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Development of a Styrene-Isobutylene-Styrene (SIBS) and Carbon Black Thermoplastic Elastomer for Biomedical Pressure Sensing Applications

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DEVELOPMENT OF A STYRENE-ISOBUTYLENE-STYRENE (SIBS) AND CARBON BLACK THERMOPLASTIC ELASTOMER FOR BIOMEDICAL PRESSURE SENSING APPLICATIONS

By

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A DISSERTATION

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DEVELOPMENT OF A STYRENE-ISOBUTYLENE-STYRENE (SIBS) AND CARBON BLACK THERMOPLASTIC ELASTOMER FOR BIOMEDICAL PRESSURE SENSING APPLICATIONS

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Poly(Styrene-block-Isobutylene-block-Styrene) is a phase-separated tri-block thermoplastic elastomer known for having excellent biocompatibility and flexibility. The mechanical properties of this material can be tailored by varying its styrene content. This makes it an excellent candidate for biomedical applications. SIBS reinforced with carbon black (CB) filler particles can be used for pressure sensing external (stick-to-skin) devices. Pressure sensors made from SIBS/CB composites can be used as potential solutions for real-time monitoring of intraoperative intraocular pressure. Another target application is the detection and prevention of pressure ulcers in people suffering from peripheral neuropathy, including diabetic patients. These sensors must be sensitive to pressure, biocompatible, conformable to complex surfaces, and capable of enduring the variable mechanical stresses associated with moving and stretching. The aim of this thesis is to fabricate, tests, and develop SIBS/CB composites for pressure sensing applications. The mechanical, electrical, morphological, and rheological properties of SIBS/CB composites are characterized. Biocompatibility retention is analyzed and the suitability of SIBS/CB composites for external pressure sensing applications is determined.

Main challenges facing the development of new biomaterials include biocompatibility, good processability, flexibility, and functionality. In this thesis, SIBS/CB
composites of different loadings are fabricated through a combination of high-shear mixing, ultrasonication, and solvent-casting. It is found that nanoscale CB can be easily and effectively dispersed in a SIBS host. The relationship between mechanical and electrical properties is established through analysis via tensile testing, resistivity testing, Fourier Transform Infrared Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM). Typically, an increase in electrical properties leads to reduction in mechanical properties. These properties are affected by the fabrication method and procedures utilized, further emphasizing the tailorability of SIBS/CB composites. For this reason, processing parameters are analyzed via statistical Taguchi and screening methods, leading to regression models for maximum tensile strength and conductivity responses.

Addition of CB filler material to a polymer matrix alters the rheological properties of the material. The rheological behavior of conductive polymer composites has practical importance. It influences the final structure of the material and is valuable in determining the optimal processing conditions for manufacturing production. Rheological behavior of SIBS/CB composites is evaluated and provides insight into the interactions present in the composite. Finally, cell toxicity assays are used to determine whether addition of CB filler compromises the excellent biocompatibility present in the neat SIBS polymer. Biocompatibility testing results justify further exploration of SIBS/CB composites for biomedical testing.

This thesis and all the data provided serve as foundational knowledge in the development of SIBS/CB composites. The information provided serves as guidelines for the development and fabrication of optimally functioning biocompatible pressure sensors for biomedical applications.
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CHAPTER 1: Introduction

1.1 Background

The need for a cost-effective, reliable pressure sensor for biomedical applications remains significant despite increased research effort in this area. In most cases, these types of sensors are very application-specific. The aim of this thesis is to explore the relationship between various properties, sensing capability, and conductive particle loading percentage in order to inform design of biomedical pressure sensors for a variety of stick-to-skin applications requiring significant strain during movement, or during placement due to complex anatomical curvature. For example, the use of stick-to-skin biocompatible pressure sensors is a viable solution to the significant prevalence of pressure-based injuries, such as decubitus ulcers (alternatively known as pressure ulcers). According to the US Joint Commission on Patient safety, more than 60,000 people die from pressure ulcer complications each year [1]. Yet another example is found in the absence of intraoperative intraocular pressure monitoring due to its high cost and the resulting permanent blindness occurring in thousands of patients worldwide during routine surgeries [2]–[4]. The following work proposes a simple, cost-effective pressure sensing solution that can be adapted to these or a variety of other biomedical applications. This thesis forms the basis for the fabrication, characterization, and development of a composite material for use in pressure sensing biomedical applications.

Simple, thin, flexible, inexpensive variably-conductive nanocomposite (VCN) sensor films can be adhered to surfaces to provide real-time feedback on applied pressure [5]. Relying on quantum tunneling theory to induce a dramatic change in bulk resistivity of the film for very small strains, this signal can then be processed and analyzed to extract critical
information regarding both magnitude and duration of applied loading. These micro and nanocomposite films have the capability to accurately detect strain despite conflicting or confounding environmental effects, time-dependent material changes, or initial conditions, such as deflection or curvature [5]–[7]. In this thesis, we propose the use of a VCN based on CB dispersed in a biocompatible block thermoplastic elastomer. Each of these components are commercially available, inexpensive, and easily processed into an effective sensor film.

Conductive polymer composites (CPC) offer reliable electrical conductivity and various properties intrinsic to the polymer. These polymers are obtained by incorporating filler- usually in the form of powder, flakes, fibers, or layered forms- into the structure of the matrix consisting of one or more non-conducting polymers [8]. The fabrication of composites is typically done using melt mixing, solution mixing, or in situ polymerization [9]. For manufacturing purposes, composites are usually developed using injection molding, compression molding, or extrusion. Recently much interest has been generated in CPCs due to their low cost, efficiency, and variability in their range of possible applications [10].

1.2 Poly(Styrene-

block-

IsoButylene-

block-

Styrene) (SIBS)

Poly(Styrene-block-Isobutylene-block-Styrene) (SIBS) is a thermoplastic elastomer with tailororable mechanical properties due to its tri-block phase-separated structure, as shown in Figure 1 [11]. SIBS consists of ordered, separated, and incompatible phases of soft rubber-like isobutylene and hard glassy polystyrene [11]. The ability to customize the mechanical properties of SIBS by varying the styrene/isobutylene ratio without altering its composition offers versatility and flexibility in its range of applications. The four types of
commercially available SIBS are known as: 72T, 73T, 102T, and 103T. The morphology and microstructure of SIBS will vary depending on the composition, which differs for different SIBS types based on the styrene content (Table 1) [11], [12]. Characterization of the microstructure of SIBS has found that at lower mass fractions of styrene, the styrene is present as spherical domains. SIBS containing lower styrene content has a mechanical response similar to that of rubber. At higher mass fractions of styrene, the spherical domains become cylindrical, double gyroid structures, or lamellar [13]. In contrast to varies with low styrene content, SIBS with high styrene content behaves similar to a toughened plastic [14]–[16]. Figure 2 illustrates the microstructure for SIBS with spherical and cylindrical domains.

![Polyisobutylene](image)

**Figure 1. Styrene-Isobutylene-Styrene (SIBS) simplified structure [11]**

<table>
<thead>
<tr>
<th>SIBS Type</th>
<th>Styrene Content [%]</th>
<th>Molecular Weight [g/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>72T</td>
<td>22</td>
<td>75,000</td>
</tr>
<tr>
<td>73T</td>
<td>30</td>
<td>76,000</td>
</tr>
<tr>
<td>102T</td>
<td>15</td>
<td>117,000</td>
</tr>
<tr>
<td>103T</td>
<td>30</td>
<td>106,000</td>
</tr>
</tbody>
</table>
SIBS may be an excellent choice for external stick-to-skin pressure sensors due to its excellent biocompatibility, ability to conform to complex anatomical surfaces, commercial availability, and its ease of processing [17]. The excellent biocompatibility present in SIBS has been attributed to a lack of any cleavable moieties. Its polymeric backbone and pendant groups have been shown to not contain any unprotected groups that might be prone to oxidation, hydrolysis, or enzymatic cleavage [18]. Prior research of SIBS for use in medical devices has suggested that it: (1) does not activate platelets in the vascular system, (2) does not induce leukocytes to sites of subcutaneous eye implants, (3) no scarring, encapsulation, or inflammation is present in eye implants, (4) there is no occurrence of calcification, oxidation, embrittlement, or hydrolysis, and (5) it does not show any signs of activating a foreign body reaction [12].
There is present research being conducted for the development of lightweight, structurally sound, implantable medical devices and biocompatible coatings [19]. One potential solution is to use SIBS as a base material. This widely available, easily processed, and inexpensive material has been approved by The Food and Drug Administration for ultra-long term in vivo vascular device applications and is currently being used in the TAXUS® drug-eluting coronary stent [11], [20]–[22]. The need for an easier, safer, and more effective method for treating glaucoma led to the application of SIBS to the InnFocus, Inc. glaucoma drainage microtube. The final product, the InnFocus MicroShunt®, made by extruding a SIBS tube and molding a fixed member onto the tube, achieved an approximate 50% drop in intraocular pressure with a 100% patient success rate [12]. SIBS used for this novel device displayed no significant dimensional changes, exhibited chemical hydrolytic stability, and demonstrated through biocompatibility testing that this novel biomaterial is safe for human testing. Furthermore, SIBS has shown promise as a new alternative to silicone breast implants [20].

Commercially available SIBS has ultimate tensile strength and elongation at break values ranging from 9-18 MPa and 500-1000% [23]. The ability to customize the mechanical properties of SIBS by varying the styrene content without altering its chemical composition offers exceptional versatility. The mechanical tailorability of SIBS offers potential use in applications where extensive mechanical customization is required. However, use of SIBS for pressure sensing applications would require the use of filler material, which may be detrimental to the mechanical properties. The relationship between the mechanical and electrical properties is complex, yet its characterization is a major benefit to the in vivo applications of SIBS for conductive composites. Furthermore, if the
biocompatibility of SIBS is not compromised through addition of filler material, surface treatments, or any alterations, then the range of possible applications becomes even larger.

Despite this material’s unique versatility and robust mechanical properties, there are characteristics of the in vivo environment that greatly diminish its mechanical strength. Biological environments have harsh and dynamic conditions, consisting of ever-changing concentrations of bodily fluids, which may have detrimental effects on the performance of biological implants [24], [25]. Studies conducted previously associate the presence of lipids in vivo with the nearly universal degradation response of the SIBS polymer. One study consisted of a SIBS based trileaflet heart valve being implanted into a sheep test-animal to evaluate the feasibility of using SIBS for artificial human heart valves. The SIBS trileaflet heart valve experienced lipid-induced degradation, which resulted in viscoelastic creep leading to surface cracking. This material response eventually led to the death of the test animal [11]. This significant reduction in mechanical properties was attributed to the absorption of the lipid, its plasticizing effect, the weakening of virtual cross links, and the subsequent restructuring and realignment of the molecular structure. No further comprehensive studies were pursued in order to further understand the failure mechanics of this phenomenon or to develop potential solutions.

Recent studies exploring the effect of lipid absorption on the mechanical properties of SIBS found a direct correlation between absorbed lipid content and the loss of ultimate tensile strength [26]. This study concluded that plasticization is phase-dependent, with softer isobutylene regions being more susceptible to lipid-induced degradation. These results necessitate that the lipid resistance of the material be improved so as to fully exploit the biocompatibility of SIBS. From these studies, it is apparent that the SIBS polymer,
alone, is incapable of maintaining its mechanical properties in lipid-rich \textit{in vivo} environments. It is for this reason that filler materials are being considered as a potential solution for extending the longevity and performance of SIBS for \textit{in vivo} environments. Although external applications would not require enhanced resistivity to lipids due to the general absence of significant lipid concentration on the skin, the strain-induced changes in electrical resistance that results from conductive-particle reinforcement also provides an opportunity for expanding its use to stick-to-skin pressure sensing applications. Furthermore, the flexible, soft, and stretchable nature of neat SIBS allows it to conform to complex anatomical surfaces, providing a suitable choice for tactile sensors.

1.3 Carbon Black for Electrically Conductive Polymer Composites

Generally, polymer materials are preferred for pressure sensing applications due to their compliance. To use SIBS for sensor applications, it must be reinforced with conductive filler material. Electrically conductive polymer composites (ECPC) are obtained when conductive particles such as carbon black, graphite powder, or metal microparticles are implanted into a matrix of insulating polymer. CB is widely used as a conductive filler material in a variety of applications because it can provide excellent electric conductivity due to its graphite-type crystalline structure. Carbon black can exist as free individual particles, complex particle aggregates, or clusters of even larger agglomerates, as shown in Figure 3 [27]. Each primary particle contains up to 1,500 concentrically arranged crystallites [28]. Addition of carbon black to the polymer can be used to alter the material’s electrical properties. For this work, Carbon black particles were chosen due to their ability to provide better adhesion to polymer chains compared to microspheres or microrods, their wide availability, and their low cost [29].
When the conductive CB filler is dispersed into the otherwise non-conductive and insulating SIBS polymer, it allows the reinforced composite to be used for sensing applications as a result of its altered electrical properties. There have been many reports of successful integration of non-conductive polymers with conductive filler materials for sensing applications [8], [30]–[32]. One example of using electrically conductive polymers is in the fabrication of electronic nose gas sensor devices. Kindeldei *et al.* used four non-conductive polymers: polyisoprene, polystyrene, poly (N-vinylpyrrolidone), and polyvinylbutyrl in combination with carbon black conductive filler [32]. Similar to the work presented here, Kindeldei *et al.* used conductive polymer composites due to the high stretchability of the material and the possibility of implantation in locations where it would be impossible to install rigid sensors on silicon or glass. Carbon black polymer gas sensors changed their resistance in response to swelling upon exposure to an analyte. Such sensors were used to distinguish between gas mixtures and for measurements of relative humidity.

![Figure 3. Structure of Carbon Black [27]](image)
Another application of conductive polymers is as tactile sensors. Studies have reported fabrication of flexible conductive rubber sensor arrays capable of detecting pressure-related deformations [30]. In another study, Cheng et al. dispersed conductive polymer on a grid of sensing electrodes to create artificial skin. The conductive polymer used in this study was a mixture of PDMS and variety of conductive filler material, including carbon black [31]. Cheng et al. demonstrated that the sensor was capable of deformation without structural or functional damage [8].

Studies by Wang et al. in which carbon black was used for silicone rubber nanocomposite films found that CB filler provided a secondary reinforcement network [33]. Figure 4 represents a schematic diagram for the inner structure of the nanocomposite. Phase A shows a rubber molecule chain not absorbed by CB with active micro-Brownian motion. Phase B depicts cross-linked rubber molecule chains with restricted motion. Phase C denotes a macro-rubber molecule absorbed on the surface of CB through physiosorption. Phase D represents a CB molecule [33]. Apart from potentially forming a reinforcement network in a polymer matrix, CB particles will also form chains. When the CB particle-to-particle distance is small enough, local conductive paths will be formed. If the local conductive paths penetrate the polymer matrix, effective conductive paths which contribute to the overall composite conductivity are formed, as shown in Figure 5. In Figure 6 black chains are indicative of effective conductive paths in the composite while white chains indicate the lack of an effective conductive path [33].
Figure 4. Schematic diagram of the structure of a rubber silicone/CB nanocomposite [33]

Figure 5. Schematic view of local conductive path and effective conductive path [33]
1.4 Percolation Theory

Through the use of the principles of percolation theory, the behavior of CB particles within the SIBS matrix can be predicted. Percolation theory states that at a certain concentration of filler particles electroconductive channels will be formed within the polymer [29]. For low volume fractions of filler, the measured resistivity will be close to that of the polymer, thus, the polymer remains an insulator and very little voltage will pass through the specimen. The composite assumes the electrical properties of the matrix. Ideal electrical performance is achieved when a target middle ground or “percolation threshold” is reached. At the percolation threshold, there should be a sharp decline, known as a second-order phase transition, in the measured resistivity. This critical point is the point of maximum sensitivity for the composite [29], [34]–[36]. There is dramatic variability in electrical resistance with very small changes in inter-particle distances near the threshold. Past the percolation threshold, the measured resistivity will approximate that of the carbon black filler and the amount of conductive particles in the polymer is sufficient to form an interconnected network capable of acting as a conductor [37]. The curve in Figure 7 depicts
the three regions of electrical resistivity in filler-polymer composite systems achieved through the addition of increasing amounts of carbon black [37].

