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The effect of strain on the electrical resistivity of carbon filled elastomers

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THE EFFECT OF STRAIN ON THE ELECTRICAL RESISTIVITY OF CARBON
FILLED ELASTOMERS

A Thesis

Presented to

The Faculty of the Department of Materials and Chemical Engineering

San José State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Scott Leonard Poveromo

August 2009

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THE EFFECT OF STRAIN ON THE ELECTRICAL RESISTIVITY OF CARBON
FILLED ELASTOMERS

by

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ABSTRACT

THE EFFECT OF STRAIN ON THE ELECTRICAL RESISTIVITY OF CARBON FILLED ELASTOMERS

by Scott L. Poveromo

The effects of strain on the electrical resistivity of particulate composites were investigated. The resistivities of two carbon-loaded silicones, SC-Consil-861 and CHO-SEAL-6370, were measured as they were pulled uniaxially in tension up to 10% strain. It was determined that the electrical resistivity for both conductive silicones was sensitive to small strains. It was also determined that the change in electrical resistivity due to strain depends on the filler particle size distribution and distribution of the fillers in the elastomer. Hysteresis was found in the initial part of the resistivity-strain curve for both materials after repeat testing. Seven different theoretical models that predict electrical resistivity values for particulate composites at 0% strain were considered and compared against the SC-Consil-861 experimental data. The Scarisbrick model proved to be the most accurate model to predict an electrical resistivity value within an order of magnitude of the experimental data.

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CHAPTER ONE

INTRODUCTION

1.1 Background/Significance

Particulate composites or particle filled polymers continue to be developed over time as the need for advanced material properties increase [1]. These types of materials can range from toughened thermoplastics to flame retardant filled elastomers, and are used in a wide variety of industrial applications. The filler materials found in particulate composites range from minerals such as calcium carbonate to metallic powders such as silver or organic materials such as carbon black [1]. The type of filler determines the properties the composite material will exhibit. For example, carbon black and metallic powder fillers increase the electrical conductivity of polymers and have been utilized to create electromagnetic interference (EMI) shielding and electrostatic discharge (ESD) devices. The filler type, shape, size, and interparticle contacts all play a role in defining the electrical properties of the composite [2].

A potential application for carbon or metal filled polymers is in producing a low cost sensor material to assess building damage caused by earthquakes. According to Housner *et al.*, very little information is currently known about the changes in stresses and strains in buildings due to earthquakes [3]. The capability to gather strain data from a structural health monitoring system in real time would be invaluable in determining the structural integrity of a building after an earthquake. The sensor chosen must have the sensitivity to pick up small variations in the strain of a structure to aid civil engineers in

determining the extent of damage. Also, the sensor material needs to be easily installed, especially for a large scale structure, to make the system economically feasible.

One of the more unique methods being developed to measure strain in a component via electrical resistance is to use electrically conductive reinforced polymer composites. Carbon fiber and or carbon powder have been added to different composites to improve their electrical properties with the goal of using the hybrid material as a sensor for strain. These carbon filled sensors are attractive because they are easy to install, simple to manufacture, and low in cost compared to the standard strain sensors. Matsubara *et al.*, used carbon fiber and carbon powder filled polymer composites to detect damage in concrete structures. The authors measured strain of a concrete block in bending by monitoring the changes in electrical resistance of a carbon filled composite. The results of the experiment performed are illustrated in Figure 1 [4]. The change in resistance was measured against time for a carbon powder and carbon fiber filled composite. The relative resistance difference of the carbon fiber filled specimen did not change due to small strains in the concrete. The relative resistance difference only changed at larger strains and the change was abrupt, illustrating its poor characteristics as a sensor. On the other hand, the carbon powder filled specimen was very sensitive to small strain changes in the concrete as the relative resistance difference began to change at around the time the strain started to increase [4]. Also, the carbon powder filled specimen continued to register the strain changes in the concrete as the load increased. This trend illustrates that the sensor can be used to track large strain changes [4]. Matsubara *et al.* concluded that the reason the carbon powder filled specimen performed

so well at small strain changes was because of the flexibility of the structure due to the dispersion of the carbon particles [4].

Figure 1. (a) Load (kN) vs time (seconds) for the concrete block. (b) strain (μ) vs time (seconds) for the concrete block (c) percent relative resistance difference vs time (seconds) for the carbon powder filled specimen and (d) percent relative resistance difference vs time (seconds) for the carbon fiber filled specimen [4]. (Reprinted with permission from SPIE, for full citation see References)

Carbon powder loaded polymers have the potential to be sensor materials in a structural health monitoring system to solve the problem of assessing building damage caused by earthquakes. The advantage of using carbon in a particulate composite is that it is inert, generally adheres well to the matrix elastomer and is low in cost [2]. The focus of this investigation was to characterize the electrical resistivity as a function of strain for carbon filled silicone materials at low strains ($\leq 10\%$). The theoretical models used to predict the electrical resistivity properties of particulate composites and comparisons of experimental data to the models are reviewed in Chapter 2. The research objectives, including the basis for a hypothesis, are discussed in Chapter 3. The procedures and methods followed to perform the experimentation are summarized in Chapter 4 and the results from the experimentation are presented in Chapter 5. Sources of error in the experimentation and a comparison of the experimental data to the literature are reviewed in Chapter 6. Finally, the findings based on the experimental results are concluded in Chapter 7.

CHAPTER TWO

LITERATURE REVIEW

In order to characterize the relationship between strain and electrical resistivity for carbon-loaded elastomers it is necessary to understand the variables that influence these properties. A review of the electrical resistivity models for particulate composites is needed. The basic models for electrical conduction in particulate composite materials are described in Chapter 2. Experimental data from literature, for different carbon-loaded elastomers, is compared to the individual models. One model, that predicts the resistivity changes with strain for a carbon-loaded silicone, is also examined. Finally, literature examining the effects of strain on the electrical resistivity of carbon-loaded elastomers is reviewed.

2.1 Summary of Electrical Resistivity Models

The electrical conductivity of a multi-phase system depends on a variety of factors such as filler type, particle size, volume fraction, surface contamination, polymer matrix type, and strain applied to the composite [1,5]. Many models characterizing the electrical properties of a composite exist; however, no one single relationship has been found to describe the behavior of all particulate composites [6]. Also, very few models take into account how resistivity changes with strain in a polymer.

Mathematical models used to predict changes in electrical resistivity of particulate composites are summarized in Table 1. These models can be divided into 4

Table 1. Summary of models predicting electrical conductivity of particulate composites.

Group Name	Model Name	Model Description	Equations	Equation Variables	Reference
Maxwell// Bruggeman	Maxwell's Equation	Assumes spherical filler particles and non-interaction between particles. Does not predict correct behavior when the volume fraction of the filler reaches the maximum packing volume fraction.	$\sigma_r = 1 + 3 * ((\lambda - 1) / (\lambda + 2)) * \Phi$	σ_r = conductivity ratio of composite to matrix, λ = conductivity ratio of filler to matrix and Φ = volume fraction of filler	[6]
	Bruggeman Equation	Assumes spherical filler particles and non-interaction between particles. Does not predict correct behavior when the volume fraction of the filler reaches the maximum packing volume fraction.	$((\sigma_d - \sigma) / (\sigma_d - \sigma_m)) * (\sigma_m / \sigma)^{1/3} = 1 - \Phi$	σ_d = conductivity of filler, σ_m = conductivity of matrix, σ = conductivity of composite and Φ = volume fraction of filler	[6]
	Pal Corrected Maxwell Equation #1	Describes conductivity of particulate composites for low to moderate filler volume fractions. Assumes all volume in matrix is free volume for filler to occupy. Uses correction factor for non-spherical shaped fillers.	$(\sigma / \sigma_m)^{1/3} * ((\sigma_d - \sigma_m) / (\sigma_d - \sigma)) = \exp(\alpha * \Phi)$	σ_d = conductivity of filler, σ_m = conductivity of matrix, σ = conductivity of composite, Φ = volume fraction of filler and α = correction factor for shape of particle	[6]
	Pal corrected Maxwell Equation #2	Takes into account the packing factor of the particles. Uses a correction factor for non-spherical shaped fillers.	$(\sigma / \sigma_m)^{1/3} * ((\sigma_d - \sigma_m) / (\sigma_d - \sigma)) = (1 - (\Phi / \Phi_m)) - \alpha \Phi_m$	σ_d = conductivity of filler, σ_m = conductivity of matrix, σ = conductivity of composite, Φ = volume fraction of filler, Φ_m = maximum packing factor and α = correction factor for shape of particle	[6]

Table 1 Continued. Summary of models predicting electrical conductivity of particulate composites.

