THE EFFECTS OF ADDING INHERENTLY CONDUCTIVE POLYMERS TO SILVER-FILLED EPOXIES

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THE EFFECTS OF ADDING INHERENTLY CONDUCTIVE POLYMERS TO SILVER-FILLED EPOXIES

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Thesis

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Abstract

The demands for electrically conductive materials continue to increase, and this has driven an interest in polymers filled with silver particles that can deliver improved electrical performance and reduced cost. Since polymers form an insulation barrier around the silver particles, the conductive composite cannot deliver the intrinsic conductivity of the silver metal. By introducing inherently conductive polymers (ICPs) to a silver-filled epoxy polymer, the conductivity of the epoxy matrix can be potentially increased, and hence conductivity of the silver-filled composite enhanced. Substantial improvements in the conductivity of a silver-filled composite have been observed with the introduction of undoped polyaniline, a popular ICP, to the system. The significant gains in the composite conductivity were dependent on the crosslink density of the epoxy, the type of silver particle, the level of silver, and the amount of polyaniline.
DEDICATION

To my lovely wife, Carrie, and my 4 wonderful children, Samuel, Seraiah, Solomon, and Sophia. Your patience and encouragement kept me focused. You truly are gifts from God.
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CHAPTER I
INTRODUCTION

Highly-conductive metals and polymers represent extremes of electrical conductivity separated by approximately 20 orders of magnitude in their respective conductivity values. Although diametric in electrical properties, insulating polymers and micron-sized particles of highly-conductive metals can be blended to render electrical properties between the extremes. These electrically-conductive compositions can be tuned to a myriad of conductivity values with the selection of the metal, particle size, particle shape, and loading level into the polymer. Gold filler is often cost prohibitive, and the electrically insulating copper oxide layer on copper particles establishes silver as the most attractive conductive particle for promoting conductivity in a polymer matrix.

Silver-filled polymers serve in a variety of applications requiring electrical conductivity. When high electrical conductivity is required, silver-filled polymers are found as interconnects for printed circuit boards, ground planes for silicon die, antennas for radio frequency tags, and conductive traces for low cost electronics.\(^1,2\) When intermediate conductivities are necessary, silver-filled polymers are utilized for shielding electronics from electromagnetic radiation and radio frequencies.\(^3\)

Silver-filled polymers possess a host of advantages over pure metallic conductors. Primarily, they represent an efficient method of applying and processing. Silver-filled polymers can be easily molded, dispensed, screened-printed, or stenciled in the desired
place or pattern. After application, a subsequent heat step polymerizes or sets the polymer creating the desired physical and electrical properties. Processing times and temperatures for polymers are more appealing than some of the stringent high temperatures employed for metal processing. In addition, manufacturers can enjoy the physical properties of a polymer such as light weight, ductility, fatigue resistance, adhesion strength, and elongation. Only a minor conductivity penalty of 1-3 orders of magnitude is observed compared to highly-conductive metals.4

In the market for silver-filled polymers, the requirements are evolving. Many applications are requiring improved silver-filled polymers that exceed the current conductivity values. The solution is not as simple as increasing the silver loading. Because of the high cost of silver, additional silver loading is not preferred. Physical properties also suffer with high loadings of silver. Adhesion is reduced, the modulus is increased, and impact and toughness properties are decreased.5 In addition, instances occur when increased silver-loading may result in only a negligible improvement in electrical conductivity or in some cases, the optimum silver-level is surpassed resulting in a decrease in electrical conductivity.

Though silver is the most effective filler for conductivity in a polymer, inherently conductive polymers (ICPs) and carbon nanofibers exhibit interesting electrical properties.6 Though both materials possess significantly less conductivity than silver, their inclusion in a silver-filled composition should have a minimal effect on the physical properties maintaining good adhesion. The purpose of this study is to examine the potential synergisms with blending carbon nanofibers and ICPs to enhance the electrical conductivity of a silver-filled polymer composition. Potential enhancements in the
electrical conductivity of the composition could also open up new possibilities to displace metals in applications that require the highest conductivity. Conductivity improvements can be instrumental in cost reduction by attaining target conductivity values with less silver.

