can have a large impact on the cure rates of compounds. An investigation was completed on the present samples to determine the activation energy as a function of carbon black loading. In the interest of time, the samples tested were 0 PHR, 10 PHR, 30 PHR, and 50 PHR carbon black. In practice, the creation of this data is quite complicated and subject to the investigator's judgment. First, the sample should be cured in a curemeter at no less than 2 different temperatures. The present study completed 4 different temperatures, 150°C, 160°C, 170°C, and 180°C. The state of cure for each curve must be calculated using the relationship,

$$SOC = \frac{I_i}{I_{\text{max}} - I_{\text{min}}}$$  \hspace{1cm} (21)
where $\Gamma_i$ is the torque at a given time and $\Gamma_{\text{max}}$ and $\Gamma_{\text{min}}$ are the maximum and minimum torque at that given temperature, respectively. Each curemeter curve is then converted into a plot of $\ln(1 - SOC)$ as a function of time. At this time, the rate constant is being investigated and an analysis of this curve must result in a tangent line being created at the point of maximum curvature (which is also the point at which the vulcanization reaction is at its maximum velocity). The slope of this line is the negative of the rate constant $k$ in equation 15. Once the rate constant is determined for each compound at each temperature, they are charted on a logarithmic graph, with $\ln[k(T)]$ as a function of $1/T$. This resulted in figure 3.18, where the slope of the line is the activation energy divided by the rate constant.

Figure 3.18: Activation energy plots for 4 compounds at 0 PHR, 10 PHR, 30 PHR, and 50 PHR.
A plot of these activation energies against carbon black loading shows a direct, negative relationship as seen in figure 3.19.

As the carbon black loading was increased, the activation energy decreased. This means that as more carbon black is mixed into the compound, increasing the energy conductivity of the compound, less energy is required from the external heat source used to cure the compound. At low loading, even at no carbon black, the energy required to initiate the vulcanization reaction is at its highest. This confirms the trends established in the curing kinetic models, four of which are listed in table 3.3: the nth order kinetic model, the Isayev-Deng model, the Piloyan model, and the Kamal-Ryan model. Each of these kinetic equations is given for reference ($\alpha$ represents the degree of cure). This table is not exhaustive of the kinetic models that exist in the literature.

Figure 3.19: Activation energy as a function of carbon black level.
Table 3.3: Kinetic equations modeling the vulcanization reaction.

<table>
<thead>
<tr>
<th>Name of Model Limitations</th>
<th>Model Equation</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>nth Order (n \geq 1)</td>
<td>(\frac{d\alpha}{dt} = k(1 - \alpha)^n)</td>
<td>[\alpha = 1 - e^{-kt}] (\text{when } n = 1) [\alpha = 1 - \frac{1}{[1 + kt(n - 1)]^{n-1}}] (\text{when } n &gt; 1)</td>
</tr>
<tr>
<td>Isayev-Deng(^{87}) (n \geq 1)</td>
<td>(\frac{d\alpha}{dt} = \frac{n}{k}t^{-(n+1)}\alpha^2)</td>
<td>(\alpha = \frac{kt^n}{1 + kt^n})</td>
</tr>
<tr>
<td>Piloyan(^{88}) (n \geq 1, m &lt; 1)</td>
<td>(\frac{d\alpha}{dt} = k\alpha^m(1 - \alpha)^n)</td>
<td>(t = k \int_{0}^{\alpha} \frac{d\alpha}{\alpha^m(1 - \alpha)^n})</td>
</tr>
<tr>
<td>Kamal-Ryan(^{89}) (n \geq 1, m &lt; 1)</td>
<td>(\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n)</td>
<td>(t = k \int_{0}^{\alpha} \frac{d\alpha}{(k_1 + k_2\alpha^m)(1 - \alpha)^n})</td>
</tr>
</tbody>
</table>

Note that the degree of reaction, \(n\), is always positive. To this point, it was assumed that \(n = 1\) in the present study. A solution for \(\alpha\) is available for each model, which provides the investigator with an equation solved for the rate of reaction. However solutions are easiest for the nth Order and Isayev-Deng equations, where \(\alpha\) can be solved directly. In the Piloyan and Kamal-Ryan models it is best to solve for \(t\) since there are two orders of reaction, \(m\) and \(n\). Figure 3.20 shows the experimental cure curves matched with the Isayev-Deng equation to compare to theory.
Figure 3.20: Curemeter data compared to Isayev-Deng equation.