Group Name	Model Name	Model Description	Equations	Equation Variables	Reference
Volume Averaging	Arithmetic mean	Electric field is parallel to conductive network. Does not take into account percolation limit. Assumes conductive network is formed at all filler volume fractions	$\sigma_c = V_f^* \sigma_f + V_r^* \sigma_r$	V_f = volume fraction of filler, V_r = volume fraction of matrix, σ_c = conductivity of composite, σ_f = conductivity of filler and σ_r = conductivity of matrix	[7]
	Harmonic mean	Electric field is perpendicular to conductive network. Does not take into account percolation limit. Assumes conductive network is formed at all filler volume fractions	$\sigma_c = ((\sigma_m^* \sigma_f) / (V_m^* \sigma_f + V_f^* \sigma_m))$	V_f = volume fraction of filler, V_m = volume fraction of matrix, σ_c = conductivity of composite, σ_f = conductivity of filler and σ_m = conductivity of matrix	[7]
Statistical Percolation	McLachlan model	Similar to a statistical model. Used to predict conductivity of a material that has high conductive filler in a low conducting matrix. Assumes conductive particles form discrete chains.	$\begin{aligned} &((1-\Phi)^* ((\rho_m)^{1/t} - (\rho_h)^{1/t}) / ((\rho_m)^{1/t} + ((1-\Phi_c)/\Phi_c)^* (\rho_h)^{1/t}) + \\ &((\Phi)^* ((\rho_m)^{1/t} - (\rho_l)^{1/t}) / ((\rho_m)^{1/t} + ((1-\Phi_c)/\Phi_c)^* (\rho_l)^{1/t})) = 0 \end{aligned}$	ρ_h = resistivity of filler, ρ_l = resistivity of matrix, ρ_m = resistivity of composite, Φ = volume fraction of filler, t = critical exponent and Φ_c = percolation threshold	[8]
Scarbrick Model	Scarbrick model	Assumes the conductive particles in the composite are touching and follow ohms law. Based on probability functions.	$r_{VR} = V_c^* P^* c^2$	r_{VR} = resistivity of the composite, V_c = volume fraction of filler, P = the probability of chain formation and c = the geometrical factor	[9]

different groups: Maxwell/Bruggeman, volume averaging, statistical percolation, and the Scarisbrick model. These four groups are described in the following section.

2.2 Maxwell/Bruggeman Models

One of the first electrical conductivity models derived for multi-phase materials was created by James Maxwell in 1881 [6]. Maxwell derived an equation relating the electrical conductivity of a particulate composite to the individual conductivities of the filler and matrix and the volume fraction of the filler. The resulting relationship, called Maxwell's equation, is shown in Equation 1:

$$\sigma_r = 1 + 3 * ((\lambda - 1) / (\lambda + 2)) * \Phi \quad \text{Equation 1}$$

where σ_r is the conductivity ratio of the composite to the matrix, λ is the conductivity ratio of the filler to the matrix and Φ is the volume fraction of filler. Equation 1 may be reduced to Equation 2 as λ decreases to zero.

$$\sigma_r = 1 - (3/2)\Phi \quad \text{Equation 2}$$

Also, Equation 1 reduces to Equation 3 as λ increases to infinity.

$$\sigma_r = 1 + 3\Phi \quad \text{Equation 3}$$

Another electrical conductivity model developed using the same variables as the Maxwell equation is the Bruggeman equation published in 1935 [6]. The Bruggeman equation is shown in Equation 4:

$$((\sigma_d - \sigma) / (\sigma_d - \sigma_m)) * (\sigma_m / \sigma)^{1/3} = 1 - \Phi \quad \text{Equation 4}$$

where σ_d is the conductivity of the filler, σ_m is the conductivity of the matrix, σ is the conductivity of the composite and Φ is the volume fraction of filler. As λ decreases to zero, the Bruggeman equation simplifies to Equation 5.

$$\sigma_r = (1 - \Phi)^{3/2} \quad \text{Equation 5}$$

As λ increases to infinity, the Bruggeman equation simplifies to Equation 6.

$$\sigma_r = (1 - \Phi)^{-3} \quad \text{Equation 6}$$

The drawback of using either the Maxwell or the Bruggeman equation is that they assume that the particles in the composite material are spherical. This is not always the case in a particulate composite as the particles will vary in shape and size in the matrix. There also will always be a fraction of the matrix volume that contains voids, inclusions, or other defects. The other assumption made in the Maxwell and Bruggeman equations is that there is no interaction between the particles. This means how the particles are distributed in the matrix is not accounted for in the model. As a result of these assumptions, the electrical conductivity of the composite becomes more difficult to predict as the volume fraction of the filler increases. The models are very inaccurate when compared to experimental data of composites with either high volume fraction filler loadings or non-spherical fillers [6].

Many scientists have tried modifying both the Maxwell and Bruggeman equations for varying applications in order to predict electrical properties more accurately. For example, Rajinder Pal created two new models based on Maxwell's equation [6]. The two equations, Pal Corrected Maxwell Equation #1 and #2, are summarized in Table 1. Pal uses a correction factor, α , in both equations to account for non-spherical shaped fillers. In the first modified Maxwell equation, it is assumed that all the volume in the matrix is 'free volume' for the conductive particles to occupy. As more conductive particles are added to the matrix, the conductivity of the composite will change

incrementally. This equation is acceptable for moderate to low filler loadings, but does not work well for high filler loadings. The reason being that as the number of particles added to the matrix increases, the amount of free volume for more particles decreases. The maximum packing loading becomes an important parameter in determining how many particles can be added into the matrix. To account for composites with high filler loadings, Pal created another model, Pal Corrected Maxwell Equation #2, and added the maximum packing volume fraction, Φ_m , as a variable [6]. The maximum packing volume fraction for spheres is 0.637. Interestingly, the Pal Corrected Maxwell Equation #2 turns into the regular Bruggeman equation when λ equals 1 and the packing factor equals 1.

A comparison of the Maxwell equation and the modified Maxwell equations are shown in Figure 2. The three models predict similar relative conductivities at low filler volume fractions, less than 0.20. However, at above a filler volume fraction of 0.2 the models begin to diverge. The relative conductivity for Maxwell's equation and Pal's Corrected Maxwell Equation #1 increases steadily up to a filler volume fraction of 1. This is because both models do not take into account the maximum packing volume fraction of the filler particles. The relative conductivity from the Pal Corrected Maxwell Equation #2 increases linearly at low volume fractions, but then displays a large increase in slope starting at around a volume fraction of 0.28. Experimental data in the literature [2] shows that the conductivity of the composite levels off at a maximum volume fraction. However, the Pal Corrected Maxwell Equation #2 does not predict this behavior. Instead, as the volume fraction of the filler gets closer to the maximum

packing volume fraction of 0.637, the conductivity of the composite is predicted to increase at a faster rate and never levels off.

Figure 2. Comparison of three different models predicting changes in relative conductivity vs filler volume fraction. M is Maxwell's equation, 1 is Pal Corrected Maxwell Equation #1 and 2 is the Pal Corrected Maxwell Equation #2 [6]. (Reprinted with permission from SAGE Publications, for full citation see References)

2.3 Volume Averaging Models

Two volume averaging models are summarized in Table 1. They are the arithmetic mean model and the geometrical mean model. Both models describe the electrical conductivity of particulate composites using the weighted averages by volume of the individual phase conductivities. The arithmetic mean model describes the conductivity of the composite when the electric field is parallel to the conductive network created by the filler [7]. The conductivity of the filler typically determines the conductivity of the composite for this model. The geometrical mean model describes the conductivity of the composite when the electric field is perpendicular to the conductive network [7]. For this model, the conductivity of the composite is typically driven by the

conductivity of the matrix. Both the geometrical and arithmetic mean models assume that a conductive path is formed at all filler volume fractions, meaning the filler particles are always in contact with each other [7]. Experimentally, this is not the case as the conductivity of a particulate composite can change drastically depending on the filler volume fraction. A plot of the resistivity as a function of filler content for a carbon black and carbon fiber filled polypropylene composite is shown in Figure 3 [10].

Figure 3. Electrical resistivity vs weight fraction of carbon black and carbon fiber filled polypropylene [10]. (Reprinted with permission from Springer, for full citation see References)

The experimental behavior for the carbon particle filled composite shown in Figure 3 is a step function. First, the resistivity of the composite changes very little at low filler loadings. Next, the resistivity decreases sharply at a specific filler content. This point is called the percolation threshold and is theoretically where a continuous conductive network is formed by the filler material [10]. The percolation threshold for

carbon particle filled composites generally occurs at higher loadings than carbon fiber filled composites since it is easier for fibers to align themselves to form a conductive path. For carbon black, the conductive network is created through agglomerations of ‘particle aggregates’ where an electrical current can flow through [11]. As the filler content increases, the resistivity of the composite continues to decrease until a minimum value is reached to complete the S curve shape. The volume averaging models do not predict the step function shaped electrical property curve since the percolation threshold of the composite is not accounted for.

2.4 Statistical Percolation Models

A statistical percolation model predicts the electrical conductivity of a composite based on the probability of particles coming in contact with one another to form a conductive path or reach their percolation threshold [8]. There are several statistical percolation models that have been created for both particle and fiber reinforced composites. One of the basic statistical models is a power law equation formulated by Kirkpatrick and Zallen [8]:

$$\sigma = \sigma_0(V-V_c)^s \quad \text{Equation 7}$$

where σ is the conductivity of the composite, σ_0 is the conductivity of the filler, V is the filler volume fraction, V_c is the filler volume fraction at the percolation threshold, and s is an exponent based on the dimensions of the filler. The critical exponent s in Equation 7 determines the slope of the curve at the percolation threshold limit. Kirkpatrick and Zallen’s model assumes that the filler particles are located in random locations in the matrix [12]. A variation of this equation was used to predict the resistivity of an

ethylene-octene carbon black filled elastomer [12]. A comparison of the experimental data with the power law model is shown in Figure 4. The solid line represents data from the power law model and shows good agreement with the experimental data at and above the percolation threshold. However, the power law model does not predict the resistivity for a composite below its percolation threshold.