![Figure 7. Percolation theory curve [37]](image)

1.5 Tunneling Theory

Tunneling theory explains the phenomenon that permits the formation of conductive paths at or near the percolation threshold. When the gap between carbon black particles is sufficiently small, electrons effectively “tunnel” between isolated conductive particles, resulting in a tunneling current and a local conductive path (Figure 8) [38], [39].
Application of pressure to filled composites alters their electrical properties as well. Since carbon black is incompressible, any variations in pressure applied to the composite will result in translation and rotation of carbon black particles. Applied pressure decreases the thickness of the sample, thus reducing the gaps between adjacent carbon black particles and inducing changes in the effective conductive paths. During compression the tunneling current increases, which decreases the electrical resistance of effective conductive paths. The reduction in gap size also leads to the formation of more effective conductive paths, which increases the overall conductivity of the composite, as seen in Figure 9. Finally, if transverse slippage of carbon black particles occurs due to compression, the result may be the destruction of effective conductive paths [33].

Figure 8. Quantum electron tunneling conduction mechanism [38]
1.6 Motivation and Scope

The primary application target for this thesis is stick-to-skin pressure sensors. These sensors must be sensitive to pressure, biocompatible, conformable to complex surfaces, and capable of enduring the variable mechanical stresses associated with movement and stretching. One potential use is for the prevention of pressure ulcers in people suffering from peripheral neuropathy, including diabetic patients. Another target application for this particular SIBS/CB composite and sensor construction is real-time intraoperative intraocular pressure monitoring. Permanent or partial blindness has been associated as a consequence occurring in thousands of patients worldwide during routine surgeries, particularly prone position spinal surgeries [2]. This blindness is a result of external pressure from a headrest, as well as internal pressure due to the forward translation
of the globe, known as proptosis. For both of these potential applications, a SIBS/CB composite is proposed as a solution due to the degree of biocompatibility exhibited by SIBS and its ability to conform to complex anatomical regions. A prototype construction of a SIBS/CB pressure sensor for the periorbital region is shown in Figures 10 and 11.

Figure 10. Prototype of sensor using SIBS/CB as base material

Figure 11. Schematic of pressure sensor located over periorbital region
To use SIBS/CB sensors for pressure sensing applications, a balance must be achieved between electric and mechanical properties; the sensors are likely to be located in areas of complex curvature which also require stretching without permanent deformation. With the addition of filler materials, the behavior of a polymer matrix is almost always altered to some degree. Chapter 2 will investigate the effect of carbon black (CB) loading on the pressure-sensing capability of a thermoplastic elastomer (SIBS) composite. The relationship between electrical and mechanical properties of SIBS/CB composites will be discussed in this chapter both for situations where detection of a small pressure range is required and for situations where detection of a large pressure range is required.

Chapter 3 will focus on the optimization of the processing conditions for fabrication of SIBS/CB composites through the solvent casting method. The electrical and mechanical performance of SIBS/CB composites fabricated under a specific set of parameters was evaluated to obtain the optimum parameters for biocompatible pressure-sensing applications. The following processing parameters related to the fabrication of SIBS/CB conductive composites for pressure sensing applications are investigated: CB loading (%), casting temperature (T), and mixing time (t). The Taguchi method, screening analysis, and ANOVA are used to make a regression models. Main interaction effects of variables are explored to understand how the processing conditions influence the mechanical and electrical capabilities of the composites. Predictions from the regression models are validated using experimental results.

The focus of Chapter 4 is to assess the morphological and rheological performance of SIBS/CB composites. The goal is to advance the knowledge of the melt rheology of the
composite material over the relevant range of shear rates and temperatures, which is essential for proper material application and identification of the proper processing conditions. Based on detailed rheological characterization, thermogravimetric measurements, and imaging, the influence of CB on the rheological response of the material is investigated. The rheological behavior of SIBS/CB composites is used to determine the limits for high-production fabrication of the composites through extrusion methods.

The scope of Chapter 5 is understanding the effect of addition of CB on the excellent biocompatibility in SIBS. A cell toxicity assay is used to evaluate the viability of SIBS/CB composites for external (stick-to-skin) pressure sensing applications. It is determined whether addition of percolation threshold quantities of CB to SIBS will compromise its biocompatibility. Future biocompatibility assays are suggested based on expansion of the target applications of SIBS/CB composites.

Chapter 6 contains concluding remarks and recommendations for future work.
CHAPTER 2: Characterizing the Mechanical-Electrical Relationship in SIBS/CB Composites

2.1 Relationship Between Mechanical and Electrical Properties of Conductive Polymer Composites

To use SIBS/CB sensors for pressure sensing applications, a balance must be achieved between electric and mechanical properties. The sensors are likely to be located in areas of complex curvature which require stretching without permanent deformation. With the addition of filler materials, the behavior of a polymer matrix is almost always altered to some degree. Due to the composite nature of the material, the interface between the styrene phase, the polystyrene phase, and carbon black is a key factor in maximizing material properties [40]. A weakened interface caused by agglomeration of CB particles may lead to premature crack propagation and failure, in addition to inconsistent pressure sensing properties.

This study represents an analysis of sensing performance as a function of carbon black content; a necessary step toward probing the interaction between the competing design goals of retained biocompatibility, suitable mechanical strength, flexibility, and sufficient carbon black content to meet or exceed the percolation threshold as required for sensor functionality. The first goal is to analyze electrical properties across a small pressure range, similar to pressures felt in the periorbital region. Small and large pressure ranges are distinguished and separated due to the greater difficulty in detecting variations in pressure when the pressure deltas are small. In consequence, the filler loading for appropriate detection of pressure across small ranges is different from that for large pressure ranges. Electrical properties across large pressure ranges are also explored to broaden the potential target applications for the material. Furthermore, mechanical properties are characterized
and a mechanism for the behavior of CB in a SIBS polymer matrix is proposed. To the best of our knowledge, this work represents the first investigation into the mechanical-electrical relationship present in SIBS/CB composites.

2.2 Materials and Methods

2.2.1 Materials and Sample Preparation

The SIBS pellets used for these experiments have a composition by weight of 22% styrene and 78% isobutylene. The commercially available block copolymer, trade name SIBSTAR™ 72T, with a molecular weight of 75,000 g/mol was used in the as-received condition from Kaneka Corporation (Figure 12). High surface area Carbon Black (CB) filler material with an average 32.2 nm particle size, trade name BLACK PEARLS® 2000, were also used as-received from Cabot Corporation (Figure 13).
SIBS is soluble in various non-polar solvents and thus, SIBS/CB particle composites were fabricated through a solvent casting procedure (Figure 14) [41]. SIBS pellets mixed with CB particles were dissolved in 8.57% w/v of toluene as the solvent. In order to ensure adequate and uniform dispersion of filler CB particles in the soft polymer matrix, a combination of high shear mixing and ultrasonication was utilized. High shear mixing of the dissolved materials was performed using an IKA Eurostar 40 Digital High-Shear Mechanical Mixer for a total of six hours at 2000 revolutions per minute with 275 mL of toluene. Due to solvent evaporation, halfway through the process, an extra 275 mL of toluene was added. Composite samples were then subjected to ultrasonication at 50 kHz for an additional 45 minutes with a QSonica® 700 Watt Ultrasonic Cell Disruptor to improve dispersion of the filler. Subsequently, solutions were poured into flat stainless-steel trays and left to cast for twenty-four hours in a fume hood at 23°C. The final VCN composites had CB concentrations of 0%, 10%, 15%, 20%, and 25% loading by weight and were approximately 0.17 mm thick.
2.2.2 Scanning Electron Microscopy

Scanning electron microscope (SEM) was utilized to observe the effect of integrating increasing amounts of CB particles by weight into the neat SIBS polymer. Specimens were sputter-coated with a Denton Vacuum Desk V TSC sputtering system and then inspected using a JEOL JSM-6010PLUS/LA analytical SEM. Of particular interest were the topographies of specimens with the lowest and highest concentrations of CB particles, by weight.

2.2.3 Composite Tensile Testing

Testing of specimens was performed using an Instron® 5966 Tensile Testing Machine equipped with a 10 kN load cell at room temperature at a rate of 500 mm/min, following ASTM D412 Test Method A. The dumbbell mold used to create the thin samples is in compliance with ASTM D412 Type C (Figure 15). Between five to ten specimens for each type of composite were mounted in an eccentric roller tensile grip (Figure 15) and tested. All values represent the average of all specimens tested for each loading. All specimen groups are identified by their percentage of CB content.
2.2.4 Small Pressure Range Conductivity Testing

The pressure sensing characteristics of the samples were examined by measuring the change in voltage (of a 5V DC maximum applied) with an Arduino Uno. Samples were placed on 6.5 x 6.5 cm substrate plates and pressed between Copper electrodes. The setup is shown in Figure 16. Initial voltage measurements were made with no pressure placed upon the samples. Subsequent measurements were made with applied pressures of 162.0, 810.1, 1620, 2430, 3240, 4050, and 4860 Pa. These pressure values were selected with the target application of eye pressure sensing in mind. Normal eye pressure typically ranges from 1599-2933 Pa [42]–[44]. Eye pressure greater than 2933 Pa is considered higher than normal and can indicate ocular hypertension or glaucoma. The pressure range tested ensures that the composite, and any sensors developed with it, is capable of detecting small but impactful variations in eye pressure or any anatomical region subjected to less than 5000 Pa.
2.2.5 Large Pressure Range Conductivity Testing

A custom-built apparatus (Figure 17) was used in order to examine the pressure sensing characteristics of the samples by measuring resistance as a function of applied pressure. A 0.5 in diameter copper disc and layer of Teflon were mounted on top of a Wagner FDX force gage platform with adhesive. A 0.5 in diameter SIBS/CB specimens was punched out and placed on the copper disc. The specimen was compressed from the top by a manual linear actuator symmetrically outfitted with another layer of Teflon and 0.5 in diameter copper disc. A Fluke multimeter’s positive and negative probes were connected to the specimen using a combination of simple alligator clips and male-ended breadboard jumper wires. When the actuator was engaged, the SIBS/CB specimen was sandwiched between the copper discs and the circuit was completed. The force gage readings allowed the compressive force exerted upon the specimen in Newtons (maximum
40 N) to be recorded and paired with the resistance reading from the multimeter in Ohms (Ω), throughout testing. Increasing amounts of pressure were exerted and the corresponding resistance readings noted. Pressure values were calculated using the following relation:

\[ P = \frac{F}{A} \]  

(1)

where \( P \) is pressure (Pa), \( F \) is compressive force (N), and \( A \) is specimen area (m²). No pressure was applied on the specimens during the initial voltage measurements. Pressures of up to 315900 Pa were applied during the subsequent measurements.

Figure 17. Custom-built apparatus for large pressure range conductivity testing

2.2.6 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was performed using a PerkinElmer® Frontier instrument (Figure 18). It was utilized to verify the presence of known bonds and inspect the composites for the presence of new bonds due to CB addition.
2.3 SEM of SIBS/CB Composites Results and Discussion

SEM imaging was performed in order to understand the dispersion characteristics of the CB particles within the SIBS substrate, as shown in Figures 19 and 20. Exploring the surface structure of the specimen allowed for correlations to be drawn between filler concentrations and the results of tensile strength and conductivity testing. In Figure 19, it can be seen that the CB particles are mostly dispersed throughout the specimen, except for a few darkened agglomerations in the top right corner. In this figure, the well dispersed particles are not overlapping. In Figure 20, black concentrations of CB particles are seen throughout, showing the increasing amount of CB particles present within the 20% specimen. This demonstrates that the increased amount of CB particles have not been dispersed properly, despite sharing the same manufacturing procedure with the 10% specimen. Agglomerated CB particles seen in the 20% specimen are thought to have
negative effects on the tensile strength of the material, as the bonding of the SIBS and CB is incomplete and agglomerations act as defects. Ultimately, SEM imaging confirmed a larger number of agglomerations were present as CB concentration increased.

Figure 19. SEM image of 10% CB composites
2.4 Mechanical Testing of SIBS/CB Composites Results and Discussion

Mechanical testing was performed to determine the effect of CB reinforcement in the SIBS 72T substrate material. Figure 21 shows the results of tensile testing performed on the neat, 10%, 15%, 20% and 25% CB/SIBS 72T specimens. Dumbbell specimens of all concentrations were tested in tension until failure (break). It is important to understand the effect of manufacturing on tensile strength of the material. Fittipaldi et. al. reported a tensile strength values of 13.4 MPa for compression molded neat SIBS 72T specimens [23]. As can be seen in Figure 21, the tensile strength for solvent-casted neat SIBS 72T specimens was approximately 22% lower than that reported in the literature for compression molded neat SIBS 72T. It is apparent from the difference in values that the manufacturing process (injection molding vs solvent casting) has a significant effect on final mechanical properties, as expected. However, because injection molding requires temperatures tailored to CB concentration to achieve uniform specimens, solvent casting
was chosen to reduce the number of confounding variables and better isolate the contributions from CB concentration.

CB/SIBS specimens were expected to have increased mechanical strength when compared to the neat SIBS 72T specimens. The 10% and 15% specimens exhibit an increase of tensile strength of approximately 46% and 13%, respectively. However, the 20% and 25% specimens exhibit a decrease of tensile strength of nearly 34% each. This indicates a shift in the role of CB somewhere beyond 15%; from reinforcement to defect as agglomerations become larger and more common. The decrease in tensile strength for the 20% and 25% CB specimens was expected after analyzing the SEM imaging in Figure 20 in which weak dispersion was present. In this experiment, the 20% and 25% CB content by weight is found to be too high for increased mechanical properties. From these results, it is clear that a reinforcement threshold exists between 0% and 15% CB particle concentration.

![Tensile Strength of CB/SIBS 72T Specimens](image)

**Figure 21. Tensile testing results of SIBS/CB composites**
It should be noted that this optimum range between 0% and 15% CB is valid only for the processing steps described here; more effective dispersion through improved processing may lead to an optimum value of CB concentration beyond 15%.