With silver as the highly-conductive metal particle, epoxy chemistry was chosen as the polymer matrix for the investigation. Silver-filled polymers can be formulated with other materials such as urethanes, cyanate esters, silicones, acrylates, and thermoplastics. Epoxies, however, are the most widely used because of their rapid-cure, long pot life, excellent adhesion, low toxicity, and low viscosity. A fundamental silver-filled epoxy (SFE) based on an acid cure (cationic) mechanism was chosen for the investigation.
Composition of Silver-Filled Epoxies

Silver-filled epoxies (SFEs) have received widespread use because of their exceptional physical properties and processing ease. With the wide selection of available epoxy resins, the physical properties such as glass transition, crosslink density, hydrophobicity, and fracture toughness can be easily tuned to achieve the desired results. Epoxies, in general, exhibit exceptional adhesion to most substrates and can be tailored to survive humidity and thermal cycling excursions. Since epoxies are thermosets, they excel in load-bearing applications, while delivering high temperature resistance, and a permanent non-flowing bond to a substrate. Where thermoplastics are subject to creep and significant flow above its glass transition temperature, epoxies exhibit permanence maintaining their elastic characteristics.

Epoxies become attractive solutions for high silver-particle loading because the epoxy is first processed as a low viscosity monomer. The silver is blended as a micron-sized particle into the monomer, and the epoxy is subjected to a subsequent heat curing process, initiating a polymerization that produces a solid 3-dimensional thermoset network. In contrast, high loadings of silver in an established high molecular weight thermoplastic will be difficult to compound as well as process because of exceptionally high viscosity. Solvents can be employed to solubilize a high molecular weight
thermoplastic and reduce the viscosity to permit high concentrations of silver. However, not all thermoplastics are soluble in common solvents, and solvent processing has limiting applicability in adhesive applications where voids and bubbles result from the solvent volatilization.

A fundamental SFE is comprised of a blend of epoxy monomers, oligomers, and perhaps diluents. Depending on the chemistry a catalyst or crosslinker will be added to either initiate a polymerization or crosslink with the functionalized epoxy resins. Predominantly, amines are used as crosslinkers to react with the epoxy constituents in a step-wise mechanism. Chain-wise polymerization can be initiated with imidazoles, tertiary amines, or with an acid catalyst. Additives are employed at low levels to enhance adhesion, modify flow properties, enhance temperature stability, impart crack resistance, reduce viscosity or create a desired color. Most commercial SFEs utilize silver with a flake-like geometry. Silver flake has a large aspect ratio, the ratio of the length to diameter of the particle. The large aspect ratio enables efficient particle-to-particle contact at lower loadings than with irregular or spherical-shaped particles. Lower loadings are desirable since there are fewer high resistance particle-to-particle contact points. Finally, to assist in the processing of the SFE, solvents that volatilize during the cure process can be utilized to reduce the viscosity of the mixture.

Cationic Cure Mechanism

The chain-wise epoxy reaction by an acid, often called a cationic mechanism, is a popular way to deliver a rapid cure while offering good chemistry stability at ambient temperatures. The cationic cure mechanism is described extensively in literature.
Superacids based on hexafluoroantimonate and hexafluorophosphate, that initiate the cationic cure, typically exhibit exceptional thermal stability to temperatures as high as 150°C. Once the activation temperature is attained, a rapid thermal decomposition ensues creating unstable radicals that abstract hydrogen atoms from molecules in the mixture. This hydrogen is eventually liberated as a Brønsted acid with a pKa value greater than -12, which is considerably more acidic than sulfuric acid.12 Depending on the absorption characteristics of the superacid, UV radiation can initiate the reaction, as well. The generation of the acid, or initiation process, is shown in Figure 2.1.