Figure 4. Electrical resistivity vs percent volume fraction (v/v) of filler of ethylene-octene carbon-loaded elastomers. The solid line represents data from the statistical model [12]. (Reprinted with permission from Elsevier, for full citation see References)

Another statistical model that is used to predict the electrical behavior of particulate composites is the McLachlan model. This model is referred to as the general effective media model and is commonly used to predict the conductivity of multiphase systems where the filler has a high conductivity and the matrix has a low conductivity [6]. The disadvantage of using the McLachlan model, which is the case for all statistical models, is that the model assumes the carbon particles form discrete chains in the matrix.

This, however, is not always the case as the particles can form multiple contacts and therefore create multiple conductive paths [9].

2.5 Scarisbrick Model

The models that have been discussed so far all assume either no interaction between particles or discrete chains of the particles are formed to create the conductive pathway in the composite. Scarisbrick developed a model to account for particle to particle interaction in a composite material [9]. The model is made up of three main variables: the probability of the constituents conducting, the probability of chain formation, and a geometrical factor which factors in how the conductive chains interact with one another in the composite [9]. All three variables are functions of the volume fraction of the filler. The probability of the composite being conductive is expressed as V_c , or the volume fraction of the filler. The probability that chain formation will occur is expressed as $V_c^{V_c^{-2/3}}$. Finally, the geometrical factor can be calculated using the relationship in Equation 8:

$$V_c = 3C^2 - 2C^3 \quad \text{Equation 8}$$

where C represents the dimension of a conductive chain in the composite. For Scarisbrick's model to be accurate, the composite must have a high enough conductivity where the material will follow Ohms law [2]. In other words, the particles in the composite must be touching. Scarisbrick's model was compared with experimental data for a carbon-loaded polyethylene composite [9]. The resistivity, plotted as a function of volume fraction, is shown in Figure 5. The Scarisbrick model predicts a trend similar to the experimental data presented in Figure 5. The largest difference in the analytical

results and the experimental results appear to occur at around the volume fraction of 0.1 where the analytical results are higher in resistivity by a factor of 3 [2].

Figure 5. Comparison of experimental and analytical data based on Scarisbrick's model for a carbon-loaded polyethylene composite [9]. (Reprinted with permission from the Institute of Physics, for full citation see References)

2.6 Model Summarizing Resistivity Behavior as a Function of Strain

The previous models predicted electrical resistivity behavior of particulate composites at 0% strain. Also of interest are models which describe how resistivity changes with strain for different composites. One such model was developed by Kost *et al.* and examined the electrical resistivity-strain-time relationship of carbon black filled polymers [13]. The model was based upon a quasi-linear viscoelastic model used by Fung to predict the mechanical properties of living tissues (stress-strain-time). According to this model:

$$P = P[\epsilon(t), t] = G(t)E[\epsilon(t)] \quad \text{Equation 9}$$

where P is the electrical resistance relaxation function, ε equals the strain, t equals the time, $G(t)$ equals the reduced relaxation function and E equals the elastic response [13]. Equation 9 can then be integrated to form the following resistance-strain-time relationship:

$$\delta(t) = G(t)E[\varepsilon(0)] + \int_0^t G(t-\tau) * ((\partial E[\varepsilon(\tau)]) / (\partial \tau)) * d\tau \quad \text{Equation 10}$$

where $\delta(t)$ equals the relative resistance difference [13]. Kost *et al.* were able to formulate analytical equations for the electrical resistance relaxation function and the elastic response and compared analytical predictions to experimental data for 8 wt% and 12 wt% carbon black-loaded silicone elastomers. The results of the comparison are shown in Figure 6. The relative resistivity difference for the carbon-loaded silicone tested increases at low strains. The relative resistivity difference then peaks around 10% to 15% strain, depending on the filler volume fraction and strain rate, before decreasing slightly. The Kost model agrees well with both carbon-loaded silicones that were strained at medium to fast strain rates. Interestingly, for the slowest strain rate tested the model starts off predicting a higher relative resistivity difference value than the experimental data. However, as the strain reaches 0.30 the predicted values match with the experimental data. This lag at the slower strain rates may be the result of the model not taking into consideration the structure of the carbon black particles. The structure refers to the aggregate chains formed when carbon particles interact with one another [11]. These aggregates form agglomerations which in turn forms a conductive pathway throughout the matrix. The formations and destructions of the carbon chains dominate at low strains and will be highly dependent on the structure [14]. At slower strain rates the

structure may play a more vital role in determining how the resistivity changes due to the lower stress exerted on the interparticle connections.

Figure 6. Comparison of relative resistivity difference vs strain data of carbon black-loaded silicone at three different strain rates; 0.0667 s⁻¹(triangles), 0.0033 s⁻¹(diamonds) and 0.00033 s⁻¹(squares). Plot (a) is 12 wt% carbon black and plot (b) is 8 wt% carbon black. The data points represent the experimental data and the curve fit to the data points represent what the Kost model predicts [13]. (Reprinted with permission from John Wiley & Sons, Inc., for full citation see References)

2.7 Review of Experimental Data

As discussed in Section 2.6, Kost *et al.* conducted experiments examining the effects of strain on the electrical resistivity of carbon-loaded silicones. Other researchers also examined the effects of strain on the electrical resistivity of carbon-loaded elastomers. A summary of their investigations are presented in this section.

Verhelst *et al.* have written about the effect of morphology and structure of different carbon blacks on the electrical properties of styrene butadiene rubber (SBR) [15]. The effect of strain on the electrical resistivity of three different carbon-loaded SBR materials was also examined. Plots of the log of electrical resistivity as a function of strain for the SBR materials are shown in Figure 7. A uniaxial tension test was performed on several test specimens at a constant rate of 20 mm/min [15]. The HAF and Vulcan specimens behaved similarly over the strain range tested. The electrical resistivity for both specimens increased to a maximum point which occurred at a relatively low strain value. The electrical resistivity then steadily decreased as the strain increased. The EC Black test specimens behaved significantly differently. The electrical resistivity for these specimens remained relatively constant over the strain range tested.

The difference in electrical properties as a function of strain may be the result of the different filler loadings for each test specimen. Plots of the log of resistivity as a function of carbon black loading for the three carbon-loaded SBR specimens are shown in Figure 8. The filler loading was measured by the number of parts by weight of filler with respect to 100 parts of SBR and expressed as the units phr or per hundred parts.

Figure 7. The log of electrical resistivity plotted as a function of % extension for three different carbon black-loaded SBR materials [15]. (Reprinted with permission from Rubber Chemistry and Technology. Copyright © 2009, Rubber Division, American Chemical Society, Inc., for full citation see References)

Figure 8. The log of electrical resistivity plotted as a function of loading for three carbon black-loaded SBR materials: 1 = EC Black, 2 = Vulcan XC 72, and 3 = HAF [15]. (Reprinted with permission from Rubber Chemistry and Technology. Copyright © 2009, Rubber Division, American Chemical Society, Inc., for full citation see References)

A small filler loading of EC Black decreases the electrical resistivity of the polymer significantly. For example, the EC Black SBR polymer has an electrical resistivity of about 1 ohm-meter at a loading of 15 phr. A greater filler loading of Vulcan XC 72 and HAF is needed in order for the SBR material to reach a similar electrical resistivity as the EC Black loaded specimen. As a result, the EC Black filler material was more conductive than the other two carbon blacks at the same filler loadings. The experimentation completed by Verhelst *et al.* proved that the types of carbon black as well as the filler loading are important variables to consider when characterizing the electrical resistivity as a function of strain for carbon-loaded elastomers.

Another investigation which examined the effect of mechanical strain on the electrical resistivity of carbon-loaded elastomers was performed by Flandin *et al.* In this study the electrical properties of carbon black filled ethylene-octene or EO elastomers were examined. The electrical resistivity was measured as a function of strain for several EO test specimens and the results are shown in Figure 9. The specimens were filled with Conductex 975 Ultra carbon black at different filler loadings and tested in tension at a constant machine rate of 20% per minute [12]. As the carbon content increased in the EO elastomer, the electrical resistivity was less affected by large strains. In other words, the slopes of the curves decreased as the carbon content increased. Interestingly, the initial parts of the curves in Figure 9 were all very similar in shape as the carbon content changed. The differences in the trends became apparent at around 50% strain.

Figure 9. The effect of carbon black loading on the electrical resistivity as a function of percent strain for EO elastomers [12]. (Reprinted with permission from Elsevier, for full citation see References)

Flandin *et al.* also tried to model the electrical resistivity changes with strain by defining the trends into four distinct regimes as summarized in Figure 10 [12]. The four regimes were labeled the following; initiation, reversible, recoverable damage and depercolation. The initiation stage occurs roughly from 0% to 3% strain where the electrical resistivity increases significantly. Flandin *et al.* attributed this increase to breakage of the carbon black network [12]. The reversible stage occurs roughly from 3% to 20% strain where the electrical resistivity decreases significantly to a minimum value. Flandin *et al.* did not observe irreversible electrical properties of the EO material in this regime during cyclic testing [12]. The next stage, called the recoverable damage regime, occurs between 20% to 600% strain. Up to 100% elongation the properties of the EO material can be recovered, but above 100% elongation will cause permanent damage to the EO material [12]. Finally, the last regime is depercolation which occurs above 600%

elongation. In this regime the percolating structure completely breaks down and the material loses its conductivity.