2.4 FTIR Testing of SIBS/CB Composites Results and Discussion

Due to the fact that a change in the role of CB from reinforcement to defect (in terms of tensile strength) is observed with increasing loads, FTIR was performed on the composite samples. Figure 22 shows the results of FTIR completed on the neat polymer, 10% CB, 15% CB, 20% CB, and 25% CB composites. The spectra for the 10% CB composite appears to be identical to that of the neat polymer. The spectra for 15%, 20%, and 25% CB show a broad peak around 2113 cm\(^{-1}\) not present in the neat polymer or the 10% CB composite. Peaks at 2113 cm\(^{-1}\) correspond to carbon-carbon triple bonds, indicating triple bond formation at CB loading above 15%. Triple bonds are stronger bonds than single or double bonds, making molecules stiffer and reducing freedom of rotation [45], [46]. A chemical and functional mechanism, which influences the mechanical properties, is proposed based on the results of the FTIR spectra. It is likely that for low CB loadings the particle-polymer interactions are not strong enough for bond formation to occur. Higher CB loadings increase the amount and magnitude of filler-particle interactions due to a decrease in the particle-to-particle distance. This results in the formation of triple bonds in the composite. Triple bonds are known to cause steric hindrance, resulting in changes in the physical and mechanical properties of a material [47]. At 15% CB, bonds created are causing material strengthening. However, for higher loadings triple bonds may be leading to embrittlement, voids, and defects which lead to an earlier onset of failure.
2.5 Conductivity/Pressure Sensing Testing of SIBS/CB Composites Results and Discussion

2.5.1 Small Pressure Range Conductivity Testing

The carbon black content-dependent variation in sensitivity for SIBS/carbon black composites exhibited behavior consistent with percolation theory. Low carbon black loadings led to very low measured voltages (high resistivity), and are therefore likely not suitable for applications with operating pressures on the order of what was tested here: up to 5 kPa.

Figure 23 shows the average voltage with varying pressure from 0-4860 Pa across various samples of 10% by weight CB composites. For the 10% carbon black sample the increase in voltage with pressure is nearly linear. For all samples tested both the initial and final voltages measures were less than 0.045 V. This indicates that for a 10% carbon...
black/SIBS composite the resistance is near that of the insulating polymer. Thus, this is not an optimum carbon black loading for pressure sensing applications.

Figure 24 illustrates the average voltage with varying pressure across various samples of 15% by wt carbon black composites. This data displays a more exponential relationship. Composites with 15% CB exhibit a much higher voltage when no initial pressure is present when compared with 10% CB composites, indicating the presence of conductive channels in the absence of external loading.

![Figure 23. 10% CB/SIBS average voltage-pressure curve](image)
Increases in carbon black up to 15% and 20% display a significant voltage change (and therefore, resistivity change), indicating an increased formation of conducting chains of carbon black throughout the polymer matrix. As the percentage of CB is increased from 10% to 15% there is a significant increase in voltage. This behavior implies that this is the vicinity of the percolation threshold. A critical and relatively unique requirement for a sensor constructed using these composites for biomedical applications is the ability to conform to a complex anatomical structure, such as the periorbital region around the eye. As a result, the range of voltage available becomes important; the act of deforming the sensor to fit an anatomical region cannot drive the resistivity of the composite to zero and the voltage drop to the maximum applied 5V (thereby eliminating pressure detection after application). Thus, the applicable CB loading cannot significantly exceed the percolation threshold.
Figures 25 and 26 depict the average voltage variation with pressure for 20% and 25% filler composites, respectively. These curves show an exponential relationship, similar to that for 15% CB composites in Figure 24. It can be seen in Figure 26 that 25% carbon black loadings have the highest overall initial voltage and subsequently reach the highest measured voltage of all samples at 486 Pa. In accordance with percolation theory, at 25% CB loadings the resistance of the composite is very near that of the conductive filler. At the highest applied pressure, films with this carbon black loading nearly reach the upper limit of voltage drop across the film (5V). In effect, 25% CB loadings are not ideal for detection of small pressures.
Figure 26. 25% CB/SIBS average voltage-pressure curve

Figure 27 presents the voltage range for all carbon black loadings. It can be seen that 20% carbon black composites display the largest voltage range and sensitivity to pressure. Figure 28 shows the behavior of each composite when placed under pressure. In this graph, $\Delta V$ is the change in voltage, which has occurred through the application of pressure, and $V_o$ is the original voltage for each respective carbon black loading. Samples with 15% and 20% carbon black showed the greatest pressure sensitivity. Figures 27 and 28 indicate that for the range of pressures tested, composites with 20% carbon black filler would optimize pressure sensitivity. Samples with 25% carbon black loading were less sensitive to applied pressure. This suggests that when pressure is applied to samples with 25% carbon black, any new conductive chains, which may be formed by the addition of conductive filler, do not significantly affect the overall sensor conductivity.
Figure 27. Voltage range observed with increasing CB loading

Figure 28. Normalized voltage change throughout the pressure range
For the sensor application pursued, the voltage drop in the undeflected, pre-application state must be minimized and sensitivity, defined as voltage drop per unit applied pressure or deflection, must be maximized. Composite films fabricated with 10% CB exhibit a voltage drop very close to zero, indicating that the resistivity of the composite is very near that of the polymer matrix. Application of pressure does not significantly alter the voltage drop through the sample. The maximum sensitivity rate achieved for these samples was 0.0071 mV/Pa. Samples containing 15% CB and 20% CB have an initial detectable voltage drop of 1.16 V and 1.86 V, respectively. Films with 15% CB achieved a maximum rate of 0.25 mV/Pa, whereas 20% CB loadings attained 0.380 mV/Pa. The aforementioned results validate that 20% CB loading maximized sensitivity for the pressure range tested.

2.5.2 Large Pressure Range Conductivity Testing

The electrical resistance of 10%, 15%, 20%, and 25% CB/SIBS 72T specimens as a function of various applied pressures were obtained using a custom-built apparatus. The relationship between applied pressure and composite resistance is an important indicator of the performance of the sensor film. Table 2 shows the specific resistance, defined as resistance per unit thickness, of SIBS/CB specimens at minimum and maximum applied pressure, as well as the associated absolute resistance decrease. The table highlights how the ability to differentiate between the amount of applied pressure is related to the overall change in resistivity throughout the pressure range. For excellent pressure sensing capabilities, the pressure range of the material and therefore, the “resolution” of the specific resistance value acquired between these ranges are of principal importance. The 15% specimen has the largest resistance difference between the highest and lowest applied
pressures, whereas the 25% specimen exhibits the lowest. The 25% specimen demonstrates a drastically lower absolute difference in comparison, as expected.

Apart from the values for the absolute resistance decrease for each composite type, the trend seen as loading increases is also of importance. With few CB particles present, a high resistivity is anticipated. At any specific pressure value, it is expected to see a decreasing trend in resistivity as CB loading increases. This pattern is true between 15% CB and 20% CB specimens. However, an unexpected phenomenon occurs between 10% CB and 15% CB composites. The specific resistivity of 10% CB specimens is 63 times lower than that of 15% CB specimens. It is probable that the processing steps utilized in the fabrication of these composites are more suited to favor large resistivity differences for 15% CB concentrations. The processing conditions likely resulted in distributed conductive particles with fewer complete conductive pathways at low pressures, which subsequently yielded a very large absolute difference. It is apparent that the pressure-resistivity relationship for SIBS/CB composites is very sensitive to the quality of the dispersion.

Table 2. Specific resistance of composites at maximum and minimum pressure and the associated absolute resistance decrease

<table>
<thead>
<tr>
<th>Specimen (% CB)</th>
<th>Specific Resistance at 7,900 Pa (kΩ/mm)</th>
<th>Specific Resistance at 355,450 Pa (kΩ/mm)</th>
<th>Absolute Decrease (kΩ/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%</td>
<td>161.7</td>
<td>2.9</td>
<td>158.8</td>
</tr>
<tr>
<td>15%</td>
<td>10,284.2</td>
<td>46.2</td>
<td>10,238</td>
</tr>
<tr>
<td>20%</td>
<td>586.5</td>
<td>4.6</td>
<td>581.9</td>
</tr>
<tr>
<td>25%</td>
<td>7.3</td>
<td>0.2</td>
<td>7.1</td>
</tr>
</tbody>
</table>
Utilizing a 2nd order polynomial fit, the resistance data adheres to the line of best fit exceptionally well, as shown by the coefficients of determination in Figure 29. Following Table 2, the large resistivity difference can also be seen here in the 15% specimen. While there seem to be behavioral similarities between the 10% and 20% specimens in Figure 29, it can be seen from the table that they are significantly different in range of specific resistance.

![Figure 29. Specific resistance versus applied pressure for SIBS/CB composites](image)

In Figure 30, the 15% CB/SIBS 72T pressure-resistivity relationship is shown. With an impressive 10.2 (MΩ/mm) absolute difference between the minimum and maximum pressures applied, this particular version of the composite is very well-suited for sensing applications. In Figure 31, the 25% CB/SIBS 72T pressure-resistivity relationship is shown. With only a 7.1 (kΩ/mm) absolute difference between the minimum and
maximum pressures applied, this version of the composite is much less suitable for sensing applications due to the decreased ability to discern between small pressure differences.

Figure 30. Specific resistance versus applied pressure for 15% CB/SIBS composites

Figure 31. Specific resistance versus applied pressure for 25% CB/SIBS composites
2.6 Conclusion

One of the main challenges in the fabrication of conductive composites for biomedical applications is to simultaneously achieve both high conductivity and mechanical toughness. Higher carbon black loadings lead to higher conductivity as can be seen in the results presented here. However, increased filler loading results in large agglomerates. Micro-voids may be formed due to agglomerates. Mechanical strength and flexibility may thus be compromised due to structural flaws and stress concentration in the polymer.

Tensile testing results show an optimum CB content for maximum tensile strength exists between 0% and 15% CB particle concentration by weight, beyond which tensile strength begins to decrease as CB starts to function as a defect rather than reinforcement. This optimum range is valid only for the processing steps described here; more effective dispersion through alternate processing conditions may lead to an optimum value of CB concentration beyond 15%. Pressure testing across a large pressure range shows that 15% CB composites are very well-suited for pressure sensing applications. The obvious and significant improvement in sensing performance at this CB content warrants a more thorough investigation into the underlying mechanism responsible, which is explored in Chapter 3. The dependency on processing parameters of pressure sensitivity demonstrates yet another level of tailorability to SIBS-based composites, apart from styrene content and molecular weight. To the best of our knowledge, this is the first investigation into the mechanical-electrical relationship of SIBS/CB composites and the potential tailorability based on the intended application of the material.
Variables affecting composite properties include preparation method, volume fraction of filler material, distribution of filler material, and the size and shape of both the insulating and conducting phases within the composite. Results from the mechanical and electrical testing highlight the need for a full design of experiment, which should encompass multiple processing parameters at various levels.
CHAPTER 3: Optimization of the Processing Parameters of SIBS/CB Composites for Maximum Pressure Sensing Capacity and Tensile Strength

3.1 Design of Experiments for Maximum Mechanical and Electrical Properties

The interface between the styrene phase, the polystyrene phase, and carbon black in SIBS/CB composites is a key factor in maximizing material properties [48]. A weak interface due to agglomeration of CB particles may lead to premature crack propagation, early onset of failure, and inconsistent pressure sensing abilities [23], [48], [49]. Thus, achieving an adequate dispersion of filler material is a significant concern during the fabrication of these materials. For this reason, the primary goals influencing the fabrication and development of these conductive composites are the achievement of a maximum pressure sensing range as well as the retention of sufficient mechanical strength. Some processing parameters and conditions involved in the fabrication of SIBS/CB composites through the solvent casting method that can affect the mechanical-electrical behavior of the material are CB content, mixing time, and casting temperature. To determine whether an individual factor is of importance in composite fabrication and whether interaction effects between different factors exist, a statistical approach is required. This allows us to achieve optimal conductive composite sensor performance with minimal amount of experimentation.

Design of experiments (DOE) is a mathematical method implemented to solve complicated problems in a cost and time-effective way through the reduction of the number of experimental runs necessary [50]. This method is designed to yield valid and objective conclusions. The Taguchi method is the robust DOE method implemented in this work to
investigate how different parameters affect the mean and variance of a performance characteristic. The overall objective of the method is to identify the processing parameters that will yield a maximum absolute resistance decrease while not causing a reduction in mechanical strength. The Taguchi method uses orthogonal arrays to organize the fabrication factors and the levels at which they should be varied [51], [52]. Using an L8 array allows for the collection of sufficient data to determine which factors most influence and determine material performance with a reduction in the number of experimental runs.

The electrical and mechanical performance of SIBS/CB composites fabricated under a specific set of parameters was evaluated to obtain the optimum parameters for biocompatible pressure-sensing applications. Therefore, the aims are to explore the most important processing parameters related to the fabrication of SIBS/CB conductive composites for pressure sensing applications and to make a regression model based on main interaction effects of variables to understand how they influence the mechanical and electrical capabilities of the composites.

3.2 Materials and Methods

3.2.1 Materials and Sample Preparation

The SIBS pellets used in this experiment have a composition by weight of 22% styrene and 78% isobutylene. The commercially available block copolymer, trade name SIBSTAR™ 72T, with a molecular weight of 75,000 g/mol was used in the as-received condition from Kaneka Corporation. Carbon black filler material with an average 32.2 nm particle size, trade name BLACK PEARLS® 2000, were also used as-received from Cabot Corporation. SIBS/CB particle composites were fabricated through a solvent casting procedure. SIBS pellets mixed with CB particles were dissolved in 8.57% w/v of toluene
as the solvent. In order to ensure adequate and uniform dispersion of filler CB particles in the soft polymer matrix, a combination of high shear mixing and ultrasonication was utilized. High shear mixing of the dissolved materials was performed using an IKA Eurostar 40 Digital High-Shear Mechanical Mixer for periods of 2 and 6 hours at 2000 revolutions per minute with 275 mL of toluene. A few samples were fabricated using a mixing time of 4 hours for extra analysis, comparison, and validation. Due to solvent evaporation in solutions mixed for 6 hours, halfway through the process, an extra 275 mL of toluene was added. Composite samples were then subjected to ultrasonication at 50 kHz for an additional 45 minutes with a QSonica® 700 Watt Ultrasonic Cell Disruptor to improve dispersion of the filler. Subsequently, solutions were poured into flat stainless-steel trays and left to cure for twenty-four hours either in a fume hood at 23°C or in an oven at 60°C. The final conductive composites had CB concentrations of 0%, 15%, and 20% loading by weight. Specimens produced were approximately 0.17 mm thick.

### 3.2.2 Tensile Testing

Testing of specimens was performed using an Instron® 5966 Tensile Testing Machine equipped with a 10 kN load cell at room temperature at a rate of 500 mm/min, following ASTM D412 Test Method A. The dumbbell mold used to create the thin samples is in compliance with ASTM D412 Type C. Between five to ten specimens from each combination of parameters in the orthogonal Taguchi array were mounted in an eccentric roller tensile grip and tested. All values represent the average of all specimens tested for each loading, and all specimen groups are identified by their unique combination of fabrication parameters.
3.2.3 Scanning Electron Microscopy

Scanning electron microscope (SEM) was utilized to observe the effect of varying the processing parameters on the surface of the SIBS/CB composites. Specimens were sputter-coated with a Denton Vacuum Desk V TSC sputtering system and then inspected using a JEOL JSM-6010PLUS/LA analytical SEM. Of particular interest were the topographies of specimens fabricated utilizing the same mixing time but different casting temperatures.