The Isayev-Deng equation needed a slight adjustment due to the fact that cure measurements were taken on cold compound, thus accounting for the higher initial torque requirements. This is very common in industrial cure measurements taken on standard equipment, such as oscillating (ODR) and moving die rheometers (MDR) as well as rubber process analyzers (RPA).

\[
\alpha = X_1 + \frac{kt^n}{1 + X_2(kt^n)} \quad (22)
\]

In equation 22, where \(X_1\) is a factor added to account for the torque needed for compound breakdown and \(X_2\) is a scaling factor used to scale the fitting curves to account for...
conversion not exceeding 1, superb fits are noted in figure 3.20. As a rule of thumb, 
\( X_1 \approx 4X_2 \). In general the fit is quite good. At lower part loadings it is much easier for 
the modified Isayev-Deng model to describe the vulcanization reaction, however as 
reactive carbon black is added, this relationship becomes less accurate at long times due 
to slight reversion seen in the higher loaded compounds.

### 3.4 Conclusion

Carbon black presented many interesting points of interest when studying its 
effects on the shape memory behavior of elastomers. As predicted, the fixity was 
increased until plateauing while the recovery exhibited a negative monotonic relationship 
by adding carbon black to a simple rubber formulation. Since carbon black creates its 
own reinforcing network with the cross-linked network, these shape memory swelled 
elastomers have three effective networks when the crystalline stearic acid is taken into 
account. Above the melt point of the stearic acid only two networks are active and as 
elongation enters the system, the elastic force dominates. When the sample is held for 5 
minutes after cooling with a constant 0.1 MPa stress, the sample is allowed to relax, in 
which case the elastic force transfers some of its dominance to the innate network formed 
by the carbon black. Thus, as the parts of carbon black increase and a highly reinforced 
network is formed, it overcomes the elastic energy, decreased as a result of the relaxation, 
and enables the compound to exhibit more shape fixity upon cooling.

It is noteworthy that the tensile strength trend with increased parts of carbon black 
showed a clear percolation point at which the tensile strength was at a minimum. This is 
profound when determining a starting point for the ultimate objective goal of shape
molding and identifying a formulation that will allow one to have malleability but also exhibit strength. Likewise, the DMA elongation measurements, mimicking the tensile testing previously reported, also shows a percolation point, with maximum elongation at the same percolation point of between 10 and 20 PHR as the results from elongation tensile strength tests. This is encouraging for the validation that formulations incorporating reactive carbon black must account for the effects of carbon black on the state of cure.

Clearly there is an effect that carbon black has on the activation energy, namely decreasing the energy required to active the vulcanization reaction as the parts of carbon black are increased. Future studies would do well to study the effects that the internal carbon black network has on the overall cross-link density, which showed to increase steadily before leveling out at very high loadings in excess of about 50 PHR. Likely related to the decreased activation energy, it was notable that the thermal expansion also increased with increased carbon black loadings. This was likely caused by increased conductivity, a natural response to an increase in the primary conductive material, carbon black, in the compound.

With this study, it is expected that a future set of experiments will be designed to continue investigation into the effects that carbon black have on shape fixity, as well as other fillers that may allow a more economical industrialization of this technology. For instance, kaolin clay, a very inexpensive filling material, may provide similar reinforcing properties even though it is non-reactive. Further investigations into the effect of different cure systems on shape memory would also enable the investigative community
to better understand how to fine tune the various physical properties to enable a particular shape memory effect.
CHAPTER IV
SUMMARY AND RECOMMENDATIONS

The present design of experiments has enabled the investigation of how levels of curatives affect polymers and their shape memory related elastomers that are swollen with stearic acid. In addition, the effects of carbon black on simple rubber compounds and their stearic acid-swollen counterparts were also investigated.