Figure 10. Identification of four different stages in the electrical resistivity behavior as a function of strain for an EO composite with a carbon black volume fraction of 20% [12]. (Reprinted with permission from Elsevier, for full citation see References)

2.8 Summary of Literature Review

Several mathematical models have been formulated to help understand the electrical resistivity behavior of particulate composites. Only one model that describes how resistivity changes with strain, for a composite material, was found. However, several investigators have carried out experiments examining the effects of strain on the electrical resistivity of carbon-loaded elastomers. These authors focused on examining the change in resistivity of the composite over a large strain range. There is a gap in the literature in understanding how small strains affect the electrical resistivity properties of carbon-loaded elastomers. Also, previous researchers focused on characterizing the behavior of carbon black-loaded composites and did not look at the effects of adding

graphite particles to the composite. Finally, only Kost *et al.* measured the electrical resistivity as a function of strain for a carbon-loaded silicone material. As a result, this research will focus on understanding the effects of small strains on the electrical resistivity of carbon-loaded silicone materials.

CHAPTER THREE

RESEARCH OBJECTIVES

3.1 Hypothesis

The effects of strain on the electrical resistivity of carbon-loaded elastomers have been investigated in the literature. The results from the experimentation in the literature showed that large strains significantly changed the electrical resistivity of the carbon-loaded elastomer material. Based on these findings, it was hypothesized that the resistivity of carbon filled silicone elastomers will change appreciably at low strain values as well.

3.2 Research Objectives

The main objective of this research was to characterize the electrical resistivity behavior of carbon filled silicone elastomers in the strain range of 0% to 10%. To accomplish this objective, several specific research objectives were defined. The first was to measure the electrical resistivity of two different carbon-loaded elastomers under a constant rate of tension. The second objective was to determine the effect of strain rate and hysteresis on the electrical resistivity of the composite specimens. The third objective was to compare the electrical resistivity of unstrained specimens to the values predicted by the mathematical models reported in the literature.

CHAPTER FOUR

EXPERIMENTAL MATERIALS AND METHODS

4.1 Experimental Approach Overview

The electrical resistivities of two different carbon particle loaded silicone elastomers were evaluated in tension at a constant rate of strain. The test matrix that was followed for the two different composite materials is summarized in Table 2. The SC-

Table 2. Test matrix used to evaluate the change in electrical resistivity as a function of strain for two carbon-loaded silicone materials [16, 17].

Vendor Information	Specimen Description	Volume Resistivity (ohm-m)	Uniaxial Tension Test @ 0.10 inch/min (# of specimens)	Uniaxial Tension Test @ 0.05 inch/min (# of specimens)	Uniaxial Tension Hysteresis Test @ 0.10 inch/min (# of specimens)
Tecknit P/N: SC-Consil-86-10041	Silicone elastomer filled with carbon particles thickness = 0.125 in	0.08	10	10	2
Chomerics P/N: CHO-SEAL 40-50-0505-6370	Silicone elastomer filled with nickel coated graphite particles. thickness = 0.125 in	0.001	3	NA	1

Consil and CHO-SEAL materials were chosen for this study because they are both established products produced by two of the largest US companies which make EMI shielding conductive elastomers, Tecknit and Chomerics. The goal was to use off-the-shelf materials for the experimentation to ensure the conductive elastomer product was

made in a manufacturing environment and variables such as dispersion of the conductive particles in the matrix are provided for. The number of specimens that were tested for each experiment is also shown in Table 2. In the first two experiments, both materials were strained uni-axially in tension at two different cross-head speeds, 0.10 inch/min and 0.05 inch/min. The electrical resistance was measured at different load intervals and used to compute the electrical resistivity of the material. The third experiment was a hysteresis test which tested how the electrical resistivity changed for a specimen that was strained in tension multiple times. The experimental procedure and data analysis for each experiment are discussed in this chapter. Finally, the procedures used to determine the particle size and volume percent of the fillers in the SC-Consil-861 are described.

4.2 Specimen Materials and Preparation

Two 12 inch x 12 inch x 0.125 inch molded sheets of the SC-Consil-861 material were procured for testing. Both sheets were ordered at the same time and were assumed to be from the same batch of material. The SC-Consil-861 specimens contained carbon particles dispersed in a silicone elastomer. Only one 5 inch x 5 inch x 0.125 inch molded ‘sample’ sheet of the CHO-SEAL 6370 was procured from Chomerics for testing due to a large minimum order requirement. The CHO-SEAL 6370 specimens contained nickel coated graphite particles dispersed in a silicone elastomer. The 0.125 inch thickness was chosen so that the specimens would be easier to handle during tension testing. Tensile specimens were die cut in ‘dogbones’ using die C called out in the test method. Before performing the experiments, each test specimen’s thickness was measured in the gauge length using calipers and recorded.

4.3 Description of Experimental Procedure

The test specimens, described in Section 4.2, were pulled uni-axially in tension following ASTM D412 for elastomers. The mechanical tension testing for the experimentation was performed at SJSU on a 33R4204 INSTRON tester. The electrical resistance for each specimen was measured using a Fluke 114 ohmmeter while the specimen was pulled in tension. The experimental set-up is shown in Figures 11, 12 and 13. An overall view of the test apparatus is shown in Figure 11. An angled view illustrating the different equipment used is shown in Figure 12. A close-up view of a specimen ready to be tested is shown in Figure 13.

A one inch distance was marked off in the gauge length of each test specimen where alligator clips from the ohmmeter were attached. The electrical resistance was measured through the volume of the specimen between the two alligator clips. Drill bits, to be used as markers on a measuring scale as shown in Figure 13, were bonded onto the alligator clips. The top edge of the bottom drill bit and the bottom edge of the top drill bit marked the distance traveled by the specimen during the tension test. The drill bits were visually checked to be straight and parallel and lined up over the scale, roughly an inch apart, prior to starting the experiment. A 25 pound load cell set at 5 pounds was used for accurate load measurements during the experiments. A V/E-20A digital strain indicator was used to record the output from the load cell. The indicator was calibrated using a 1 pound weight on the top grip area and was adjusted so that the 1 pound weight would register close to 1000, as shown in Figure 14.

Figure 11. Photograph of overview of experimental set-up.

Figure 12. Angled view of experimental set-up showing a specimen ready to be tested.

Figure 13. Close-up view of test specimen with drill bit markers, scale, and ohmmeter in the background. The electrical resistance was measured through the volume of the specimen using the alligator clips from the ohmmeter.

Figure 14. Photograph showing the calibration of the digital strain indicator. A one pound weight, shown above the top grip, gives a value of 0.998 lbs on the strain indicator.

Once the experiment started, electrical measurements were taken at 0.1 pound load intervals, up to 2 pounds, for each test specimen. This small measuring interval allowed for the determination of how sensitive the specimen's electrical properties were to small strains. In order to record the change in extensions of the specimens during the loading, the experiments were videotaped and transferred onto a mini-DVD using a Sony

camcorder. The camcorder was set-up on a tripod and placed as close to the INSTRON as possible. The camcorder was zoomed into the specimen, scale, and ohmmeter at the highest resolution possible, to read both length changes and resistance values. An example of a still image of a specimen being recorded during testing is shown in Figure 15. An ohmmeter was placed on top of a support structure behind the specimen so that the digital screen could be read in between the markers in the video. Load increments of 0.1 lbs were called out in the video as a point of reference to record data points. The scale used to measure the extensions had increments down to 0.01 inch; therefore, data points were recorded to the nearest 0.01 inch. The changes in length were documented when the markers clearly moved from one 0.01 increment to another.

The use of the scale and video equipment was determined to be the best and most convenient method to measure strain and electrical resistance of the test coupons at low extensions. A mechanical contact extensometer is typically used for particle filled elastomers to measure strain and construct a stress-strain curve. However, the goal of this study was to examine the effects of electrical resistivity at low strains that are less than 10%. It has been shown in the literature [18] that a mechanical extensometer is not very sensitive to small changes in strain. Also, a contact extensometer would be difficult to isolate from the test specimen and not influence the electrical resistance measurements. A video or laser extensometer would be good choices for this type of specimen and experiment, but they are very expensive to purchase and were not available for use. The test set-up utilized was cost effective and provided repeatable results.

Figure 15. Photograph of a specimen being tested. This is a still image from a video of one of the experiments performed.

4.4 Data Analysis for Uniaxial Tension Testing

Once the electrical resistance and thickness measurements had been measured and compiled for each specimen, the electrical resistivity was calculated. The electrical resistivity can be calculated using the following equation:

$$\rho = RA/L \quad \text{Equation 11}$$

where R is the electrical resistance, L is the length of the specimen, and A is the cross sectional area where the electrons will flow through [19]. However, this equation accounts for changes in electrical resistivity due to length changes as well as changes to the electron path created by the conductive particles [5, 20]. For example, as L increases,

A decreases and the electrical resistivity will decrease regardless of what is happening to the conductive particles in the composite matrix. In order to determine how the electrical resistivity of the specimen behaves due to only changes in the conductive filler, another equation needs to be utilized. Kost *et al.* assumed the volume change to be constant for a carbon-loaded silicone specimen, when loaded in tension [20]. The following relationship was used to determine electrical resistivity:

$$\rho = (RV_o)/(L_o^2(1+\epsilon)^2) \quad \text{Equation 12}$$

where R is the electrical resistance, V_o is the initial volume, L_o is the initial length, and ϵ is the strain [20]. This equation was assumed to be valid for this study especially since the test specimens would not be strained more than 10% and the volume of the specimens should remain relatively constant.