3.2.4 Conductivity Testing

A custom-built apparatus was used to examine the pressure sensing characteristics of the samples by measuring resistance as a function of applied pressure. A 0.5 in diameter copper disc and layer of Teflon were mounted on top of a Wagner FDX force gage platform with adhesive. SIBS/CB specimens of a 0.5 diameter were punched out and placed on the copper disc. The specimens were compressed from the top by a manual linear actuator symmetrically outfitted with another layer of Teflon and 0.5 in diameter copper disc. A Fluke digital multimeter was connected to the specimen to measure the resistivity. The force gage readings allowed the compressive force exerted upon the specimen in Newtons (maximum 40 N) to be recorded and paired with the resistance reading from the multimeter in ohms (Ω), throughout testing. Increasing amounts of pressure were exerted and the corresponding resistance readings noted. No pressure was applied on the specimens during the initial voltage measurements. Pressures of up to 315900 Pa were applied during the subsequent measurements.
3.2.5 Design of Experiments: Taguchi Method

Taguchi method was implemented to develop an experimental plan designed to insure data analysis and extrapolation from obtained experimental results with valid statistical inferences. The method extracts maximum information through the use of minimal experimentation by utilizing standard orthogonal array techniques to form a matrix of the processing parameters and their results [53], [54]. Using an orthogonal array technique it is possible to study the influence of CB content, mixing time, and casting temperature on the conductivity and the specific resistance decrease with applied pressure. Taguchi method allows us to determine interaction effects, analyze their significance, and minimize response variation [55].

The method is design to minimize noise (N) and maximize changes dependent on signal factors (S). It accomplishes this by using the S/N ratios. The S/N ratio has three main targets: smaller-is-better, larger-is-better and nominal-is-best [53], [55]. The relevant equations for each criterion are:

\[
\frac{S}{N} = -10 \log_{10} \left[ \frac{1}{n} \sum_{i=1}^{n} \frac{1}{y_i^2} \right] \text{ Larger is Better } \tag{2}
\]

\[
\frac{S}{N} = 10 \log_{10} \left[ \frac{y_i^2}{\sigma^2} \right] \text{ Nominal is Best } \tag{3}
\]

\[
\frac{S}{N} = -10 \log_{10} \left[ \frac{1}{n} \sum_{i=1}^{n} y_i^2 \right] \text{ Smaller is Better } \tag{4}
\]
In all equations $y_i$ is the response to the signals, $n$ is number of repetitions, and $\sigma^2$ is the standard deviation. In this study the objective is to maximize tensile strength and resistance change and thus, the Larger-is-Better criterion is used. An $L_8$ array was constructed with 3 factors at two distinct levels. Based on this design, an eight experiment plan was constructed. The factors and levels tested are summarized in Table 3. After the experiments listed in Table 3 were conducted, all statistical analysis of the results was performed in Minitab 18 software.

3.2.6 Design of Experiments: Screening Analysis

Screening designs were used to detect important factors and screen out unimportant factors for a regression analysis. This reduction allows process improvement and optimization to be concentrated on the vital fabrication parameters that may indicate major trends [50], [56]. Screening designs are an economical and efficient way of screening and ranking variables with a low number of experimental runs [57]. As was done for the Taguchi method, two levels were selected for each of the three relevant processing parameters. A two-level fractional factorial design was utilized which resulted in twelve experimental runs, as can be seen in Table 6. Analysis of Variance (ANOVA) and Pareto Charts are used to determine the significance of terms in the regression analysis. It is important to note that a limitation of a fractional factorial design is the use of only two levels for each factor, which assumes that responses are approximately linear across the range of potential levels for the processing factors chosen [50]. Prior work supports the linearity assumption in both tensile strength and overall resistance decrease as a function of curing temperature, mixing time, and carbon black content in the ranges investigated here [58]. All statistical analysis was performed using Minitab 18 software.
3.3 Processing Parameters Optimization Results and Discussion

3.3.1 Taguchi Method

The goal of the experiments was to attain the fabrication conditions which maximize the pressure sensing range (measured as an absolute decrease in resistivity) while maximizing the tensile strength of the composites, based on the Taguchi optimization method. Table 3 shows the processing parameter combinations, the results of the two measured responses, and the performance indicator of S/N ratio. Parameter levels used were: CB content 15% and 20%; mixing time 2 hours and 6 hours; and casting temperature 23°C and 60°C. The CB content levels were selected based on previous studies from Chapter 2 indicating that the CB content at the percolation threshold for conductivity in SIBS/CB composites lies between 15% and 20% by weight, based upon the intended pressure range applied and the target material application.

Table 3. Taguchi analysis response for Signal-to-Noise ratios

<table>
<thead>
<tr>
<th>Mixing Time [Hrs]</th>
<th>Casting Temperature [°C]</th>
<th>CB Content [%]</th>
<th>Resistance Decrease [kΩ/mm]</th>
<th>S/N</th>
<th>Tensile Strength [MPa]</th>
<th>S/N</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>23</td>
<td>15</td>
<td>2522</td>
<td>68.034</td>
<td>9.504</td>
<td>19.558</td>
</tr>
<tr>
<td>2</td>
<td>23</td>
<td>20</td>
<td>1736</td>
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<td>6.838</td>
<td>16.698</td>
</tr>
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<td>60</td>
<td>15</td>
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</tr>
<tr>
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<td>5.298</td>
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</tr>
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<td>23</td>
<td>15</td>
<td>1278</td>
<td>62.131</td>
<td>9.452</td>
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</tr>
<tr>
<td>6</td>
<td>23</td>
<td>20</td>
<td>477</td>
<td>53.570</td>
<td>8.103</td>
<td>18.172</td>
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<tr>
<td>6</td>
<td>60</td>
<td>15</td>
<td>460</td>
<td>53.255</td>
<td>9.103</td>
<td>19.183</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>20</td>
<td>1293</td>
<td>62.232</td>
<td>7.945</td>
<td>18.001</td>
</tr>
</tbody>
</table>

Main effects plot for tensile testing for the main effect terms of mixing time, casting temperature, and CB loading are shown in Figure 32. From Figure 32 it can be observed that tensile strength increases with increased mixing time and decreases with temperature
from 23°C to 60°C, as well as with increasing CB content. The decrease in tensile strength with higher casting temperatures is likely indicative of stress build-up sites due to dehydration at higher temperatures. Parameters yielding the highest tensile strength are circled, as predicted by the Taguchi method. Figure 33 shows SEM images of 15% CB samples fabricated using a mixing time of two hours but set with different casting temperatures. The composites with a casting temperature of 23°C show a relatively smooth surface through the entire section, whereas the composites at 60°C show multiple cracks, increased agglomerations, and a rougher surface. Additionally, the decrease in tensile strength with higher CB loadings is to be expected due to the higher likelihood of agglomerations which have a weakening effect on the overall polymer. However, the lower tensile properties must be balanced against the potentially higher and desirable conductive properties of the composite.

Figure 32. Main effects plot of fabrication parameters on tensile strength of SIBS/CB composites
Analysis of the effect of curing temperature on tensile strength across mixing times of 2, 4, and 6 hours for 20% CB composites is illustrated in Figure 34. There is a decrease in tensile strength between samples cast in a fume hood at 23°C and those cast in an oven at 60°C, regardless of mixing time. Higher temperatures are causing dehydration and thus, more stress concentrations at certain sites. Fundamentally, stress build-up is present in composites cast at higher temperatures, which lowers the ultimate tensile strength.

Figure 35 shows the change (Δ) in ultimate tensile strength across mixing time between 20% CB samples cast at 23°C and 60°C. The difference in tensile strength between samples cast at different temperatures is smaller as the mixing time increases. Essentially, for long mixing times the effect of casting temperature becomes more negligible. It seems that although the higher temperatures are creating more porosity and stress concentration sites, the increased mixing time is dispersing the particles in such a way that the particles reinforce the polymer more and can counteract the stress concentration effect. This experimental finding is reinforced by statistical analysis ranking through the Taguchi
method, as shown in Table 4. Table 4 shows the rank of each of the fabrication parameters selected for the experiment in terms of the signal-to-noise ratios for tensile strength with larger-is-better criterion. In accordance with the experimental runs, it can be observed from Table 4 that CB loading and mixing time have the largest effect on tensile strength, while casting temperature has the smallest.

Furthermore, another experimental finding from the fabrication runs is that the rate of decrease in delta strength between samples set at 23°C and those at 60°C is slower for 15% CB samples. Figure 36 depicts the change in tensile strength between 15% CB and 20% CB samples left to solidify at 23°C and those at 60°C as a function of mixing time. From Figure 36 it can be seen that the drop in tensile strength effect, shown as a delta, is smaller as the mixing time increases. This can be explained by the fact that because the amount of CB is less, it needs to be better dispersed to achieve homogeneity and thus, processing parameters have a greater effect on ultimate tensile strength.

![Figure 34. Effect of casting temperature on tensile strength across various mixing times](image)
Figure 35. Delta ultimate tensile strength between 23°C and 60°C 20% CB samples across mixing time

Figure 36. Plot of the difference in tensile strength between 15% CB and 20% CB samples fabricated at 23°C and 60°C across various mixing times
Table 4. Tensile strength response for Signal-to-Noise ratios

<table>
<thead>
<tr>
<th>Level</th>
<th>Mixing Time</th>
<th>Casting Temperature</th>
<th>CB Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.31</td>
<td>18.49</td>
<td>19.19</td>
</tr>
<tr>
<td>2</td>
<td>18.72</td>
<td>17.55</td>
<td>16.84</td>
</tr>
<tr>
<td>Delta</td>
<td>1.40</td>
<td>0.94</td>
<td>2.35</td>
</tr>
<tr>
<td>Rank</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
</tbody>
</table>

Main effects plot for resistance decrease and processing parameter rankings are shown in Figure 37 and Table 5. Unlike for the tensile strength where the most important parameter is the CB loading, the most significant parameter to achieve a maximum resistance decrease is mixing time. For both responses, casting temperature proved to be the least significant parameter. As Figure 37 shows, the largest specific resistance decrease was achieved for the following fabrication parameters: 15% CB loading mixed for 2 hours at 23°C casting temperature. It is worth noting that samples with 20% CB loading had a lower resistivity in the absence of pressure than 15% CB samples, meaning a higher conductivity. Despite this, upon application of pressure 20% CB samples were not able to achieve as large a range for resistivity and are thus, are less suited for our external stick-to-skin pressure sensing applications. Additionally, samples fabricated at a 60°C casting temperature had lower resistivity regardless of applied pressure. A possible explanation for this observation is that higher temperatures cause particle volumetric shrinkage, leading particles to assemble closer together (Figure 38) [59]. Ultimately, this phenomenon results in a reduction in the particle tunneling distance. The outcome is an increase in the tunneling current and the creation of more effective conductive paths. Although greater conductivity is evident at higher temperatures, it does not result in a larger range of values for the
specific resistance decrease. This is explained by the fact that the overall composite conductivity is increased to such an extent that small changes in pressure do not significantly yield new conductive paths or increase the tunneling current. Consequently, lower casting temperatures are optimal for pressure sensing applications where large resistance ranges are needed.

Figure 37. Main effects plot of fabrication parameters on specific resistance decrease of SIBS/CB composites

Table 5. Absolute resistance decrease response for Signal-to-Noise ratios

<table>
<thead>
<tr>
<th>Level</th>
<th>Mixing Time</th>
<th>Casting Temperature</th>
<th>CB Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>63.23</td>
<td>62.13</td>
<td>62.33</td>
</tr>
<tr>
<td>2</td>
<td>57.80</td>
<td>58.89</td>
<td>58.69</td>
</tr>
<tr>
<td>Delta</td>
<td>5.43</td>
<td>3.24</td>
<td>3.64</td>
</tr>
<tr>
<td>Rank</td>
<td>1</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>
Figure 38. Casting temperature effect on particle size [59]

Whether interactions exist or not between factors can be visualized using a matrix of interaction plot. An interaction occurs when the effect of one independent variable is impacted by the level of another input variable. In an interactions plot, parallel lines are indicative of no interaction occurring between the factors. Nonparallel lines suggest the occurrence of an interaction [60], [61]. The less parallel that two lines are, the greater the strength of the interaction. The matrix of interactions plot for tensile strength is shown in Figure 39. Visually it can be seen that interactions exist between mixing time and casting temperature, as well as between mixing time and carbon black loading. Casting temperature and CB loading do not show any significant interactions. From the interactions plot for the resistance decrease in Figure 40 it is apparent that the fabrication variables hold a more intricate relationship in determining this response. All of the parameters seem to interact with each other. This demonstrates that determining a model for conductivity optimization is likely to involve more assumptions and approximations, especially considering the greater probability for variation in electrical responses.

Contour plots for the tensile strength response and the specific resistance decrease response are shown in Figures 41 and 42, respectively. The interaction effects of individual processing parameters on the responses are shown visually in contour plots [62]. Each contour plot shown depicts the response surface for tensile (Figure 41) and for resistance
decrease (Figure 42) as a function of two independent processing parameters, maintaining the third processing parameter constant. The levels that are kept constant are shown as “hold values.” The contour plots for the tensile strength response show the substantial difference in tensile strength when the CB level is held constant at 15% loading. The greatest response is achieved in the plot where CB is held at this level, which is in agreement with experiments resulting in the highest tensile strength when 15% CB is utilized. Furthermore, plots where the CB loading varies show a greater number of contour regions, thus highlighting the importance of CB loading for the tensile strength response. Contour plots representing the absolute resistance decrease of the composites emphasize the importance of mixing time in achieving greater values. Curves where mixing time is not held constant display more response regions, indicating that differences in mixing time can lead to more response variation.

Figure 39. Interactions plot for the processing parameters for the tensile strength response
Figure 40. Interactions plot for the processing parameters for the resistance decrease response

Figure 41. Contour plots for the processing parameters at different levels for the tensile strength response
**Figure 42. Contour plots for the processing parameters at different levels for the specific resistance decrease response**

### 3.3.2 Screening Analysis

Screening designs were utilized to identify which processing parameters are significant for determining regression equations for prediction of tensile strength and absolute resistance decrease as functions of CB loading, mixing time, and casting temperature. Table 6 shows the combination of processing parameters used for the twelve experimental runs done for screening analysis, as well as the results for the resistance decrease and the tensile strength. In a screening analysis, Pareto charts indicate the relative magnitude of the effects and evaluate their statistical significance [56], [63], [64]. Pareto charts display the absolute value of the effects of each factor and a reference line which corresponds to $\alpha = 0.05$ (95% confidence). Any effects that extend past this reference line
are potentially important in determining regression equations. When the response is tensile strength, it can be seen that all of the processing factors taken into account are significant at the 0.5 $\alpha$-level, as shown in Figure 43. The Pareto chart in Figure 44 for absolute resistance decrease displays that CB loading has the greatest effect on the response, followed by mixing time. Casting temperature does not seem to have a significant effect on the resistance decrease response.