In chapter 2 it was determined that the state of cure can have a tremendous effect on the physical properties, as well as the shape memory properties, of vulcanized rubber compounds. Curemeter curves suggested that as long as a sufficient amount of free sulfur was added, all formulations could attain a maximum state of cure. Thus the determination of which cure system would be best for further experimentation rested in its ability to exhibit suitable shape memory properties. The shape memory properties were highly predictable by the relative cross-link density, as calculated by the Flory-Rehner equation. In this case, the lowest cross-link density provided optimal fixity and recovery compared to the other samples tested, with fixity of 73%. LF-NMR data was used to verify the swollen cross-link density calculations and showed acceptable agreement. Finally, it was determined that the number of minutes a sample was allowed to swell in molten stearic acid had a large impact on the sample’s ability to exhibit shape
memory behavior. Experiments showed that when a compound attained about 45 minutes of swelling time it reached its maximum fixity.

Variations in carbon black loading provided surprising results pertaining to each sample’s fixity and recovery metrics as well as simple elongation and tensile results. A percolation point for this particular compound formulation allowed the investigator to pinpoint a carbon black loading of minimal tensile strength. In addition, an analysis of the vulcanization properties as carbon black levels were varied showed that carbon black had a direct impact on the amount of energy required to initiate the vulcanization reaction. As carbon black loading increased, the shape fixity appeared to find a maximum and then plateau at loadings above 20 PHR filler. Alternatively, the recovery showed to have a direct negative relationship to carbon black PHR. There was a slight decrease in the thermal expansion as levels of carbon black increased until about 20 PHR after which the thermal expansion rose steadily. This was also explained in light of percolation point theory.

There are many avenues of research that remained left untouched. One of those areas is around types of filler. It is known that carbon black fillers do not interact with a vulcanized polymer backbone in the same way as silica, kaolin clay, carbon nanotubes, or other common fillers utilized in the rubber industry. Silica has long been used in the rubber industry as alternative filler due to its unique hydrophobicity, allowing it to have superior wet traction to its carbon black counterpart, and the study of silica-filled rubber’s rheological properties is an active area of investigation. Liu, Zhao, et al. have shown that the addition of silica can have a very positive impact on the elastomer’s ability to form crosslinks due to interactions from the silica hydroxyl groups. Furthermore, when a
polymer functionalized with reactive end groups is used, silica fillers can aid in creating suitable flow and improved processability. Kaolin clay has shown to flocculate in a different manner to carbon black and, thus, after it is cured through vulcanization, the resulting physical properties may turn out to be different than expected\textsuperscript{91}.

The vulcanization reaction is an area of rubber chemistry that is only recently being investigated with any vigor. There are many types of curing reactions. The MBDS cure system utilized in the present research is just one curative among dozens of other industrially used chemicals to hasten the vulcanization reaction. However, there are alternative cross-linking materials. Peroxide cures have been used to successfully link polymer backbone chains with carbon-carbon linkages\textsuperscript{92}. This presents an interesting area of potential research. Carbon-carbon linkages have shown to be much more stable and resistant to extremes in temperature when cured at an optimal temperature and with an optimal concentration of peroxide additive\textsuperscript{93}. Further investigation has shown that a balancing of sulfur vulcanization with peroxide vulcanization in the same compound results in unique tensile properties, blending the permanence of the peroxide cure with the improved elasticity of the sulfur cure system\textsuperscript{94}. Investigation into an alternate cure system may show improved shape memory properties.

There was an interesting percolation point phenomenon observed in chapter 3. Changes in carbon black type will result in carbon black fillers that have different adsorptive properties when interacting with each other and with the carbon chain polymer backbone. In the present experiment the percolation point was identified at 10 PHR, a critical concentration corresponding to the minimum tensile strength. The effect that alternative carbon blacks will have on this elongation property remains unknown and
would provide a guiding principal on the choice of filler in future shape memory elastomers.