Once the electrical resistivity data were analyzed, the data were plotted. For each test specimen, the electrical resistivity calculated from Equation 12 was plotted as a function of strain. An example of a plot of the data is shown in Figure 16. The change in electrical resistivity from 0% to 10% strain was also calculated based on these plots, and compared to one another. The data collected for each specimen included the load, electrical resistance, top marker scale reading and bottom marker scale reading. All data points, calculations, and individual plots for each specimen were organized on separate spreadsheets.

Figure 16. Example of electrical resistivity plotted as a function of percent strain for SC-Consil-861 specimen #1 at 0.1 inch/min cross head speed.

4.5 Procedure Used to Perform Hysteresis Testing

Hysteresis testing was performed for both conductive composites to determine if low strains would induce irreversible changes in the electrical properties of the material. Test specimens were first strained to a load of about 2 pounds and then unloaded. After a predetermined period of time, they were loaded again. The SC-Consil-861 specimens were tested three times. The first test was performed in the as-received condition, the second test was performed after 72 hours of aging and the third test was performed after 162 hours of aging. However, due to experimental errors, the second test results were not evaluated and only the first and third test results were reported. The CHO-SEAL

specimen was tested four times. Because there was limited CHO-SEAL 6370 material to test, specimen #2 from the uniaxial tension testing was reused in the hysteresis testing. The data from the uniaxial tension testing for specimen #2 was used as the first test in the as-received condition. The second, third and fourth tests were performed 1848 hours, 1920 hours and 2010 hours after the first test was completed. The electrical resistivity was plotted as a function of strain for all tests and compared to one another after the different time periods.

4.6 Procedure of SEM Analysis

Scanning electron microscopy (SEM) was used to determine how well the filler particles were distributed in the silicone for select SC-Consil-861 and CHO-SEAL 6370 specimens. A cross section was cut from each specimen using a razor blade and subsequently sputter coated with gold to improve the image quality. The specimens were examined under an environmental scanning electron microscope using secondary electrons.

4.7 Procedure to Determine Volume Fraction of Filler

The volume fraction of filler for SC-Consil-861 was measured for two reasons. One, the volume fraction of filler was an input variable for the theoretical models. Two, verification that carbon black was the filler in the SC-Consil 861 material was needed. The volume fraction was determined using the weight fraction of filler and then calculating the volume fraction using the densities of the constituents. Specimen #9, which was tested at the 0.1 inch/min cross head speed, was submitted for testing to Akron Rubber Development Laboratory (ARDL). ARDL determined the weight fraction of

carbon black in the silicone elastomers, following ASTM D 297-93. The specimen was pyrolyzed in a nitrogen atmosphere and the residue left over was cooled to room temperature and weighed. The carbon black was then burned off in an air atmosphere and the residue left over was weighed. The weight of carbon black is the weight of residue left over after the pyrolysis in nitrogen minus the weight of residue left over after the pyrolysis in air. Once the weight fraction was determined, the volume fraction of carbon black was determined by using the density and weight fractions for each constituent.

4.8 Procedure to Determine Particle Size of Filler

The particle size distribution of the filler used in SC-Consil-861 and CHO-SEAL 6370 was quantified by the University of Minnesota Characterization Facility using X-ray diffraction. The parameters used in the X-ray diffraction instrument are summarized in Table 3. Three specimens were characterized using XRD; two SC-Consil-861 specimens and one CHO-SEAL 6370 specimen. The test specimens were examined in two directions, as shown in Figure 17. It was discovered during testing that the filler particles were easier to observe in the perpendicular direction. As a result, the filler particle size was determined by examining the specimen in this direction. For each specimen, the intensity of the diffraction pattern was measured and plotted against two-theta. The resulting plot was then fitted using a software program. The area underneath the fitted curve was then reported as the particle size distribution. An average particle size was estimated based on which two-theta value recorded the highest intensity value.

Table 3. Summary of X-ray diffraction parameters used to determine particle size of fillers [21].

	Power	Collimator	Start/Stop Angle	Step Size	Counts
XRD Parameters	50Kv, 100mA	0.8 mm	10°/90°	0.06	600s per frame

Figure 17. Schematic explaining how the specimens were examined under XRD [21].

CHAPTER FIVE

RESULTS

5.0 Overview of Results

The electrical resistivity was calculated and plotted as a function of strain for the SC-Consil and CHO-SEAL materials based on the experimental procedures described in Chapter Four. The experimental data for the SC-Consil 861 material varied significantly from specimen to specimen. The data scatter was attributed to the variation in the distribution of the filler particles for each specimen. As a result of the scatter in the data, the effect of strain rate on the SC-Consil 861 specimens could not be determined. The experimental data for the CHO-SEAL 6370 material was consistent from specimen to specimen. The electrical resistivity for the CHO-SEAL 6370 material increased as the strain increased to 2%. From 2% strain to 10% strain, the electrical resistivity for the specimens decreased to about 3×10^{-7} ohm-m. Hysteresis in electrical resistivity behavior was observed in both materials tested in the initial electrical resistivity-strain curve. Finally, the Scarisbrick model proved to be the most accurate model predicting electrical resistivity values for the SC-Consil-861 specimens in the unstrained condition.

5.1 The Effect of Strain on Electrical Resistivity for SC-Consil-861 at 0.1 inch/min

A plot of electrical resistivity as a function of strain for SC-Consil-861 specimens at 0.1 inch/min cross head speed is shown in Figure 18. The results show a large scatter of electrical resistivity from specimen to specimen. The initial electrical resistivity data range from 5.5×10^{-5} ohm-m to 7.5×10^{-5} ohm-m. The final electrical resistivity, at

Figure 18. Electrical resistivity plotted with strain at 0.1 inch/min for SC-Consil-861.

roughly 10% strain, ranges from 9.5×10^{-5} ohm-m to 7.5×10^{-5} ohm-m. The common trend exhibited an increase in electrical resistivity followed by the electrical resistivity leveling off to a relatively constant value. The magnitude of the electrical resistivity increase in the beginning of the experiment varied from specimen to specimen. Some specimens showed a steep initial electrical resistivity increase, while others exhibited more of a gradual transition. The extremes in electrical resistivity behavior are shown in Figure 19. The electrical resistivity for specimen #8 increased sharply over the entire strain range and did not level off. The electrical resistivity for specimen #9 increased slightly up to 4% strain and then began to level off. The results shown in Figure 20 illustrate that the change in electrical resistivity varies from specimen to specimen. For

example, the change in electrical resistivity for specimen #8 was almost 80%, while the change in electrical resistivity for specimen #9 was around 10%.

Figure 19. Illustration of extremes of electrical resistivity vs % strain behavior for SC-Consil-861 tested at 0.1 inch/min.

Figure 20. Percent change in electrical resistivity from 0%-10% strain for 0.1 inch/min SC-Consil-861 specimens.

The logical question is why did the electrical resistivity data vary significantly from specimen to specimen? To answer this question, properties of the filler in the matrix need to be examined. The results from the weight fraction determination of the filler in SC-Consil-861 showed that there were both carbon black and graphite particles in the silicone elastomer. The volume fractions of the fillers in SC-Consil-861 are presented in Table 4. The total volume fraction of filler (carbon black + graphite) in SC-Consil-861 was 21.07%. This material was not expected to contain graphite as well as carbon black particles. Since both fillers will contribute to the electrical resistivity of the composite, both fillers need to be distributed evenly across the composite sheet. If the distribution of the composition of the filler particles varies from specimen to specimen, this could result in significantly different electrical resistivity measurements.

Table 4. Percent volume fraction of carbon and graphite fillers in SC-Consil-861.

% Volume fraction of carbon black in SC-Consil-861	% Volume fraction of graphite in SC-Consil-861
15.21	5.86

Filler particle size is also an important factor in determining the consistency of the material's electrical properties [14, 20]. For example for carbon black particles, the smaller the particle size, the lower the electrical resistivity [15]. Carbon black particles form complicated aggregate structures which can vary in structure based on the composite manufacturing process [14]. The distance between each of these aggregates (interaggregate distance) and how they align to each other determines the bulk electrical

resistivity of the composite [14]. Small changes in the interaggregate distance will affect the electrical resistivity of the composite [15]. Furthermore, how well the particle size distribution is controlled will also determine how much the interaggregate distance will vary. This variation will affect the electrical resistivity of the composite and how it behaves under strain. X-ray diffraction was used to characterize the particle size distribution for SC-Consil-861 specimen #8 and specimen #9 in the 0.1 in/min experimentation. A trimodal distribution for the filler particles used in SC-Consil-861 is shown in Figures 21 and 22. This shows the particle size was not controlled within a tight range and that the average particle size varied from specimen to specimen. The variation in particle size caused the initial electrical resistivity and electrical resistivity under strain to vary because the interaggregate distances change. The other item of interest from the XRD results was that an average particle size of 1992 angstroms was calculated for specimen #8 which was lower than the average particle size of > 5000 angstroms calculated for specimen #9. The lower particle size explains why specimen #8 has a lower initial electrical resistivity than specimen #9. This difference in electrical properties can be seen in the 0% strain electrical resistivity values shown in Figure 23.