The residuals plots for the screening analysis for the tensile strength response are displayed in Figure 45. Residuals in a screening analysis are defined as the deviations of the results of the experimental runs from the results of the model’s fitted values. Residuals are used to evaluate the accuracy of the model resulting from a screening analysis. In a normal probability plot, if the residuals are normally distributed, then they should approximately follow a straight line [62]. The normal probability plot for the tensile strength response shown in Figure 45 shows that residuals do not deviate from a normal distribution. From the residuals versus fits plot it is verified that residuals are randomly distributed about zero with no recognizable pattern, which indicates constant variance. Furthermore, from the residuals plots it can be inferred, due to the lack of any trend or pattern in the residuals versus order plot, that the data collection order, or order of experimental runs, does not influence the error. Residuals are dispersed and prove the suitability of the model for tensile strength. From Figure 46 we can see from the normal probability plot for the resistance decrease response that the data also approximately follows a straight line. However, unlike for the tensile strength response, the resistance decrease response data seems to have a slightly downward curve, implying a skewed distribution. The histogram also proves that the data might be slightly skewed. It is likely
that the data for resistance decrease has more variability due to factors such as particle-to-particle distance, dispersion, sensitivity, and testing setup affecting the results. Despite this, the vast majority of residuals are normally distributed and thus, the model would still provide a good approximation for determining the best processing parameters to obtain the optimal resistance decrease.

Table 6. Screening analysis experimental results and model fits

<table>
<thead>
<tr>
<th>Mixing Time [Hrs]</th>
<th>Casting Temperature [°C]</th>
<th>CB Content [%]</th>
<th>Resistance Decrease [kΩ/mm]</th>
<th>Fits</th>
<th>Tensile Strength [MPa]</th>
<th>Fits</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>60</td>
<td>15</td>
<td>1736</td>
<td>1927.8</td>
<td>8.432</td>
<td>8.148</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>15</td>
<td>1070</td>
<td>1172.5</td>
<td>9.103</td>
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<tr>
<td>2</td>
<td>23</td>
<td>15</td>
<td>2522</td>
<td>2494.2</td>
<td>9.504</td>
<td>9.125</td>
</tr>
<tr>
<td>6</td>
<td>23</td>
<td>20</td>
<td>477</td>
<td>832.8</td>
<td>8.103</td>
<td>8.089</td>
</tr>
<tr>
<td>2</td>
<td>23</td>
<td>20</td>
<td>1972</td>
<td>1588.2</td>
<td>6.838</td>
<td>6.958</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>15</td>
<td>1280</td>
<td>1172.5</td>
<td>9.237</td>
<td>9.279</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>15</td>
<td>1280</td>
<td>1172.5</td>
<td>9.237</td>
<td>9.279</td>
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<td>23</td>
<td>20</td>
<td>618</td>
<td>832.8</td>
<td>8.261</td>
<td>8.089</td>
</tr>
<tr>
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<td>23</td>
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<td>9.452</td>
<td>10.256</td>
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<td>20</td>
<td>512</td>
<td>1021.8</td>
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<td>5.981</td>
</tr>
<tr>
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<td>60</td>
<td>20</td>
<td>692</td>
<td>1021.8</td>
<td>5.762</td>
<td>5.981</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>20</td>
<td>1293</td>
<td>266.5</td>
<td>7.945</td>
<td>7.111</td>
</tr>
<tr>
<td>2</td>
<td>23</td>
<td>15</td>
<td>3114</td>
<td>2494.2</td>
<td>9.482</td>
<td>9.125</td>
</tr>
</tbody>
</table>
Figure 43. DOE Pareto chart of the standardized effects for tensile strength response

Figure 44. DOE Pareto chart of the standardized effects for resistance decrease response
Figure 45. Residual plots of SIBS/CB samples for the tensile strength response

Figure 46. Residual plots of SIBS/CB samples for the specific resistance decrease
3.3.3 Regression Modeling

A general regression for the models for both tensile strength and resistance decrease was performed using MINITAB 18 software. The regression method in Minitab uses the least squares method to derive the equation. In this study, there are three processing parameters at two levels each. The number of terms in the regression models depend on the degrees of freedom of the main effect terms and the p-values of each term. The analysis of variance (ANOVA) tables for the tensile strength response and the absolute resistance decrease response (Table 7 and Table 8) contain the effect of each factor and the experimental error. The level of confidence used for the ANOVA analysis is 95% and thus, for significance of the processing parameter in the regression equation the p-value should be less than 0.05. If the p-value is less than 0.05, it is possible to conclude that the model explains any variations in the response [65]. Since residuals for both models approximately followed a normal distribution, linear regression equations were deemed appropriate.

The final linear regression model for tensile strength is as follows:

\[
T(m, t, c) = 15.67 + 0.2827 \cdot m - 0.02641 \cdot t - 0.4334 \cdot c
\]  

(5)

where T is the tensile strength (MPa) of the composite, \( m \) is the mixing time (Hrs) used for fabrication, \( t \) is the casting temperature (°C), and \( c \) is the CB content (%) in the conductive composite. \( R^2 \) values for a model indicate the degree of agreement between the experimental results and the results predicted by the model [65]. The model has an \( R^2 = 91\% \), indicating that the model can explain the variation in tensile strength to the degree of 91%. In other words, with 91% confidence, increase of one unit of mixing time (Hrs) will
increase the tensile strength by 0.2827 MPa, whereas increase of one unit of casting temperature (°C) and CB loading (%) will decrease the tensile strength by 0.02641 and 0.4334, respectively. As seen in Table 7, p-values for all three processing parameters are less than 0.05 and thus, all factors are significant and relevant to the model. P-values, the R² value, and the residuals all imply that the model is adequate for optimization of tensile strength of CB/SIBS conductive composites.

### Table 7. Analysis of variance for tensile strength regression equation

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>3</td>
<td>24.28</td>
<td>0.00</td>
</tr>
<tr>
<td>Mixing Time</td>
<td>3</td>
<td>13.44</td>
<td>0.006</td>
</tr>
<tr>
<td>Casting Temperature</td>
<td>1</td>
<td>10.04</td>
<td>0.013</td>
</tr>
<tr>
<td>CB Loading</td>
<td>1</td>
<td>49.36</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack-of-Fit</td>
<td>4</td>
<td>16.65</td>
<td>0.009</td>
</tr>
<tr>
<td>Pure Error</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The final linear regression model for resistance decrease is as follows:

$$RD(m, t, c) = 5942 - 188.8 \cdot m - 15.31 \cdot t - 181.2 \cdot c$$ (6)

where RD is the resistance decrease (kΩ/mm) of the composite, m is the mixing time (Hrs) used for fabrication, t is the casting temperature (°C), and c is the CB content (%) in the conductive composite. This model is less adequate in explaining variations in response than that for tensile strength, as seen by the parameter $R^2 = 71\%$. Despite a lower $R^2$, this model is still important for drawing important conclusions regarding how changes in the
statistically significant processing parameters are associated with changes in the response. In accordance with the Pareto charts for the resistance decrease response, the p-values denote that the significant parameters are mixing time and CB loading. Casting temperature does not show statistical significance with this number of experimental runs. Regardless, the term will be kept in the regression equation due to the greater potential for variation in the resistance decrease response caused by material properties and external factors.

Table 8. Analysis of variance for specific resistance decrease regression equation

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>F-Value</th>
<th>P-Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>3</td>
<td>5.71</td>
<td>0.022</td>
</tr>
<tr>
<td>Mixing</td>
<td>3</td>
<td>5.71</td>
<td>0.044</td>
</tr>
<tr>
<td>Time</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Casting Temperature</td>
<td>1</td>
<td>3.21</td>
<td>0.111</td>
</tr>
<tr>
<td>CB Loading</td>
<td>1</td>
<td>8.21</td>
<td>0.021</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack-of-Fit</td>
<td>4</td>
<td>9.74</td>
<td>0.024</td>
</tr>
<tr>
<td>Pure Error</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

According to the Taguchi method, when composites are fabricated using the optimal parameters for a maximum tensile strength response (15% CB under 6 hours of mixing time and cast at 23°C) the fitted value for the tensile strength and the S/N ratio are 9.369 MPa and 19.344, respectively. Experimental validation of composites under those parameters yielded an average tensile strength of 9.504, indicating that Taguchi under predicts the tensile strength by less than 1%. Taguchi method prediction of resistance decrease for the optimal parameters for a maximum delta (15% CB under 2 hours of mixing time and cast at 23°C) results in a value of 2810.5 kΩ/mm and S/N ratio of 71.286. Experimental validation shows that Taguchi over predicts the specific resistance decrease.
Additionally, response optimization was done using the regression models from the screening analysis. Results for the multiple response prediction can be seen in Table 9. With 95% confidence, regression models predict that the optimal parameters for maximum tensile and absolute resistance decrease are: 2 hrs mixing time, 23°C casting temperature, 15% CB loading. Using these models and this analysis, optimal parameters can be obtained for numerous target applications.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing Time</td>
<td>2</td>
</tr>
<tr>
<td>Casting Temperature</td>
<td>23</td>
</tr>
<tr>
<td>CB Loading</td>
<td>15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Response</th>
<th>Fit</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile</td>
<td>9.132</td>
<td>(8.369, 9.896)</td>
</tr>
<tr>
<td>Resistance Decrease</td>
<td>2297</td>
<td>(1564, 3030)</td>
</tr>
</tbody>
</table>

Validation of the model was done using alternate levels for the processing parameters. The experimental results and model fits of three other combinations of processing parameters are shown in Tables 10 and 11. The magnitude of the fits of the resistance decrease and the tensile strength for all combinations are in accordance with the experimental results. For the composites fabricated utilizing 2 hours mixing time, 42°C casting temperature, and 15% CB loading, the model only under predicts the resistance decrease by 0.4% and there is a perfect fit for the tensile strength. The maximum difference between the model fits and the experimental values occurred for the 4 hours mixing time, 60°C casting temperature, and 10% CB loading composite, with the model under predicting the resistance decrease by less than 10%. Considering the great probability for variance in
the resistance decrease due to the processing method, a greater than 90% agreement in resistance decrease between experimental values and model fits is excellent for determining the general range of the value we expect to get based on specific parameter levels. Additionally, all experimental values lie within the 95% confidence interval of the model. The tensile strength regression model fits all show greater than 92% agreement with the experimental values. The 2 hrs mixing time, 42°C casting temperature, and 15% CB loading sample model fit is the exact value found from experiments. For the tensile strength model, all experimental values also lie within the 95% confidence interval of the model. The good agreement between experimental and fitted values prove that the established model is satisfactory in predicting the optimal conditions of the composite fabrication parameters.

Table 10. Tensile Strength Regression Model: Experimental Results and Model Fits

<table>
<thead>
<tr>
<th>Mixing Time [Hrs]</th>
<th>Casting Temperature [°C]</th>
<th>CB Content [%]</th>
<th>Tensile Strength [MPa]</th>
<th>Fits</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>42</td>
<td>15</td>
<td>8.623</td>
<td>8.623</td>
<td>(8.00, 9.24)</td>
</tr>
<tr>
<td>4</td>
<td>42</td>
<td>20</td>
<td>7.146</td>
<td>7.021</td>
<td>(6.52, 7.52)</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>10</td>
<td>9.989</td>
<td>10.880</td>
<td>(9.70, 12.06)</td>
</tr>
</tbody>
</table>

Table 11. Resistance Decrease Regression Model: Experimental Results and Model Fits

<table>
<thead>
<tr>
<th>Mixing Time [Hrs]</th>
<th>Casting Temperature [°C]</th>
<th>CB Content [%]</th>
<th>Resistance Decrease [kΩ/mm]</th>
<th>Fits</th>
<th>95% CI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>42</td>
<td>15</td>
<td>2214.09</td>
<td>2203.35</td>
<td>(1571.9, 2834.8)</td>
</tr>
<tr>
<td>4</td>
<td>42</td>
<td>20</td>
<td>845</td>
<td>919.68</td>
<td>(404.09, 1435.27)</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>10</td>
<td>2710</td>
<td>2456.17</td>
<td>(1247.21, 3665.12)</td>
</tr>
</tbody>
</table>
Undoubtedly, the processing parameters involved in fabrication through solvent casting affect the mechanical and electrical properties of the composite. The parameters particularly affect the degree of dispersion of filler in the polymer matrix, thus, affecting the properties. This work explores the relationship these properties have to each other and to the overall composite performance. In this way, it leads to an optimal process for the development of flexible biocompatible pressure sensors to be used in various locations on the body. Since the polymer used is a tri-block co-polymer composed of soft isobutylene domains and hard styrene phases, future studies should investigate the effect of varying the styrene-isobutylene ratio. This can be done by using any of the commercially available SIBS with different styrene content, known as SIBS 73T, 102T, and 103T. Altering the ratio composition of the polymer matrix will potentially result in a different range of mechanical and electrical properties. It is worth exploring whether this would lead to more optimal properties of the composite. Additionally, it would be interesting to consider other processing parameters that might alter the mechanical-electrical relationship, such as: solvent used, mixing temperature, and drying time [66].

3.4 Conclusion

The present study evaluates the effect of three processing parameters on the tensile strength and specific resistance decrease of SIBS/CB conductive thermoplastic composites. Design of experiments methods were employed to reduce the number of experimental runs. A Taguchi analysis resulted in ranking of the CB loading, mixing time, and casting temperature in order of main effects for the tensile strength and specific resistance decrease response. It was demonstrated that for both responses casting temperature was the least
influential factor. Taguchi methods proved that the optimal fabrication parameters for the composite vary depending on the target response. For pressure sensing applications it is important to achieve a maximum resistance decrease to fully utilize the sensitivity capabilities of the sensor yet, it is also important to not lose mechanical integrity. A screening analysis and ANOVA were done to determine the significant parameters. As a result, a statistical regression model for each response was created. The sensitivity of the pressure-sensing capabilities of the composites to the processing parameters is proven. From SEM it is suggested that this is due to the degree of homogeneity of the dispersion, formation of agglomerations, and interphase between filler particles and polymeric phases. This research demonstrated the complex relationship that exists between the mechanical and electrical properties of SIB/CB composites. The results of these analyses can be used as guidelines for selecting the optimal fabrication conditions of SIBS/CB composites for use in biomedical pressure-sensing applications.
CHAPTER 4: Rheological Properties of SIBS/CB Conductive Composites

4.1 Rheological Properties of Conductive Polymer Composites

Addition of CB filler material to a polymer matrix alters the rheological properties of the material. A nanofiller/polymer composite will have viscoelastic behavior which will impact the rheological properties, composite processing, and microstructure [67]. The rheological behavior of conductive polymer composites has practical importance since it influences the final structure of the material and is thus, valuable in determining the optimal processing conditions and understanding the nanoscale characteristics of a material [68]. Rheological methods have been widely used to study the internal structure and physical interactions present in 3D networks in filled polymer systems [69], [70]. SIBS/CB composites have a network consisting of the following interactions influencing the material’s rheological response: CB particle-CB particle, polymer-polymer, CB particle-SIBS polymer, van der Waals, and electrostatic.