As explained in the survey of literature, there has been an immense amount of research into polymers that contain two distinct blocks, which will exhibit two unique glass transition temperatures acting as trigger temperatures for inducing shape memory behavior. The inclusion of carbon black filler into these systems remains an enigma to the shape memory community. A systematic undertaking of the effects that a carbon black network will induce will result in a substantially improved understanding of polymer chain and carbon black filler interaction behavior. The present experiment utilized stearic acid as a transition material, utilizing its melt point as an activation or transition temperature. This was suitable for experiments in chapters 2 and 3 since stearic acid remains inert in the presence of carbon black. The benefits of working with stearic acid lay primarily in its economic advantages as well as its easy handling and plentiful availability. Thus, maintaining a stearic acid transition phase, if a filler could be found that was reactive with the stearic acid, the resulting shape memory behaviors may succumb to an additional tuning mechanism. In other words, if a filler was utilized that would adjust the tensile or glass transition temperature or other physical property of the rubbery system, this filler could be used as a simple way to hone in on the compound’s desired properties.

Finally, the limits of future research are boundless. Any number of material experiments could be undertaken to identify a unique shape memory rubber. Likewise, various fatty acids and their salts could be examined to find additionally unique systems that respond at different temperatures with different transition shapes and properties. The
present research attempted to build a starting point of a known rubber compound with chemistry able to be researched and evaluated for its shape memory benefits. In the future, should shape memory elastomers find a home in the rubber molding industry or another industry that could benefit from materials able to retain temporary shapes, the building blocks of knowledge presented herein provide a foundation to continue that investigative journey.
REFERENCES


APPENDIX A

LIST OF COMPOUND RAW MATERIALS

Appendix A contains a list of all of the materials used to make compounds in this study. The list contains the chemical name, structure (where applicable), supplier, and trade name.

Table A.1: Ingredients used with detailed information.

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>Supplier</th>
<th>Trade Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic cis-1,4-polyisoprene</td>
<td><img src="image" alt="Structure" /></td>
<td>Goodyear Tire &amp; Rubber Company</td>
<td>Natsyn 2200</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>Zn=O</td>
<td>Zochem Incorporated</td>
<td>Zoco 624</td>
</tr>
<tr>
<td>4-Morpholinyl-2-Benzothiazole Disulfide</td>
<td><img src="image" alt="Structure" /></td>
<td>Emerald Performance Materials</td>
<td>CureRite® MBDS</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>C_{18}H_{36}O_{2}</td>
<td>Vantage Oleochemicals</td>
<td>VSTERAIN™ SA29</td>
</tr>
<tr>
<td>Sulfur</td>
<td><img src="image" alt="Structure" /></td>
<td>Akrochem Corporation</td>
<td>Rubbemakers Sulfur OT</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>N/A</td>
<td>Sid Richardson</td>
<td>N330</td>
</tr>
</tbody>
</table>
APPENDIX B

DYNAMIC MECHANICAL ANALYSIS RESULTS

Appendix B contains each shape memory graph produced for use in chapters 2 and 3. Compounds are referenced by their designation as shown in each chapter, respectively. The first set, figures B.1 – B.6 pertain to standard compound DMA testing while figures B.7 – B.14 show the solubility DMA testing, both from chapter 2. The second set of figures, B.15 – B.22 pertain to chapter 3 compounds. The 0.1 MPa stress was applied at approximately 40 minutes.

Figure B.1: DMA results for chapter 2, compound 1.
Figure B.2: DMA results for chapter 2, compound 2.

Figure B.3: DMA results for chapter 2, compound 3.
Figure B.4: DMA results for chapter 2, Compound 4.

Figure B.5: DMA results from chapter 2, compound 6.
Figure B.6: DMA results for chapter 2, Compound 7.

Figure B.7: DMA results for chapter 2, Figure 2.16 at 5 mins.
Figure B.8: DMA results for chapter 2, Figure 2.16 at 10 mins.

Figure B.9: DMA results for chapter 2, Figure 2.16 at 20 mins.
Figure B.10: DMA results for chapter 2, Figure 2.16 at 30 mins.

Figure B.11: DMA results for chapter 2, Figure 2.16 at 35 mins.
Figure B.12: DMA results for chapter 2, Figure 2.16 at 45 mins.