To determine if the distribution of the filler particles varied for different SC-Consil-861 specimens, SEM images were taken. SEM images of the cross sections for specimens 3, 5, 8, and 9 are shown in Figures 24, 25, 26 and 27. The bright areas in the SEM images are filler particles in the resin matrix. Figures 24 and 25 both show the filler to be very evenly distributed throughout the matrix. Clear connections between clusters of filler particles can be seen for both specimen #8 and specimen #6. The filler is not as

Figure 21. Particle size distribution of SC-Consil-861 specimen #9 tested at 0.1 inch/min [21].

Figure 22. Particle size distribution of SC-Consil-861 specimen #8 tested at 0.1 inch/min [21].

Figure 23. Electrical resistivity values at 0% strain for 0.1 inch/min SC-Consil-861 specimens.

Figure 24. SEM image of SC-Consil-861 specimen #8 tested at 0.1 inch/min using secondary electrons.

Figure 25. SEM image of SC-Consil-861 specimen #5 tested at 0.1 inch/min using secondary electrons.

Figure 26. SEM image of SC-Consil-861 specimen #3 tested at 0.1 inch/min using secondary electrons.

Figure 27. SEM image of SC-Consil-861 specimen #9 tested at 0.1 inch/min using secondary electrons.

well distributed in the matrix for specimens shown in Figures 26 and 27. There are larger “black” areas in these specimens where no clusters of particles exist.

Properties of the SC-Consil-861 specimens tested at 0.1 in/min are summarized in Table 5. The table contains a summary of the filler distribution determined from SEM images, filler size, and electrical resistivity values for specimens #3, #5, #8, and #9. The specimens that had good filler distribution also exhibited high percent changes in electrical resistivity.

Table 5. Comparison of properties of SC-Consil-861 specimens tested at 0.1 inch/min.

Specimen #	Initial Electrical Resistivity (ohm-m)	% Change in Resistivity	Average Filler Particle Size (micrometers)	Filler Particle Distribution from SEM Analysis
3	NA	36	NA	Not well distributed
5	NA	55	NA	Very well distributed
8	5.52×10^{-5}	77	0.2	Very well distributed
9	6.75×10^{-5}	9	> 0.5	Not well distributed

5.2 The Effect of Strain on Electrical Resistivity for SC-Consil-861 at 0.05 inch/min

A plot of electrical resistivity as a function of strain for SC-Consil-861 specimens at 0.05 in/min cross head speed is shown in Figure 28. The results presented in Figure 28 show a large scatter in data from specimen to specimen. The specimens appear to cluster in two major groups. One group, specimens #3, #4, #8, and #9, displayed a very small increase in electrical resistivity from 0%-10% strain. The electrical resistivity for these specimens leveled off very quickly. The second group, specimens #1, #5, #6, #7, and #10, showed a more significant increase in electrical resistivity over the strain range. Also, the electrical resistivity for some of the specimens did not appear to level off at 10% strain. There was one outlier data point, specimen #2, the behavior of which matched that of the second group. The initial electrical resistivity, at 0% strain, for specimen #2 was 1.05×10^{-4} ohm-m which is 2×10^{-5} ohm-m higher than the next closest specimen. Upon further inspection it was discovered that the thickness for specimen #2

Figure 28. Electrical resistivity plotted with strain at 0.05 inch/min for SC-Consil-861.

was around 0.126 inch which was significantly higher than the average thickness for all specimens tested, 0.115 inch. This difference in thickness will increase the area over which the electrical resistance is being measured and consequently increase the electrical resistivity. Including specimen #2, the extremes in electrical resistivity behaviors from the 0.05 inch/min experimentation are shown in Figure 29. The electrical resistivity for specimen #5 increased sharply over most of the strain range and appears to level off at around 10% strain. The electrical resistivity for specimen #9 increased only slightly over the strain range and does not appear to be sensitive to low strains. The results summarized in Figure 30 also show that the change in electrical resistivity varies from specimen to specimen.

Figure 29. Illustration of extremes of electrical resistivity vs % strain behavior for SC-Consil-861 tested at 0.05 inch/min.

Figure 30. Percent change in electrical resistivity from 0%-10% strain for SC-Consil-861 at 0.1 inch/min.

To determine if the distribution of the filler particles varied for the extreme SC-Consil-861 specimens tested at 0.05 inch/min, SEM images were taken. A SEM image of the cross sectional area of specimen #5 is shown in Figure 31. The filler particles appear to be combined into several larger clusters and are well distributed throughout the matrix. As a result, the electrical resistivity for specimen #5 is sensitive to small strains. A SEM image of the cross sectional area of specimen #9 is shown in Figure 32. The filler particles in this image appear to form smaller clusters and are not as well distributed throughout the matrix. As a result, the electrical resistivity for specimen #9 is not as sensitive to small strains as specimen #5.

Figure 31. SEM image of SC-Consil-861 specimen #5 tested at 0.05 inch/min using secondary electrons.

Figure 32. SEM image of SC-Consil-861 specimen #9 tested at 0.05 inch/min using secondary electrons.

5.3 The Effect of Strain Rate on Electrical Resistivity for SC-Consil-861

The electrical resistivity as a function of strain for both 0.1 inch/min and 0.05 inch/min SC-Consil-861 specimens has been discussed in Section 5.1 and Section 5.2. One of the experimental objectives was to determine whether the strain rate affects the electrical resistivity of the composite. If the strain rate changes, the rate at which the conducting chains are formed or destroyed can be expected to change. As a result, the sensitivity of the composite's electrical resistivity to strain should also change. To determine if this behavior is true for the experimental data, two plots of data for both 0.1

inch/min and 0.05 inch/min experiments that had similar initial electrical resistivities were compared. These graphs are shown in Figure 33.

Figure 33. Comparison of electrical resistivity vs % strain results tested at 0.1 inch/min and 0.05 inch/min.

The two specimens chosen from the 0.1 inch/min experimentation behaved similarly, while the two specimens chosen from the 0.05 inch/min experimentation did not. When compared to one another, the scatter of the 0.05 inch/min data was prominent. As illustrated in the previous section, the electrical resistivity for the 0.05 inch/min specimens were either very sensitive to strain or were not. Three of the specimens exhibited a similar trend to one another as the electrical resistivity increased with strain. However, the fourth test specimen, #10, behaved significantly different as the electrical resistivity increased at a faster rate with strain than the electrical resistivity of the other

three specimens. It was not possible to determine the strain rate sensitivity of electrical resistivity within the scope of this project.

5.4 The Effect of Strain on Electrical Resistivity for CHO-SEAL-6370 at 0.1 inch/min

The results from the CHO-SEAL 6370 experiments are presented in Figure 34.

Figure 34. Electrical resistivity plotted with strain for CHO-SEAL-6370 at 0.1 inch/min.

The change of electrical resistivity with strain for CHO-SEAL 6370 was consistent from specimen to specimen. The electrical resistivity first increased sharply during the initial strain of the specimen. Then, the electrical resistivity decreased to roughly the 0% strain resistivity value. The electrical resistivity behavior and the consistency of the data were remarkably different than the data recorded for the SC-Consil-861 material. This occurred mainly because of three reasons. First, the initial electrical resistivity of the nickel plated graphite loaded CHO-SEAL 6370 was lower than the initial electrical

resistivity of the carbon and graphite loaded SC-Consil-861. The electrical resistivity at 0% strain for the three CHO-SEAL-6370 specimens is summarized in Table 6. Second,

Table 6. Electrical resistivity of CHO-SEAL-6370 test specimens at 0% strain.

CHO-SEAL-6370 Specimen #	Electrical Resistivity (ohm-m)
1	0.00074
2	0.00059
3	0.00074

the distribution of the nickel plated graphite filler was much more uniform in the matrix than the graphite and carbon fillers in the SC-Consil-861. This can be verified by comparing SEM images taken of the cross sections of the specimens. A SEM image taken of a CHO-SEAL 6370 specimen in the as-received or unstrained condition is shown in Figure 35. This image portrays the filler material to be evenly distributed

Figure 35. SEM image of CHO-SEAL 6370 specimen in the as-received condition using secondary electrons.

through-out the matrix, creating numerous electrical paths. Lastly, the shape of the nickel plated graphite particles was not spherical like carbon black. Many of the particles were longer in one direction than another and were shaped similar to a short rod. A SEM image taken of a CHO-SEAL 6370 specimen after it was strained is shown in Figure 36.

Figure 36. SEM image of CHO-SEAL 6370 specimen after being strained using secondary electrons.

The filler particles shown in this image are more clustered together than in the image shown in Figure 35. As the CHO-SEAL 6370 specimen is stretched to 10% strain the filler particles tend to become more aligned and clustered together. This behavior results in the electrical resistivity of the composite to decrease.

The results from the X-ray diffraction analysis for the CHO-SEAL 6370 material are shown in Figure 37. Only one peak was found in the X-ray diffraction analysis

indicating a unimodal distribution of the particles. Two sieves were most likely used, +60 mesh and -65 mesh, to keep the filler particle size controlled in a tight range. The CHO-SEAL product was definitely produced by a more controlled manufacturing process, compared to the SC-Consil-861 material, which resulted in more consistent experimental data.

Figure 37. Particle size distribution of CHO-SEAL 6370 tested at 0.1 inch/min [21].

5.5 The Effect of Hysteresis on the Electrical Resistivity

The results from the hysteresis testing performed on both SC-Consil and CHO-SEAL materials are presented in this section. The effect of strain on electrical resistivity for two different SC-Consil-861 specimens, before and after aging for 6 days, is shown in Figures 38 and 39. The initial electrical resistivity for both specimens increased when they were tested after six days. The rate of increase of electrical resistivity during the initial strain also decreased for both specimens when tested after the six day period.