![Figure 2.1. Generation of acid from iodonium hexafluoroantimonate decomposition.](image)

After the generation of the acid, the polymerization is initiated and the propagation of the epoxy polymer ensues. The acid protonates the ring-strained epoxy group, and the positively-charged epoxide is now susceptible to nucleophilic substitution (SN2 reaction) from lone pairs of electrons from another epoxide ring. After the SN2 reaction, the protonated epoxide ring is opened and stabilized while the attacking epoxy assumes the positive charge allowing the process of nucleophilic substitution to continue.
to propagate. The reaction scheme for the propagation and the potential termination is shown in Figure 2.2. In order to create a 3-dimensional cross-linked structure, the average functionality of the monomer system must be >2.0. Each epoxy group has a functionality of 2.0; in other words it creates 2 crosslinks for each epoxy group. Therefore the diepoxide monomers have a functionality of 4.0 fulfilling the requirement to create a 3-dimensional network.

![Reaction Scheme](image)

**Figure 2.2.** Cationic cure mechanism: (a) propagation of the epoxide monomers (b) potential termination of cationic cure of epoxy monomers.
When the propagating species encounters a hydrogen-bearing moiety such as a hydroxyl, primary amine, or a secondary amine, a chain-transfer reaction will occur. Because the oxygen and nitrogen are weak nucleophiles, an attack on the propagating oxonium ion terminates the advancing chain and produces a Brönsted acid which is free to initiate an additional cationic reaction. Overall, the chain-transfer typically accelerates the reaction rate because of the generation of additional Brönsted acids, but thresholds exist where the crosslink density of the resulting network will be reduced with excessive hydroxyls or amines.\textsuperscript{13}

Percolation Theory

The electrical conductivity of the composite can be described by percolation phenomena, where the individual conductive particles or flakes form a continuous secondary network within the continuous polymer matrix. The silver flakes, in this case, reach a state of increased contiguity during the curing process enabling contacts between the individual flakes. The formation of percolation is contingent upon exceeding a percolation threshold, a volume fraction of conductive particles that is dependent on several variables relating to the fillers and matrix. Generally, the conductivity of the composite can be related to the volume fraction of filler by a simple power relation:

\[
\sigma = \sigma_0 (V - V_C)^S
\]

where \(\sigma\) is the conductivity of the composite, \(\sigma_0\) is the conductivity of the conductive filler, \(V\) is the volume loading of conductive filler, and \(V_C\) is the volume loading at the percolation threshold. The percolation threshold is the volume loading where a rapid step
in conductivity occurs, and the conductivity continues to rapidly ascend with only small changes in volume loading. The exponent $s$ is dependent on lattice dimensions. An example of a typical percolation curve is shown in Figure 2.2. The general shape of the curve is characteristic of any conductive media in an insulating polymer matrix.

Figure 2.3. General percolation curve for silver-filled epoxies.\textsuperscript{14}

Although much work has been done with mathematic models to validate the shape of a percolation curve, predicting the magnitude of conductivity has been an elusive goal.\textsuperscript{15} Some have found that incorporating terms to calculate interfacial tension between the conductive filler and the polymer matrix improves the predictability of the model.\textsuperscript{16} Others have shown that particle size and shape are reliable predictive parameters, where smaller particles and a larger aspect ratio for the conductive particle decrease the percolation threshold.\textsuperscript{17} Smaller particles can theoretically result in lower electrical conductivity since more high resistance particle-particle points-of-contact exist in the filler-polymer composite. Many have expressed the dependence of conductivity on pressure, where the softer conductive particles, high modulus polymer matrix, higher cure shrinkage, and larger expansion coefficient difference between filler and polymer all contribute to enhanced composite conductivity.\textsuperscript{18,19}
Cure Shrinkage

A thermoset material undergoes a significant change in volume after the curing process. Initially, the epoxy monomer is characterized by a viscosity measurement, the resistance to a shear rate. Essentially, the monomer is able to relax and dissipate any stresses applied to the system when undergoing a shear force. When the epoxy begins to crosslink, the molecular weight begins to increase until it eventually forms a gel structure. At the gel point, the polymer begins to behave more elastic and less viscous in nature.\(^{20}\) The crosslinking continues and the development of crosslinks or network junctions slow the large scale cooperative motions of the growing chains resulting in reduced entropy of the polymer network permitting enthalpic forces between molecules to densely pack the network. The resulting change in volume is a function of the packing efficiency of the chains, which is related to the crosslink density of the chemistry, the molecular characteristics of the network, and the kinetics of the cure process.\(^{21}\) In particular, a tighter or increased crosslink density creates a larger volume change after curing, and the volume change is fundamentally related to the cure shrinkage.