Figure B.13: DMA results for chapter 2, Figure 2.16 at 55 mins.
Figure B.14: DMA results for chapter 2, Figure 2.16 at 60 mins.

Figure B.15: DMA results for chapter 3, compound 1 (0 PHR).
Figure B.16: DMA results for chapter 3, compound 2 (10 PHR).

Figure B.17: DMA results for chapter 3, compound 3 (20 PHR).
Figure B.18: DMA results for chapter 3, compound 4 (30 PHR).

Figure B.19: DMA results for chapter 3, compound 5 (40 PHR).
Figure B.20: DMA results for chapter 3, compound 6 (50 PHR).

Figure B.21: DMA results for chapter 3, compound 7 (60 PHR).
APPENDIX C

TENSILE AND ELONGATION RESULTS

Figures C.1 – C.6 were taken using the method described in section 2.2 while figures C.7 – C.14 were taken using the method described in section 3.2. All tensile testing was completed on compounds that were un-swelled. Future experiments may include tensile and elongation testing of swelled rubbers.

![Stress-strain curve](image)

Figure C.1: Stress-strain curve for chapter 2, compound 1.
Figure C.2: Stress-strain curve for chapter 2, compound 2.

Figure C.3: Stress-strain curve for chapter 2, compound 3.
Figure C.4: Stress-strain curve for chapter 2, compound 4.

Figure C.5: Stress-strain curve for chapter 2, compound 6.
Figure C.6: Stress-strain curve for chapter 2, compound 7.

Figure C.7: Stress-strain curve for chapter 3, compound 1 (0 PHR).
Figure C.8: Stress-strain curve for chapter 3, compound 2 (10 PHR).

Figure C.9: Stress-strain curve for chapter 3, compound 3 (20 PHR).
Figure C.10: Stress-strain curve for chapter 3, compound 4 (30 PHR).

Figure C.11: Stress-strain curve for chapter 3, compound 5 (40 PHR).
Figure C.12: Stress-strain curve for chapter 3, compound 6 (50 PHR).

Figure C.13: Stress-strain curve for chapter 3, compound 7 (60 PHR).
APPENDIX D

MODULATING DISC RHEOMETER RESULTS

The curemeter curves presented in appendix D were taken by the method described in section 2.2. All samples were tested at 150°C. Samples D.1 – D.7 were from chapter 2 while samples D.8 – D.14 were from chapter 3.

Figure D.1: Curemeter curve for chapter 2, compound 1.
Figure D.2: Curemeter curve for chapter 2, compound 2.

Figure D.3: Curemeter curve for chapter 2, compound 3.
Figure D.4: Curemeter curve for chapter 2, compound 4.

Figure D.5: Curemeter curve for chapter 2, compound 5.
Figure D.6: Curemeter curve for chapter 2, compound 6.

Figure D.7: Curemeter curve for chapter 2, compound 7.
Figure D.8: Curemeter curve for chapter 3, compound 1 (0 PHR).

Figure D.9: Curemeter curve for chapter 3, compound 2 (10 PHR).
Figure D.10: Curemeter curve for chapter 3, compound 3 (20 PHR).

Figure D.11: Curemeter curve for chapter 3, compound 4 (30 PHR).

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Figure D.12: Curemeter curve for chapter 3, compound 5 (40 PHR).

Figure D.13: Curemeter curve for chapter 3, compound 6 (50 PHR).
Figure D.14: Curemeter curve for chapter 3, compound 7 (60 PHR).
APPENDIX E
LF-NMR RESULTS

Low field nuclear magnetic resonance (LF-NMR) results were obtained to verify cross-link density calculations using the Flory-Rehner equations for the cure variations examined in chapter 2.

Figure E.1: LF-NMR results for chapter 2, compound 1.
Figure E.2: LF-NMR results for chapter 2, compound 2.

Figure E.3: LF-NMR results for chapter 2, compound 3.
Figure E.4: LF-NMR results for chapter 2, compound 4.

Figure E.5: LF-NMR results for chapter 2, compound 6.
Figure E.6: LF-NMR results for chapter 2, compound 7.