Figure 38. Hysteresis testing of SC-Consil-861 specimen #1 at 0.1 inch/min.

Figure 39. Hysteresis testing of SC-Consil-861 specimen #2 at 0.1 inch/min.

These differences may be the result of permanent damage occurring in the aggregate network of carbon particles after the first test. However, both specimens approached similar electrical resistivity values at 10% strain before and after aging. The hysteresis seen in both SC-Consil-861 specimens was small and was observed in only the initial part of the electrical resistivity-strain curve.

The effect of strain on electrical resistivity for the CHO-SEAL 6370 material before and after several aging periods is shown in Figure 40. The peak electrical

Figure 40. Hysteresis testing of CHO-SEAL 6370 at 0.1 inch/min.

resistivity value, at around 2% strain, significantly decreased when tested after 1848 hours or the first aging period. This behavior signifies that the specimen had undergone a

‘permanent set’ in its electrical properties. Subsequent tests run on the specimen show that the trends are very similar after the first aging period. It appears that the permanent change reflected in the testing performed after 1848 hours does not get worse after more testing iterations.

5.6 Electrical Resistivity Predictions Based on Theoretical Models

The electrical resistivity values at 0% strain were calculated for the SC-Consil-861 material using 7 different models. The parameters needed to calculate these values are summarized in Table 7. In the filler volume fraction determination test, two fillers

Table 7. Table of properties needed for modeling of the SC-Consil-861 material

Constituent	Volume Fraction	Electrical Resistivity (ohm-m)	Electrical Conductivity (ohm ⁻¹ m ⁻¹)	λ (Conductivity ratio of filler to silicone)	Assumptions
Carbon black [1]	0.1521	0.01	100	1.00E+15	Typical Furnace carbon black powder
Graphite [21]	0.0586	0.00005	20000	2.00E+17	Graphite flakes
Silicone [19]	0.7893	1E+13	1E-13	NA	Elastomer

were discovered to be used to lower the electrical resistivity of the SC-Consil-861 material: carbon black and graphite particles. The properties of the constituents were found in the literature based on the assumptions summarized in Table 7. For instance, there are many types of carbon blacks sold on the market and it was assumed the carbon black used in the SC-Consil-861 material was a typical furnace carbon black powder with a resistivity of 0.01 ohm-m. To understand the impact of each of the two fillers on the

electrical properties of the material, the electrical resistivity was predicted using the carbon black as the filler and also as graphite as the filler.

The results from the electrical resistivity calculations for the seven different models are displayed in Table 8. The McLachlan model was not used since the percolation threshold and critical exponent, t , of the SC-Concil-861 material were not known. The results from the models in Table 8 were compared against the 0% strain electrical resistivity experimental results summarized in Table 9. The electrical resistivity predicted from the Maxwell and Bruggeman equations were both very similar for the carbon black and graphite filled scenarios. However, both models predicted very high electrical resistivities, approximately 6×10^{12} ohm-m for the carbon black filled silicone and approximately 8×10^{12} ohm-m for the graphite filled silicone. The measured electrical resistivity for SC-Consil-861, as shown in Table 8, is around 6 to 7×10^{-5} ohm-m. The reason these models were inaccurate was because they do not take into consideration the interaction of the particles in the matrix. These models have been

Table 8. Electrical resistivity results from seven particulate composite models using carbon black and graphite as the fillers.

Equation Name	Predicted Electrical Resistivity, Carbon Black Filler (ohm-m)	Predicted Electrical Resistivity, Graphite Filler (ohm-m)
Maxwell's Equation	6.87E+12	8.50E+12
Bruggeman Equation	6.10E+12	8.34E+12
Pal Corrected Maxwell Equation #1	6.34E+12	8.39E+12
Pal Corrected Maxwell Equation #2	5.94E+12	8.32E+12
Arithmetic Mean	0.0657	8.53E-04
Harmonic Mean	7.89E+12	7.89E+12
Scarisbrick	1.24E-05	8.63E-12

Table 9. Average electrical resistivity data for 0.1 inch/min and 0.05 inch/min SC-Consil-861 specimens.

Specimens Tested	Experimental Electrical Resistivity Data (ohm-m)	Standard Deviation
Average Value of SC-Consil-861 Specimens Tested at 0.1 inch/min	6.41E-05	6.30E-06
Average Value of SC-Consil-861 Specimens Tested at 0.05 inch/min	7.67E-05	1.25E-05

shown to be acceptable for low filler loadings and for composites where the electrical resistivity was much higher than the SC-Consil-861 [9]. The Pal corrected equations predicted similar electrical resistivities as the Maxwell and Bruggeman models. These corrected equations may be more accurate if a more representative correction factor was used for the particle shape. However, the Pal corrected equations still do not factor in how the conductive chains in the matrix are formed and distributed. The electrical resistivity predicted by the arithmetic mean model was much closer to the experimental data than the Maxwell and Bruggemen model predictions. The arithmetic mean model predicted an electrical resistivity value of 0.0657 ohm-m for the carbon black filled silicone which was about 1000 ohm-m higher than the experimental data. The same model also predicted an electrical resistivity value of 8.53E-04 ohm-m for the graphite filled silicone which was only about an order of magnitude higher than the experimental data. As expected, the electrical resistivity predicted by the harmonic mean was not as accurate. The harmonic mean assumes the electrical properties of the composite are mainly controlled by the electrical resistivity of the matrix, which is not the case for carbon-loaded silicones [7]. Finally, the Scarisbrick model predicted the most accurate

electrical resistivity data of all seven models. A comparison of the Scarisbrick model with the experimental data is shown in Table 10. The electrical resistivity predicted for the carbon black-loaded silicone was within an order of magnitude of the experimental data. The Scarisbrick model uses a geometrical factor and a probability function to determine the electrical resistivity of the composite. Both of these variables help the model predict the formation of conductive paths in the matrix and as a result yield accurate predicted results of a composite's electrical resistivity.

Table 10. Comparison of Scarisbrick predicted electrical resistivity results vs experimental electrical resistivity data for SC-Consil-861.

	Electrical Resistivity, Carbon Black Filler (ohm-m)
Scarisbrick Predicted Value	1.24E-05
Average Value of SC-Consil-861 Specimens Tested @ 0.1 inch/min	6.41E-05
Average Value of SC-Consil-861 Specimens Tested @ 0.05 inch/min	7.67E-05

CHAPTER SIX

DISCUSSION

The following section examines the accuracy of the results presented in Chapter 5. The potential sources of error from the experimental methodology and errors contributed from the test specimen material are reviewed. Next, a comparison between the experimental data and literature for carbon-loaded silicones is presented. The electrical resistivity behavior of the CHO-SEAL 6370 test specimens is also characterized by examining the arrangement of the nickel-coated graphite particles in the composite. Finally, the characteristics of an ideal sensor material are discussed.

6.1 Sources of Error

The largest source of error from the experimentation comes from the determination of strain for each test specimen. As mentioned in Chapter 4, the electrical resistance was recorded at increments of 0.1 pounds. However, the length measurements could be made only to the nearest 0.01 inch using a scale and video camera. A new length change was recorded only when the top edge of the bottom marker or the bottom edge of the top marker reached a new 0.01-inch hash mark. This was determined by watching the video on a DVD player, pausing the video, and visually determining where the markers were located on the scale. This method of strain measurement is dependent on the interpretation of the person recording the data. In order to minimize the error involved, a consistent process was developed to record the data for each specimen.

Another error in the strain measurements came from how straight the markers were throughout the experimentation. Although the markers would start off straight and

parallel to each other, they had a tendency to move upwards during the experimentation. This was true for the bottom marker as the load approached 2 pounds. If the angle of the marker changed enough to skew the data, the test specimen was removed from the test matrix and not added to the experimental data.

Another measurement made in the experimentation was the electrical resistance. Electrical data were recorded to the nearest tenth of an ohm using an ohmmeter. Metal alligator clips were applied on the silicone specimens at roughly one-inch hash marks. This distance changed slightly from specimen to specimen and varied mostly from 0.98 inch to 1.02 inch. Gauge length distances of 0.93 inch were recorded for two test specimens, but the results from both specimens were close to the average.

An additional error associated with electrical resistance measurements is inherent in the method itself. A basic 2-point probe ohmmeter was used to measure electrical resistance through the volume of the specimen. The two probes used pick up the electrical resistance of the specimen it is attached to as well as a resistance where the probes make contact to the specimen or contact resistance. The contact resistance causes slight errors in the specimen's resistance readings. It was assumed for the current study that the contact resistance is much smaller than the resistances measured for the carbon-filled specimens. One way to avoid this error in future work is to use a four-point probe, which uses two extra probes to eliminate the effect of contact resistance in the resistance measurement [2].

Experimental error was also associated with the specimen dimensions. The test specimens used were die cut out of a flat molded sheet. The die used ensured the

specimen geometry was consistent and accurate for each specimen. However, the thickness of the test specimen could vary depending on where the specimen was cut. The variation in thickness influences the determination of resistivity. Based on Equation 12, the specimen's resistivity increases as the thickness of the test specimen increases. In order to determine if the thickness variation was substantial to cause an error in the experimental data, thickness data of all specimens were reviewed. The thickness data for both the Tecknit and Chomerics test specimens are summarized in Table 11.