One of the most important rheological properties of conductive polymer composites that affects composite processing and fabrication is the viscosity. Flow behavior of a material can be designated as Newtonian, shear thinning, or shear thickening (dilatant) based on the dependence of shear viscosity on the shear rate (Figure 47) [71]. If the flow is independent of the shear rate, it is classified as Newtonian. If the viscosity decreases as the shear rate increase, then the composite exhibits shear thinning. Conversely, if the viscosity increases with increasing shear rates, the behavior is characteristic of shear thickening [71]. Polymers typically exhibit non-Newtonian behavior [72], [71], [73].
Several models, such as Einstein’s equation, have been proposed to predict the viscosity of a filled polymer [74]. Einstein’s equation integrates the volume fraction of filler in the composite:

\[
\eta = \eta_0 \cdot (1 + 0.67 \cdot f \cdot c + 1.62 \cdot f \cdot c^2)
\]

(7)

where \( \eta \) is the viscosity of the filled polymer, \( \eta_0 \) is the viscosity of the neat polymer, \( f \) is the ratio between the length and the diameter of the filler particles, and \( c \) is the volume fraction of filler [75]. The shear viscosity of a composite is affected by the type of polymer, filler type, filler size, filler shape, distribution of filler in the matrix, filler surface, and the affinity of the polymer for the filler [69]. Small particle size, as is the case for the CB nanofillers used in this study, can potentially lead to the creation of interphases which increase the material viscosity. A homogenous filler distribution can decrease the viscosity.
of a filled polymer. In contrast, network formation within the polymer can increase the viscosity and make the material more difficult to manufacture through processes like twin-screw extrusion [76], [77]. Furthermore, higher affinity between the CB particles and the polymer can lead to higher viscosities. Addition of coupling agents such as surfactants, lubricants, and dispersants can also affect the rheological properties of the composite.

The morphological and rheological performance of SIBS/CB composites are assessed in this chapter. The aim is to advance the knowledge of the melt rheology of the composite material over the relevant range of shear rates and temperatures, which is essential for proper material application and identification of the proper processing conditions. Composite rheology is important for efficient design, fabrication, and performance [78]. Based on detailed rheological characterization, thermogravimetric measurements, and imaging, we investigate the influence of CB on the rheological response of the material.

4.1.1 Theory of Viscoelasticity

The theory of viscoelasticity describes the rheological behavior of polymer solutions and melts. The rheological material value functions are determined through oscillatory experiments [79]–[81]. For controlled oscillatory measurements, periodic deformations \( \gamma(t) \) are applied and periodic strains \( \tau(t) \) are subsequently induced. The phase angle, \( \delta \), represents the difference between the stress and strain in an oscillatory test. Complex values are used in place of trigonometric functions for rheological calculations for simplification. The following equations, describing the complex shear strain (\( \tau^* \)) and complex deformation (\( \gamma^* \)), are relevant to the theory of viscoelasticity:
\[\tau^* = \tau_0 \cdot (\cos(\omega \cdot t + \delta) + i \cdot \sin(\omega \cdot t + \delta))\] (8)

\[\gamma^* = \gamma_0 \cdot (\cos(\omega \cdot t) + i \cdot \sin(\omega \cdot t))\] (9)

Viscoelastic behavior can be described by the complex modulus \(G^*\), which is defined as the ratio between complex strain and deformation. The equation for \(G^*\) is as follows:

\[G^* = \frac{\tau^*}{\gamma^*}\] (10)

Two relevant moduli for characterization of rheological behavior are the storage modulus, \(G'\), and the loss modulus, \(G''\). The storage modulus (in-phase component) represents the degree of elasticity of a material. The loss modulus (out-of-phase component) represents the viscous behavior, or energy which is irreversibly dissipated due to viscous flow [80]. The relevant equations for \(G'\) and \(G''\) are:

\[G' = \frac{\tau_0}{\gamma_0} \cdot \cos \delta\] (11)

\[G'' = \frac{\tau_0}{\gamma_0} \cdot \sin \delta\] (12)
The ratio of loss and storage modulus is the dissipation factor \( \tan(\delta) \):

\[
\tan \delta = \frac{G''}{G'}
\]  

\((13)\)

4.2 Materials and Methods

4.2.1 Materials and Sample Preparation

The SIBS pellets used in this experiment have a composition by weight of 22% styrene and 78% isobutylene; a common composition near the mid-range between rubbery and glass-like possible material behaviors. The commercially available block copolymer, trade name SIBSTAR™ 72T, with a molecular weight of 75,000 g/mol was used in the as-received condition from Kaneka Corporation. Carbon black filler material with an average 32.2 nm particle size, trade name BLACK PEARLS® 2000, were also used as-received from Cabot Corporation. SIBS/CB particle composites were fabricated through a solvent casting procedure. To enable direct comparison and to maintain consistency, nanocomposites used in the current study were fabricated according to the same procedure. A mixture of pelletized SIBS and CB nanoparticles were dissolved in 8.57% w/v of toluene as the solvent. In order to ensure adequate, uniform, and consistent dispersion of filler CB particles in the soft polymer matrix, a combination of high shear mixing and ultrasonication was used. High shear mixing of the dissolved materials was performed using an IKA Eurostar 40 Digital High-Shear Mechanical Mixer for periods of 6 hours at 2000 revolutions per minute with 275 mL of toluene. Due to solvent evaporation in solutions mixed for 6 hours, another 275 mL of toluene was added at the 3-hour point. The mixture
was then subjected to ultrasonication at 50 kHz for an additional 45 minutes with a QSonica® 700 Watt Ultrasonic Cell Disruptor to improve dispersion of the filler, based on prior success of this method. Subsequently, solutions were poured into flat stainless-steel trays and left to cure for twenty-four hours in a fume hood at 23°C. The final conductive composites had CB concentrations of 0%, 5%, 10%, 15%, and 20% loading by weight. Specimens produced were approximately 0.17 mm thick. Specimens were then cut into 25 mm diameter circles and layered to a thickness of 2.5 mm. Samples were vacuum pressed to ensure no encapsulation of air within the samples.

4.2.2 Thermogravimetric Analysis (TGA)

The thermogravimetric analysis (TGA) of the SIBS/CB composites was performed using a TGA Q50 from TA Instruments (Figure 48). Experiments ran in a nitrogen atmosphere with a 60 mL/min sample flow rate. The instrument was equilibrated at 30°C. Samples were heated from ambient temperature to 800°C at a heating rate of 10°C/min.

Figure 48. TGA Q50 from TA Instruments
4.2.3 Rheology Testing

Rheological testing was used to study the linear-viscoelastic behavior. Dynamic oscillatory rheological measurements were conducted using an HR-1 Discovery Hybrid Rheometer (DHR) from TA Instruments (Figure 49) and located in the Johnson and Johnson® 3-D Printing Center of Excellence Collaborative Laboratory at the University of Miami. Experiments were carried out in an Environmental Test Chamber (ETC) (Figure 49) connected with liquid nitrogen using a circular parallel-plate fixture geometry (25 mm in diameter). Approximately 2.5 mm thick samples (equivalent to 0.982 mL sample volume) were loaded between the two parallel plates with a gap of 2000 μm at room temperature. Before testing commenced, the temperature was set to 225°C in the ETC. Nitrogen flow between 5-10 Pa was used during this period to ensure temperature stabilization and no degradation due to air. The gap was then reduced while monitoring the axial force and observing for any material resistance. Amplitude sweep, frequency sweep, and temperature sweep tests were carried out as part of this analysis using TRIOS software.

Figure 49. HR-1 Discovery Hybrid Rheometer and ETC with SIBS/CB composite
4.2.4 Rheology Testing: Amplitude Sweep

In the amplitude test the frequency is held constant and the strain signal (or amplitude of the deformation) is varied. To avoid affecting the material viscosity due to amplitude, amplitude logarithmic sweeps were used to find the linear region. Measurements were performed at 225°C with an oscillation strain rate percentage range from 0.025% to 25% at an angular frequency of 1 rad/sec. The storage modulus $G'$ versus oscillation strain rate % plot was used to determine the linear viscoelastic region.

4.2.5 Rheology Testing: Frequency Sweep

Frequency sweeps were performed due to the extent of material rheological property variation with radial frequency [82]. For the frequency sweeps, strain-controlled experiments were completed. For all experiments, the radial frequency was varied while the oscillation strain was held at 0.5%, as determined from the amplitude sweep test. Logarithmic sweeps ranged from 0.01 to 500 rad/sec. Complex viscosity, storage modulus, and loss modulus were measured against the shear rate in double logarithmic plots.

4.2.6 Rheology Testing: Temperature Sweep

Temperature sweeps are held at constant angular frequency and deformation. Oscillation tests were run at an angular frequency of 1 rad/sec and at 0.5% oscillation strain, as determined from the amplitude sweep test. Initial temperature was set to 225°C and lowered to 25°C at a rate of 5°C per minute. The temperature dependency of the storage modulus and loss modulus were determined, as well as any potential crossover gel points ($G'=G''$).
4.2.7 Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to observe the flow pattern and surface of the SIBS/CB composites. Specimens were sputter-coated with a Denton Vacuum Desk V TSC sputtering system and then inspected using a JEOL JSM-6010PLUS/LA analytical SEM. Of particular interest were the topographies of the neat polymer and the 15% CB/SIBS composite.

4.3 Results and Discussion

The goal of the experiments was to understand the fundamental characteristics of SIBS/CB composites at the nanoscale through the use of rheological properties. Since the rheological properties of a material are related to the microstructure of the composite, an understanding of the rheological response will also aide in improving the fabrication method and processing conditions of the material. Rheological measurements were performed so that the influence of CB filler particles on the melt viscosity may be assessed. An HR-1 Discovery Hybrid Rheometer was used for the experiments. The following samples were tested and analyzed: SIBS neat polymer, 10% CB, 15% CB, 20% CB by weight. The CB content levels were selected based on previous studies from Chapter 2 indicating that the CB content at the percolation threshold for conductivity in SIBS/CB composites lies between 15% and 20% by weight. It is important to test the rheological properties at and near the electrical percolation threshold because of the materials potential use in external (stick-to-skin) biocompatible pressure sensors.
4.3.1 TGA

The results of the TGA analysis are shown in Figure 50. The results show the degradation temperature for all samples and any residual weight of the composite. With increasing CB filler amounts present in the composite, composite degradation is delayed to higher temperatures. The degradation temperature increased with increasing filler loading in all cases, implying that CB filler acts as an effective thermal barrier. Similar results regarding thermogravimetric analysis of nano clay or graphene filled polymers have been reported in the literature [83]. In one study, it was reported that graphene nanoplatelets cause the formation of charred layers on the surface of the composite, which effectively inhibits the supply of oxygen to the material [77]. In this study, carbon black nanoparticles are likely acting in the same manner thus, increasing the thermal stability of the composite by approximately 10°C. Furthermore, for each composite the residual weight of the composite was consistent with the weight percentage of the CB filler used; additional verification that the solvent-casting process utilized yielded samples with exact and expected quantities of filler. Given the temperature of onset for degradation observed in the rheological studies, we can confirm the absence of degradation during twin-screw extrusion at temperatures below 410°C. Further, the addition of carbon black nanoparticles to SIBS would enable an increase in extrusion temperature of up to 10°C.
4.3.2 Linear Viscoelastic Region: Amplitude Sweep Test

At certain amplitudes within the lower range, materials have a linear viscoelastic region in which the storage modulus, $G'$, and the loss modulus, $G''$, are independent of amplitude. In this region the idle state of the sample is not disturbed, making it desirable to conduct all subsequent rheology tests within this region. At specified amplitude values, material modulus ($G'$ and $G''$) properties will begin to decrease with increasing amplitudes [79]. If tests were conducted in the non-linear region, the viscosity and other relevant rheological properties would be affected. Hence, measurements within the linear viscoelastic regime are absolutely necessary [84]. Figure 51 shows the $G'$ versus oscillation strain percentage plot. From this plot it was determined that a 0.5% for oscillation strain
would be used for all samples tested since it is within the linear viscoelastic region of all composites.

Figure 51. Storage modulus profile with increasing shear rate for all SIBS/CB composites

4.3.3 Rheological Percolation

To fully understand the rheological behavior of a material, the rheological percolation threshold must be determined. Behavior is typically different before and after the threshold. Similar to electrical percolation, increasing amounts of filler in the composite cause carbon black particle-particle interactions to dominate polymer-particle interactions at and beyond rheological percolation [71]. In electrical percolation, the particle-to-particle distance must be sufficiently close for electrons to effectively tunnel and create a tunneling current. In contrast, particle proximity is not a requirement for rheological percolation, but
fillers should form a network. Therefore, the particle-to-particle distance required for rheological percolation is much higher than that for electrical percolation. In other words, the amount of CB required for rheological percolation should be less than that for electrical percolation. The rheological threshold can be determined from the sudden rise in the complex viscosity vs. volume fraction (or weight %) plot, as seen in Figure 52. Figure 52 illustrates the complex viscosity of samples of various CB loadings at a shear rate of 0.13 sec⁻¹. Rheological percolation for SIBS/CB composites is achieved between 5-10% CB loading, approximately 1.5-3X lower than that for electrical percolation. The overriding consideration for this material is electrical performance. As 5% CB nanocomposites behave as an insulator, this loading is removed from consideration in the remainder of this study.

**Figure 52. Variation of the complex viscosity with CB filler loading**
4.3.4 Effect of Shear Rate on Viscosity: Frequency Sweep

The viscosity data for the neat, 10, 15, and 20% CB loading samples over a shear rate range of $10^{-2}$ to $10^{2}$ s$^{-1}$ at 35°C, is illustrated in Figure 53. The viscosity of Newtonian fluids remains constant at all shear rates at a constant temperature and pressure. For non-Newtonian fluids, the viscosity varies with the shear rate and time. All samples tested exhibit a discernable non-Newtonian behavior over the range of shear rates investigated, as expected. Incorporation of carbon black nanoparticles significantly increases the melt viscosity. Complex viscosity curves for the composites containing CB start at higher values relative to the neat polymer; likely a result of particle-particle interactions playing a dominant role. The magnitude of the increase and variation in complex viscosity due to addition of CB is more shear rate dependent in composites containing an amount of CB at or near the percolation threshold. Additionally, it is important to note that at lower shear rates the number of polymer chain entanglements present is higher so there is a greater impact of disentanglement due to the flow. Hence, the influence on the viscosity due to filler is greater at lower shear rates.

Despite having comparable complex viscosities for lower shear rates, the curves for 10, 15, and 20% CB begin to show marked deviation for rates above 1 s$^{-1}$. The neat polymer exhibits linear behavior with a negative slope throughout the range of shear rates. The composites, however, exhibit deviation from the initial linear trend at higher shear rates. At the highest shear rate tested, 100 s$^{-1}$, the curves for the neat polymer, 10% CB composite, and 20% CB composite all demonstrate approximately the same complex viscosity. However, composites fabricated with 15% CB by weight (the electrical percolation threshold) exhibit shear thinning behavior and much lower complex viscosities.
at high shear rates. Thus, although all composites are shear sensitive, 15% CB composites show the greatest sensitivity in the shear rate range of interest.