Table 11. Summary of thickness data for specimens tested.

Specimen #	Thickness Data for 0.1 inch/min Tecknit Specimens (Inches)	Thickness Data for 0.05 inch/min Tecknit Specimens (Inches)	Thickness Data for 0.1 inch/min Chomerics Specimens (Inches)
#1	0.117	0.117	0.116
#2	0.115	0.126	0.118
#3	0.121	0.114	0.117
#4	0.12	0.115	
#5	0.102	0.117	
#6	0.118	0.117	
#7	0.114	0.118	
#8	0.117	0.112	
#9	0.117	0.111	
#10	0.115	0.111	
Average	0.116	0.116	0.117
Standard Deviation	0.00525	0.00444	0.001

The average thickness value for the Tecknit material is about 0.116 inch for the 0.1 inch/min and 0.05 inch/min specimens. The standard deviation for both sets of specimens is low and less than 5% of the average value. There are two “outlier” values in Table 10: 0.102 inch thickness for specimen #5 at 0.1 inch/min and 0.126 inch thickness for specimen #2 at 0.05 inch/min. The data for both of these specimens were

compared to the other specimens in the Results section. The Chomerics specimens were die cut out of a small 5 inch x 5 inch sheet and hence the thickness did not vary for the three test specimens shown in Table 10.

Lastly, a significant source of error was the material itself. As discussed in the Results section, there are many variables that can influence the electrical resistivity of a carbon-loaded elastomer. Specifically, the filler type, shape, size, and distribution can significantly change the electrical resistivity of a conductive composite. The filler in the SC-Consil-861 was comprised of both carbon black and graphite particles. The particles have different structures and subsequently different electrical resistivities. The effect of two different fillers in the silicone may have caused the electrical resistivity behavior to vary from specimen to specimen. The models that were used to predict the zero percent strain electrical resistivity also assumed that the filler was one specific carbon black type, not carbon and graphite. As a result, the data predicted from the models were not as accurate.

6.2 Comparison of Experimental Results to Literature

The experimental results presented in Chapter 5 were compared to data found in the literature presented in Section 2.6. A comparison of the relative electrical resistivity difference as a function of strain for several SC-Consil-861 specimens tested at a 0.1 inch/min cross head speed to carbon black-loaded specimens tested by Kost *et al.* is summarized in Figure 41. The dotted line represents the data reported by Kost *et al.* for an 8 wt% carbon black-loaded silicone material. The experimental data for four SC-

Figure 41. Comparison of the relative electrical resistivity difference vs strain behavior between data reported by Kost *et al.* and the 0.1 inch/min SC-Consil-861 experimental data. The Kost *et al.* data presented was for an 8 wt% carbon black-loaded silicone material tested at a strain rate of 0.0033 s^{-1} [13]. (Reprinted with permission from John Wiley & Sons, Inc., for full citation see References)

Consil-861 specimens tested at 0.1 inch/min were also plotted in Figure 40. The relative electrical resistivity difference was calculated using Equation 13:

$$\frac{(\rho - \rho_0)}{\rho_0} \quad \text{Equation 13}$$

where ρ equals the electrical resistivity and ρ_0 equals the initial electrical resistivity. The large scatter in the experimental data for the SC-Consil-861 test specimens make it difficult to compare to values in the literature. The change in the relative electrical resistivity difference as a function of strain for specimen #5 closely matches the data from the literature. However, the data plotted for specimens #6, #7, and #9 do not match

the literature. This difference can be attributed to the variation of the distribution of filler from specimen to specimen, as discussed in Chapter 5.

6.3 Analysis of the Electrical Resistivity Behavior of CHO-SEAL 6370

As described in Chapter 5, the electrical resistivity as a function of strain for the CHO-SEAL 6370 test specimens was very different from the experimental behavior displayed by the SC-Consil-861 test specimens. Initially, the electrical resistivity for the CHO-SEAL 6370 specimens increased up to 2% strain. However, the electrical resistivity decreased with increasing strain, at strains greater than 2%, as shown in Figure 34. This can be explained by examining the particle to particle connections in a CHO-SEAL 6370 specimen. A test fixture was created to stretch a test specimen at a known strain and hold it in place for examination under a microscope. A photograph of the fixture with a test specimen is shown in Figure 42. A thin cross section of the CHO-SEAL-6370 material was cut and placed between two aluminum brackets that were tightened down using two screws on each side of the bracket. The brackets helped distribute the load during straining to ensure the specimen was stretched uniformly. The initial length of the specimen at zero percent strain was one inch. The specimen was then stretched to different lengths using the knob on the right of the fixture. A scale was added to the fixture to record the actual length changes in millimeters. Images of the surface of the cross section of the CHO-SEAL 6370 test specimen were taken at different strains using a stereoscope.

Figure 42. Photograph of test fixture used to characterize CHO-SEAL 6370 test specimen.

The nickel coated graphite particles in the CHO-SEAL 6370 specimen in the as-received condition are shown in Figure 43. These particles are mixed uniformly in the composite, are aligned in random directions and are non-spherical. Examples of the alignment of different particles in Figure 43 are outlined with red circles. An image of the nickel coated graphite particles in the CHO-SEAL 6370 specimen after being strained 19.7 % (5 mm stretch) is shown in Figure 44 and after being strained 31.5% (8 mm stretch) is shown in Figure 45. The same particles that were highlighted in Figure 43 were also labeled in Figure 44 and Figure 45 with red circles. The nickel coated graphite particles become more aligned in the direction of stretching as the strain increased from the as-received condition to 19.7% and 31.5%. It is thought that the alignment of the

particles creates more electrical connections and as a result causes the electrical resistivity of the composite to decrease.

Another observation made is that the nickel coated graphite particles are more densely packed together in Figure 45 than in Figure 44 and Figure 43. As the specimens are strained, the distance between the nickel coated graphite particles initially increases. However, as the strain on the specimen increases, the width of the specimen decreases and the density of the points of contact between particles increases. The end result is that the electrical resistivity of the composite decreases due to an increase in the density of points of contact. The images of the nickel coated graphite particles show how the electrical resistivity changed from increasing with strain to decreasing with strain.

Figure 43. Image taken of CHO-SEAL 6370 test specimen in the as received condition.

Figure 44. Image taken of CHO-SEAL 6370 test specimen after being strained 19.7% (5mm stretch).

Figure 45. Image taken of CHO-SEAL 6370 test specimen after being strained 31.5% (8mm stretch).

6.4 Ideal Resistivity Behavior for a Sensor Material

One of the potential applications for carbon-loaded elastomers is to use the material as a sensor. In order for the material to work effectively as a sensor, the electrical resistivity of the material must be sensitive to strain. Possible trends of electrical resistivity as a function of strain for conductive particulate composites are shown in Figure 46. The yellow curve represents a material that has a very high

Figure 46. Comparison of trends of electrical resistivity as a function of strain.

electrical resistivity change at low strain. The blue curve represents a material that has a low electrical resistivity change at low strain. The pink curve represents a material that exhibits a linear relationship between electrical resistivity and strain. The ideal sensor material needs to have a very high electrical response to low strain. The yellow curve shown in Figure 46 is the most desirable electrical resistivity behavior while the blue

curve is the least desirable. The electrical resistivity behavior as a function of strain for the carbon-loaded silicones described in this report varies from matching the pink line to closely matching the desired yellow profile.

6.5 Future Work

Future work should focus on determining whether a carbon-loaded elastomer can be a viable sensor material in a structural health monitoring system to help understand the impact of earthquakes on civil infrastructures. An experiment should be developed to evaluate the performance of the sensor material on actual welded steel H-beam test specimens. A correlation between the electrical resistivity of the sensor material and the strain of the welded steel specimen should be plotted in the range of 0% to 10% strain. A carbon-loaded elastomer that has a uniform distribution of carbon particles should be chosen to complete the experimentation. Also, work should be performed to understand how carbon and graphite particles mixed together in elastomers effect the electrical resistivity as a function of strain. Finally, the effect of strain rate on the electrical resistivity of carbon-loaded elastomers at low strains is not fully understood and should be examined in more detail.

CHAPTER SEVEN

CONCLUSIONS

In this study the change in electrical resistivity with strain was found to depend on the distribution of the filler in the elastomer and the particle size distribution of the filler. The electrical resistivity as a function of strain for the SC-Consil-861 specimens varied significantly due to poor filler distribution and poor control of filler particle size. The scatter of the SC-Consil-861 data made it too difficult to determine the effect of strain rate on the electrical resistivity. The electrical resistivity as a function of strain was consistent for CHO-SEAL 6370 specimens due to good filler distribution and tight control of filler particle size. The change in electrical resistivity with strain was also found to be dependent on the shape of the filler particles. The electrical resistivity decreased above 2% strain for the CHO-SEAL 6370 specimens due to an increase in alignment of the non-spherical nickel plated graphite particles and an increase in the density of points of contact between the particles. Hysteresis of electrical resistivity data was found to occur at low strains for both SC-Consil-861 and CHO-SEAL-6370 specimens. Electrical resistivity models must take into account particle to particle interaction in the elastomer to be consistent with experimental data. The Scarisbrick model was the most accurate of all the electrical resistivity models examined because the model uses a probability function, geometrical factor, and filler volume fraction to compute electrical resistivity. The Scarisbrick model predicted a 0% strain electrical resistivity value within an order of magnitude of the experimental data.

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