The rheogram for 10% CB and 15% CB composites in Figure 53 display non-linear shear thinning behavior predominantly at high shear rates, with the non-linearity being more distinct for the 15% CB composite. The greater sensitivity to shear rate in 15% CB composites is attributed to the particle-to-particle distance and the change in structure present in these composites versus the neat polymer or composites above or below the electrical percolation threshold. As is shown in Chapter 2, tensile testing of SIBS/CB composites has indicated that 15% CB composites have higher tensile strength than other CB loadings, implying that carbon black more readily creates a 3-D reinforcing network in the polymer at this loading percentage. Shear stresses on 15% CB composites cause a disruption of this 3D network and contribute to the change in rheological properties relative to other carbon black loadings. In filled systems, particle arrangement will always be in favor of the lowest resistance to flow. When the shear rate increases, structural changes occur (Figure 54), which result in a decrease in the viscosity. Additionally, rheological behavior is affected by particle dispersion and material processing conditions. Dispersion necessarily influences the particle-to-particle distance and, subsequently, the particle-particle interactions. Insufficient dispersion and the associated presence of agglomerates is expected to increase the resistance to flow, especially at low deformation rates which may be insufficient to break particle clusters [85]. Due to the rupture of the microstructure and any agglomerations in 15% CB composites at high shear rates, the resistance to flow decreases significantly in this range. It should be noted that complex viscosity curves are consistent with the extent of agglomerations in these composites as observed by
microscopy in Chapter 2. Since at high shear rates the 15% CB composite complex viscosity steeply decreases, it has the best dispersion, least amount of agglomerations, and highest permissibility for flow. In contrast, 10% CB composites are the curve with the highest viscosity values, implying the greatest likelihood for agglomerations and the most difficult material to process regardless of shear rate. These observations are also consistent with microscopy indications of agglomerations. The lower resistance to flow in the 15% CB composites can also be observed visually. Post-testing flow pattern images for the neat polymer and 15% CB composite are illustrated in Figure 55 at the same magnification level. The 15% CB image shows clear flow lines that are not present in the neat polymer, consistent with the lower complex viscosity of the composite relative to the neat version.

![Graph](image)

**Figure 53. Complex viscosity versus shear rate for all composite types**
The frequency sweep oscillation test was also used to observe the frequency-dependent (or shear-rate dependent) behavior of $G'$ and $G''$. Figure 56 shows the moduli for the neat polymer. Figure 57 contains the results for the 10% CB composite and Figure 58 depicts the moduli for the 15% CB composite. Any section of the plots where the curves for storage modulus and loss modulus intersect is referred to as the crossover region and the respective value for the moduli is known as the crossover modulus [79], [80]. The crossover region is telling of a potential structural breakdown. The oscillation frequency sweep showed that in the neat polymer there is no crossover point in the shear rate range.
tested. Throughout the range, G’ is higher than G’’, implying elastic solid-like behavior. In contrast, both the 10% CB composite and the 15% CB composite exhibit crossover phenomena. In the lower shear rate regime, G’’ is higher than G’ for both 10% and 15% CB composite, demonstrating viscous liquid-like performance. For both composite types, the crossover point and modulus is associated with the onset of the elastic dominant domain. For the 10% CB composite, the crossover point is shifted into the lower frequency region and occurs before the moduli have reached a maximum value. In contrast, for 15% CB composites the crossover point occurs at a higher shear rate but the crossover modulus is 2.4 times smaller than that for 10% CB composites. Hence, the magnitude of the crossover shear rate increases with increasing filler concentration. The crossover point for the storage and loss moduli, found from the frequency sweep test, can be used to determine the relaxation time of the material, given by the inverse of the crossover frequency [86]. The higher crossover point for composites with higher CB loadings indicates smaller relaxation times. Additionally, a higher shear rate crossover region for 15% CB composites signifies material with a lower average molar mass and a narrower molecular weight distribution [87], which is desirable for pressure-sensing applications. Furthermore, addition of carbon black filler increased the magnitude of G’ and G’’ compared to that of the neat polymer.
Figure 56. Frequency dependence of the storage modulus and loss modulus for the neat SIBS 72T polymer

Figure 57. Frequency dependence of the storage modulus and loss modulus for 10% CB composites
4.3.5 Temperature Sweep

Figure 59-62 illustrate the temperature sweep results for all SIBS/CB composite types tested. The plots in Figure 59-62 show the storage modulus (G’), loss modulus (G’’), and tan delta as a function of temperature. In temperature sweep tests, crossover points, defined as points where G’=G’’ (or tan $\delta$= 1 or $\delta$ = 45°), designate a transition in viscoelastic behavior from viscous, liquid-like to elastic solid-like behavior [88]. In rheology, crossover points are referred to as gel points [89]-[92]. Over the temperature range tested, none of the samples show this crossover behavior. For all samples, both G’ and G’’ show a plateau for temperature below 100°C, a sharp decrease around 112°C, and a gradual decrease as temperature increases further. G’ remains higher than G’’ throughout the temperature range for all composites, implying that the behavior of the composites is predominantly elastic and solid-like. Tan delta values are lower than 1 throughout the
temperature range for all samples tested. Since there is no visible crossover point in any of the composites from the temperature sweep, it is likely that any crossover event in SIBS/CB composites from the frequency sweep is associated with the particle-particle interactions. Interactions between adjacent CB particles may not be temperature sensitive. Interactions also exist between CB particles and both the styrene and isobutylene phase of the polymer. The absence of a crossover point in samples containing CB shows that filler-polymer interactions with either polymer phase are also not temperature sensitive. This may also suggest that CB/SIBS composites are stable during storage.

Figure 59. Temperature sweep for neat SIBS 72T polymer
Figure 60. Temperature sweep for 10% CB composites

Figure 61. Temperature sweep for 15% CB composites
Figure 62. Temperature sweep for 20% CB composites

From an industrial perspective, twin-screw extrusion (Figure 63) is the method of choice for fabrication for production of conductive polymer composites due to the resulting product quality and high production volumes [76], [77]. However, unlike in the method utilized in this work (solvent casting), in twin-screw extrusion materials will be subjected to high temperatures and thus, it is important to observe the relationship between temperature, viscosity, and CB content. From Figure 59-62 it can be seen that addition of CB filler, regardless of the quantity, does not change the performance of the composites relative to that of the neat polymer. Due to this observation, SIBS/CB composites can sustain the temperatures involved in twin-screw extrusion without causing polymer degradation.
Figures 64 and 65 show the results of the complex modulus $G^*$ and the phase angle $\delta$ from the temperature sweep. Both of these variables help assess material texture under deformation. The complex modulus is a measure of resistance to deformation. The complex modulus measures stiffness, where a higher value of $G^*$ indicates a stiffer structure. It provides a measure of the total resistance to deformation when the composite is subjected to shear loading [93]. The phase angle, defined as the phase lag between the wave forms of shear stress and shear strain, denotes the degree of elasticity [88]. The complex modulus and the phase angle can be used to predict the storage stability for the different SIBS/CB composite types [94]. Through the range of temperatures tested, the neat polymer shows greater change in $G^*$. Since changes in $G^*$ are smaller with addition of CB to SIBS, SIBS/CB composites are likely to have a more stable shelf life.
Figure 64. Temperature variation of the complex modulus ($G^*$) of SIBS/CB composites

From Figure 65 it can be seen that for most of the temperature range, the phase angle for each composite remains between 10 and zero degrees. This behavior is characteristic of an elastic material. In the middle of the temperature range, all curves reach a maximum phase angle between 15°C and 28°C. The increase in the phase angle between 100°C and 150°C for all composites suggests that here resistance to deformation is resulting from a combination of friction and interconnected structures in the composites. Since the phase angles never reach 90°C for any of the composites, behavior is never purely viscous. At 110°C neat polymer and 15% CB samples both reach their maximum phase angle, whereas 10% CB and 20% CB reach a maximum at higher temperatures closer to 140°C. The neat polymer reaches a higher maximum phase angle and shows more variation in phase angle with temperature. This is interpreted to mean that the neat polymer is more sensitive to temperature and thus, likely has a shorter shelf life. In effect, addition of carbon black increases the likelihood of a stable shelf life. As a result, permanent deformation is less likely to occur in samples with CB filler.
Figure 65. Temperature sweep analysis of phase angle

4.4 Conclusion

To explain the variation of the rheological properties of SIBS/CB composites with CB loading, shear rate, and temperature, it is important to understand the combination of filler-filler, polymer-polymer, and polymer-filler interactions. Processing conditions, filler dispersion, and filler-polymer compatibility can also change the rheological properties observed. This work explores the relationship between CB loading (under, at, and above the electrical percolation threshold) and the material’s rheological properties. Electrical and rheological percolation are both of importance for the use of these composites for external pressure sensors. They are also necessary for deciding the most efficient, low cost production method that does not compromise material integrity and desired properties.

Thermogravimetric analysis resulted in the evaluation of CB filler as a thermal barrier for the composite. All of the SIBS/CB composites exhibited non-Newtonian viscosity behavior. It was demonstrated that incorporation of CB filler significantly
increases the melt viscosity, the storage modulus, and the loss modulus. Major increases in the viscosity were found at filler loadings beyond 5%. Composites with 15% CB manifested non-linear shear thinning behavior, particularly at high shear rates, which is attributed to the dominance of particle-particle interactions. These composites demonstrated particle cluster rupture and low resistance to flow at high shear rates. Temperature sweep tests illustrated that elastic behavior is dominant in all composites.

Rheological analysis of SIBS/CB conductive composites provides insight into the internal structure present, which aides in determining the suitability of using alternative processing methods, such as twin-screw extrusion or injection molding, for long-term production. During fabrication utilizing these methods, the shear rate is proportional to the injection speed. If the shear rates are in the non-Newtonian region of the curve, small variations in shear rate may result in large variations in viscosity. This leads to inconsistent mold filling, incomplete penetration, and the occurrence of short shots. Knowledge of the appropriate shear rates and temperature ranges will permit development of consistent composite material with minimal defects.
CHAPTER 5: Biocompatibility Retention Analysis of SIBS/CB Composites

5.1 Biocompatibility Background

SIBS has become an increasingly important material in the biomedical field due to its high degree of biocompatibility [12], [95]. The biocompatibility of SIBS alone is well-documented and one of the primary reasons it is selected as the material of choice for the intended pressure sensing applications of this work. To be able to use SIBS/CB composites for biomedical pressure sensing applications the composites must retain the same excellent biocompatibility present in the neat polymer. Before any material for a biomedical device can be used clinically, not only efficacy but also safety must be evaluated [96], [97].

Biological testing methods for materials and devices are particular to the end-use application [98]. The necessary and required biocompatibility testing will depend upon material type, expected duration of material use, and location of application [99]–[101]. The composite material developed in this work has the potential to be used both for external (stick-to-skin) and internal (implantable) pressure sensing applications. The type of biological testing required for implantable use includes: systemic toxicity, gene toxicity, immune response, lipid-induced degradation, and carcinogenicity [98], [99]. Suggested biocompatibility testing for external use applications, such as the one presented in this work, include: cell toxicity, irritation, and sensitization [99]. Additionally, the material is expected to not induce immunological or foreign body reactions.

The focus of this chapter is to determine whether addition of CB to SIBS permits retention of biocompatibility. This study provides an understanding as to whether loadings
at and above the percolation threshold for electrical conductivity cause any effects which would restrict the material’s use in biomedical applications. In this chapter, any potential cell toxicity caused by addition of CB to SIBS is evaluated and the viability of using SIBS/CB composites for external stick-to-skin applications is determined. A second objective is to recommend subsequent necessary and sufficient biological testing to establish confidence concerning the biological response of SIBS/CB composites.

5.2 Materials and Methods

5.2.1 Materials and Sample Preparation

The SIBS pellets used in this experiment have a composition by weight of 22% styrene and 78% isobutylene. The commercially available block copolymer, trade name SIBSTAR™ 72T, with a molecular weight of 75,000 g/mol was used in the as-received condition from Kaneka Corporation. Carbon black filler material with an average 32.2 nm particle size, trade name BLACK PEARLS® 2000, were also used as-received from Cabot Corporation. SIBS/CB particle composites were fabricated through a solvent casting procedure. SIBS pellets mixed with CB particles were dissolved in 8.57% w/v of toluene as the solvent. In order to ensure adequate and uniform dispersion of filler CB particles in the soft polymer matrix, a combination of high shear mixing and ultrasonication was utilized. High shear mixing of the dissolved materials was performed using an IKA Eurostar 40 Digital High-Shear Mechanical Mixer for periods of 6 hours at 2000 revolutions per minute with 275 mL of toluene. Due to solvent evaporation in solutions mixed for 6 hours, halfway through the process, an extra 275 mL of toluene was added. Composite samples were then subjected to ultrasonication at 50 kHz for an additional 45 minutes with a QSonica® 700 Watt Ultrasonic Cell Disruptor to improve dispersion of the
filler. Subsequently, solutions were poured into flat stainless-steel trays and left to cure for twenty-four hours in a fume hood at 23°C. The final conductive composites had CB concentrations of 0%, 15%, 20%, and 25% loading by weight. These loadings were selected with the intent of determining whether percolation loadings (and loadings slightly above it) are achievable without biocompatibility loss. Specimens produced were approximately 0.17 mm thick.

5.2.2 Cell Toxicity Assay

The SIBS/CB composites of various loadings, as well as the neat sample, were tested for cell viability. This test evaluates in vitro toxicity of substrate material (SIBS/CB composite) to cultured cells [41], [99]. The cells utilized for this experiment were a sub-population of Mesenchymal Stem Cells, Marrow-Isolated Adult Multilineage Inducible (MIAMI) cells, derived from human bone marrow. Neat polymer and composite scaffolds were sterilized in 70% Ethanol for two hours. Each scaffold was rinsed three times with Phosphate-Buffered Saline (PBS). Scaffolds were then placed into MIAMI cells expansion medium consisting of the following: DMEM-low glucose, 3% FBS, 100 μM ascorbic acid, and a mix of fatty acids. Subsequently, samples were incubated in a tissue culture incubator for two hours. After two hours, 15k MIAMI cells were plated on top of the scaffolds and placed into a 24-well plate in expansion medium. Medium was changed after three days. During the incubation period, cells were monitored to observe any toxicity effect of the scaffolds on the cells. Control samples, consisting of MIAMI cells in expansion medium but in the absence of composite scaffolds, were also tested for cell viability. Following the 7-day incubation period, microscopy images were taken and SIBS/CB scaffolds were removed. To assess cell toxicity, cells were then trypsinized and counted.
5.3 Cell Toxicity Assay Results and Discussion

The effects on the biocompatibility of CB particle reinforced SIBS polymer were analyzed. MIAMI stem cells were incubated with CB/SIBS 72T scaffolding for a seven-day period. Cells were monitored and counted to ascertain any potential toxicity effects from the CB particles. Table 10 shows the final cell count (after the 7-day incubation period) for well 1, well 2, the mean, and the standard deviation across each scaffold that was plated with cells. The cell count results shown in Table 10 are for the following samples: control, neat polymer, 15% CB, 20% CB, and 25% CB. Based on these results, it is clear that cells proliferated in each of the samples tested. It is expected that the cell count will increase under the control conditions (only cell expansion medium present). It is also expected that cells will proliferate in the neat polymer sample due to the excellent biocompatibility observed in SIBS. The results summarized in Table 10 do not indicate any signs of cell toxicity in any of the scaffolds containing CB loadings.

Table 12. Summary of cell viability after 7-day incubation period

<table>
<thead>
<tr>
<th>Samples</th>
<th>Well 1</th>
<th>Well 2</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  Control</td>
<td>41000</td>
<td>49000</td>
<td>45000</td>
<td>5656.854</td>
</tr>
<tr>
<td>2  Neat Polymer</td>
<td>42500</td>
<td>-</td>
<td>42500</td>
<td>-</td>
</tr>
<tr>
<td>3  15% CB</td>
<td>37500</td>
<td>48750</td>
<td>43125</td>
<td>7954.951</td>
</tr>
<tr>
<td>4  20% CB</td>
<td>40000</td>
<td>50500</td>
<td>45250</td>
<td>7424.621</td>
</tr>
<tr>
<td>5  25% CB</td>
<td>35000</td>
<td>45000</td>
<td>40000</td>
<td>7071.068</td>
</tr>
</tbody>
</table>

In Figure 66 the initial and final cell count for each sample tested are illustrated. It can clearly be seen that the most favorable conditions for cell proliferation were the control conditions and the 20% CB loading conditions. This is a favorable result to obtain because
Chapter 2, on the relationship between conductivity and carbon black loading, indicates that the percolation threshold for conductivity (small pressure range) in SIBS/CB composites and the associated peak in sensor performance is at approximately the same loading percentage. Thus, fabrication of CB/SIBS composites using the percolation threshold necessary for optimum sensing performance is not likely to preclude the biocompatibility requirement for biomedical applications.

![Figure 66. Total cell count for SIBS/CB specimens of various loadings at day 0 and day 7 of the incubation period](image)

Figure 67 shows that the final average cell count for each scaffold incubated with MIAMI cells. All scaffold conditions were cultured with an initial 15,000 cell count. It was expected that the control group would achieve maximum cell proliferation. Data shows no significant variation in cell viability across the various loadings.
A comparison of cell growth for each day of the 7-day incubation period across all of the samples tested is shown in Figure 68. All of the loadings tested show a linear relationship for cell growth. The conditions with the steepest slope (fastest rate of growth) are the control condition and the 20% CB conditions, followed by the 15% CB specimens. Cell growth was observed as expected despite the presence of nano-filler. No cell toxicity was observed in any of the samples tested.
Figure 68. Comparison of cell count throughout 7-day incubation period for all samples tested

Figure 69 contains the microscopy images for each sample tested. The images were taken after the scaffolds had undergone a 7-day incubation period with MIAMI cells and expansion medium. Microscopy images show no signs of toxicity due to the presence of CB, regardless of loading percentage. The images verify the results from the cell count and indicate that CB does not visibly affect composite biocompatibility.
5.4 Further Biocompatibility Testing Suggestions

As the potential applications for medical devices, both external and internal, have increased, the need for biocompatible materials with a variety of capabilities has become crucial. Prior studies using electrically conductive polymers for biomedical applications have tested for cytotoxicity, skin irritation, and skin sensitization [41]. The assays and procedures below regarding irritation and sensitization should be used as guidelines for future biocompatibility testing of SIBS/CB composites for pressure sensing applications.

5.4.1 Irritation Assay

The goal of this type of biocompatibility testing is to determine the level of irritancy, if any, of SIBS/CB composites. This test should be done with a minimum of four test groups, two of which should be 15% CB composites and 20% CB composites (percolation threshold range values). The neat polymer SIBS 72T should be used as a
negative control. A positive control, such as 1-Chloro-2, 4-Dinitro Benzene (DNCB), must also be used. A minimum of eight to ten mice should be used per group tested to ensure accurate and adequate results.

As part of the preparation step, the hair from 4 different areas of mice should be clipped. Epidermal incisions should then be made on 2 sites. Test material should be placed on one intact site and one incised site. Control material should also be placed on one intact site and one incised site. Subsequently, gauzes should be placed on all sites and wrapped with a polyethylene sleeve. After 24 hours, gauzes, test material, and control material should be removed. One hour after removal, sites should be scored for erythema and edema. Sites should then be rescroed at 48 hours and 72 hours after test application. The test procedures are in accordance with ASTM F719-81.

An alternative method for conducting this test is using a patch test on the skin of rabbits, utilizing Test Practice F719. After 24 hours, the patch is removed and skin is observed and evaluated for erythema and edema.

5.4.2 Sensitization Assay

The objective of the sensitization assay for SIBS/CB composites is to assess the propensity of the material to stimulate delayed contact hypersensitivity. A modification of a murine (mice) local lymph node assay can be utilized for this purpose. Similar to the irritation assay, the sensitization test should be done with a minimum of four test groups, two of which should be 15% CB composites and 20% CB composites (percolation threshold range values). The neat polymer SIBS 72T should be used as a negative control. A positive control, such as 1-Chloro-2, 4-Dinitro Benzene (DNCB), must also be used. A
minimum of eight to ten mice should be used per group tested to ensure accurate and adequate results.

As part of the preparation step, the hair from the back of the mouse ear should be clipped. SIBS/CB composites should be dissolved in DMSO for topical application. Test material and control material should be applied topically and allowed to dry. This should be repeated after 24 hours and again after 48 hours. Seven days after the final topical application, test and control solutions will once again be applied. Between 24 to 48 hours after this final application, sites should be scored for erythema and edema and ears should be measured for swelling. The test procedures are in accordance with ASTM F72148-13. Histology tests should also be completed as part of the testing procedure.

Two types of sensitization assays are normally used for biological testing. The type described here is the cell mediated type (Type IV). The other kind, Type I, is known as the atopic type and involves measurement of IgE antibodies.

5.5 Conclusion

In this study, the effects on the biocompatibility of CB particle reinforced SIBS polymer were analyzed. MIAMI stem cells were incubated with CB/SIBS 72T scaffolding for a seven-day period. Cells were monitored and counted to ascertain any potential toxicity effects from the CB particles. Results indicate that none of the samples demonstrated any toxicity. Cell viability was >90%. From the data, it can be seen that the 20% CB scaffold exhibited cell growth similar to that of the control culture, though all loading percentages exhibited similar behavior. This likely indicates an effective, complete encapsulation of the CB particles. A comparison across various CB loadings indicates that despite higher CB
loadings, cells continue to grow and proliferate as expected. These preliminary results indicate that the presence of CB particles, whether in low or higher quantities, may not alter the excellent biocompatibility observed in the neat polymer. Although these results do not limit the use of CB/SIBS composites for stick-to-skin pressure sensors, further sensitization and skin irritation testing is needed to definitively prove viability for external medical applications. Given the performance of SIBS/CB for detecting pressure and deformation, the results of this first-level biocompatibility testing suggest that SIBS/CB composites may be well-suited for biomedical sensing applications and that further immune response, genotoxicity, and carcinogenicity testing is justified.

Recommendations and procedures for further biocompatibility testing of SIBS/CB composites are given in this Chapter. For biomedical pressure sensors constructed with this type of composite, it is suggested that irritation and sensitization assays be done. Recommendations and procedures should be modified as necessary and may not constitute the only testing that is required for SIBS/CB composites.
CHAPTER 6: Concluding Remarks and Recommendations for Future Work

6.1 Concluding Remarks

Thin films have recently emerged as excellent candidates for biomedical devices due to their ability to target sensitive and complex anatomical sites. There is a need for extensive studies to optimize the performance of thin films accurately. This thesis provides the fundamental knowledge to develop a novel type of composite, composed of the tri-block copolymer SIBS and carbon black filler particles, for pressure sensing biomedical applications using variable changes in resistivity. It provides guidance for the fabrication, characterization, and manufacturing of conductive thin films made of SIBS reinforced with CB filler.

6.1.1 Balance Between Mechanical and Electrical Properties

The relationship between processing, CB dispersion, mechanical properties, and pressure-induced resistivity changes is complex. The sensitivity of four SIBS/carbon black composites was evaluated and compared so that the optimum carbon loading for pressure sensing applications could be found. The results followed expectations based on percolation theory. Composites of all carbon black loadings exhibited a change in voltage with increasing pressure. For small pressures, the highest sensitivity was achieved for 20% carbon black loading, which exhibited a 1.9 V voltage drop (of max 5V) at the maximum loading of 4860 Pa. At this carbon loading, the maximum sensitivity was recorded as 0.38 mV/Pa.
6.1.2 Processing Parameters Optimization of SIBS/CB Composites

The effect of three processing parameters on the tensile strength and specific resistance decrease of SIBS/CB conductive thermoplastic composites was investigated. Design of experiments methods were employed to reduce the number of experimental runs. A Taguchi analysis resulted in ranking of the CB loading, mixing time, and casting temperature in order of main effects for the tensile strength and specific resistance decrease response. It was demonstrated that for both responses casting temperature was the least influential factor. Taguchi methods proved that the optimal fabrication parameters for the composite vary depending on the target response. A screening analysis and ANOVA were used to determine the significant parameters. A statistical regression model for each response was created and validated with experimental results. The sensitivity of the pressure-sensing capabilities of the composites to the processing parameters is proven. From SEM it is suggested that this is due to the degree of homogeneity of the dispersion, formation of agglomerations, and interphase between filler particles and polymeric phases. The regressions models from this analysis can be used as guidelines for selecting the optimal fabrication conditions of SIBS/CB composites for use in biomedical pressure-sensing applications.

6.1.3 Rheological Properties of SIBS/CB Composites

The rheological characteristics of SIBS/CB composites with various loadings of CB were determined. The following methods were employed: thermogravimetric analysis, amplitude sweeps, frequency sweeps, temperature sweeps, and SEM. The effect of CB on the SIBS and the effect of temperature are evaluated. Thermogravimetric analysis resulted
in the evaluation of CB filler as a thermal barrier for the composite. All of the SIBS/CB composites exhibited non-Newtonian viscosity behavior. It was demonstrated that incorporation of CB filler significantly increases the melt viscosity, the storage modulus, and the loss modulus. Major increases in the viscosity were found at filler loadings beyond 5%. Composites with 15% CB manifested non-linear shear thinning behavior, particularly at high shear rates, which is attributed to the dominance of particle-particle interactions. These composites demonstrated particle cluster rupture and low resistance to flow at high shear rates. Temperature sweep tests illustrated that elastic behavior is dominant in all composites. Complex modulus and phase angle plots indicate that filled composites exhibit less temperature sensitivity and potentially greater shelf life than the neat polymer. Rheological analysis of SIBS/CB conductive composites provides insight into the internal structure present, which aides in determining the suitability of using alternative processing methods such as twin-screw extrusion for long-term production.

6.1.4 Biocompatibility Retention Assessment of SIBS/CB Composites

The effects on the biocompatibility of CB particle reinforced SIBS polymer were analyzed. MIAMI stem cells were incubated with CB/SIBS 72T scaffolding for a seven-day period. Cells were monitored and counted to ascertain any potential toxicity effects from the CB particles. Results indicate that none of the samples demonstrated any toxicity. Cell viability was >90%. From the data, it can be seen that the 20% CB scaffold exhibited cell growth similar to that of the control culture, though all loading percentages exhibited similar behavior. This likely indicates an effective, complete encapsulation of the CB particles. A comparison across various CB loadings indicates that despite higher CB loadings, cells continue to grow and proliferate as expected. These preliminary results
indicate that the presence of CB particles, whether in low or higher quantities, may not alter the excellent biocompatibility observed in the neat polymer. Although these results do not limit the use of CB/SIBS composites for stick-to-skin pressure sensors, further sensitization and skin irritation testing is needed to definitively prove viability for external medical applications. Given the performance of SIBS/CB for detecting pressure and deformation, the results of this first-level biocompatibility tests suggest that SIBS/CB composites may be well-suited for biomedical sensing applications.

6.2 Recommendations and Future Work for SIBS/CB Composites

6.2.1 Suggestions for Improvement of Mechanical and Electrical Properties

Variables affecting composite properties include preparation method, volume fraction of filler material, distribution of filler material, and the size and shape of both the insulating and conducting phases within the composite. It has been shown that depending upon sample preparation method, samples with higher carbon black concentrations may be more prone to agglomerations with larger distances from each other. The use of a surfactant may have ensured a more homogenous dispersion. The sensitivity of the pressure-resistivity relationship is likely a cause of the dispersion. For the conductivity measurements, the processing steps were held constant regardless of CB content, rather than attempting to achieve a consistent quality of dispersion. It is suggested that the fabrication method be altered depending upon the desired properties. This may lead to the ability to select certain CB concentrations to specifically tailor the pressure sensor to application-specific resolution environments.

Another method for improving the electrical properties without compromising the mechanical properties of the material might be to use a multiphase polymer blend.
Multiphase polymer blends have previously been used in the literature to reduce the amount of CB necessary for percolation. The reduction in the percolation threshold is due to the affinity between the particles and the different polymer phases [102]. This method could be used to increase composite conductivity with minimal detrimental impact on the mechanical and rheological properties. For improvement of mechanical properties, doping with large molecules is suggested. This may however, cause interference of electron tunneling and a reduction of electrical properties. This would have to be studied in further detail so as to improve mechanical properties without compromising electrical properties.

6.2.2 Suggestions for Further Optimization of Desired Material Properties

For this work, the parameters that were varied either related to the fabrication process or to the filler loading. The type of polymer remained the same. Since the polymer used is a tri-block co-polymer composed of soft isobutylene domains and hard styrene phases, future studies should investigate the effect of varying the styrene-isobutylene ratio. This can be done by using any of the commercially available SIBS with different styrene content, known as SIBS 73T, 102T, and 103T. Altering the ratio composition of the polymer matrix will potentially result in a different range of mechanical and electrical properties. It is worth exploring whether this would lead to more optimal properties of the composite. Additionally, it would be interesting to consider other processing parameters that might alter the mechanical-electrical relationship, such as: solvent used and drying time.
6.2.3 Suggestions for Developing Improved Interactions in Composites

The improvement and application of these composites will depend on future studies resolving the challenges of better filler dispersion and good matrix-filler interphase. In future studies, a potential way to develop improved structure, interactions, and properties is through the use of surface treatment for the CB particles. Another solution may be to use one of the alternate SIBS types available.

6.2.4 Suggestions for Future Biocompatibility Testing

Given that SIBS/CB did not show any signs of cell toxicity, further biocompatibility testing is validated. Despite no signs of cell toxicity for any of the CB loadings tested, the rate of growth and proliferation of cells was slightly higher for composites containing 15% and 20% CB. The precise reasoning for why higher loadings had faster growth rates is unknown but it may be due to the greater surface area contact present between cells and the CB filler. It may also be due to a greater strength of filler-filler interactions affecting the cells. Further investigation into this mechanism is needed. The following biological tests are suggested for external (stick-to-skin) pressure sensing applications: irritation assay and sensitization assay. These tests are described in more detail in Chapter 5. Additionally, for safety improvement, safe coating of the composite with materials, such as polyethylene glycol (PEG) and polydimethylsiloxane (PDMS), is suggested. Furthermore, for pressure sensing applications, SIBS/CB composites would require the use of Tegaderm adhesive. Potential effects of Tegaderm adhesive on the biocompatibility of the composite should be explored.
6.2.5 Suggestions for Pressure Sensing Applications

Other considerations that should be accounted for in future studies of SIBS/CB composites for pressure sensing applications are the viscoelastic properties of the composite. Given that for biomedical applications SIBS/CB composites would require placement in anatomical regions with complex curvatures, the stress relaxation effects of the composite are of importance. Stress relaxation of SIBS alone has previously been studied [18] but the effects of CB filler on stress relaxation are unknown, though it is likely that the structural network due to SIBS will cause an effect similar to that seen for the tensile properties. Furthermore, hysteresis and creep properties should be explored for pressure sensing applications.
References