It has been shown that the conductivity of a SFE is related to the cure shrinkage of the epoxy network. Cure shrinkage could be calculated by measuring the density before and after cure by the relationship:

\[
\% \text{ Cure} = \frac{1/d_l - 1/d_s}{1/d_l}
\]

where \(d_l\) is the density of the liquids system before cure and \(d_s\) is the final density of the cured system. Wong and Lu demonstrated that by increasing the crosslink density of a model SFE, the cure shrinkage is increased and the resulting conductivity is improved.
The interrelated variables of crosslink density, volume change, and cure shrinkage effectively contribute to the pressure on the conductive particles in the cured state. With the use of dynamic mechanical analysis (DMA), Wong and Lu calculated the crosslink density of the SFE using the equation of rubber elasticity:22

$$\rho_{(E')} = \frac{E'}{3\phi RT}$$

where $\rho_{(E')}$ is the crosslink density in mol/cm$^3$, $E'$ is the elastic modulus by DMA, $\phi$ is a front factor $\sim 1$, $R$ is the universal gas constant, and $T$ is the absolute temperature.

According to the theory, the crosslink density is determined by taking the $E'$ at 10 °C above the tan delta peak of the elastic modulus curve. Since silver metal has a higher modulus than polymers, it is necessary to measure the modulus of only the polymer to truly capture the crosslink density of the polymer.23

Another characterization of the crosslink density utilizing data from dynamic mechanical analysis evaluates, $M_c$, the number average molecular weight between crosslinks. The $M_c$ is inversely proportional to crosslink density, $\rho_{(E')}$. Instead of stipulating a specific temperature to measure the modulus, the following equation simply evaluates the elastic modulus in the rubbery plateau above the glass transition:

$$M_c = 3q \frac{\rho RT}{E_R}$$

where $q$ is the front factor $\sim 1$, $E_R$ is the elastic modulus in the rubbery plateau, $\rho$ is the specific gravity, $T$ is the temperature, and $R$ is the universal gas constant. In the expression, the elastic modulus is typically generated by DMA where the material is deformed in tensile mode. Fundamentally, this elastic tensile modulus can be related to the elastic shear modulus of a material enabling shear metrologies such as a parallel plate
rheometer to generate crosslink density data. The relationship between the elastic shear modulus, $G'$, and the elastic tensile modulus, $E'$, has been expressed as:

$$E' = 2G'(1 + \nu)^2.$$ \textsuperscript{24}

Lubricants

Silver flake is nearly always coated in a mono-molecular layer of lubricant to prevent agglomeration of the flakes, improve disperability, and impute the appropriate rheology to the epoxy resin system.\textsuperscript{25} Typical lubricants are stearic acid, oleic acid, and palmitic acid. The acid functionality will adsorb to the silver surface and the aliphatic tail is left to dangle from the silver flake. Pigment dispersants operate in similar fashion minimizing contact of the particle surfaces due to stearic interference from the aliphatic tails.\textsuperscript{26} Structures of the typical lubricants for silver flakes are shown in Figure 2.4.

![Structures of lubricants: (a) stearic acid, (b) oleic acid, (c) palmitic acid, (d) isostearic acid.](image)

Though crosslink density is the most prominent polymer attribute that affects the electrical conductivity, the lubricant on the silver flake is another factor that contributes to the electrical conductivity of the SFE. Obviously, the lubricant creates an insulating
barrier between silver flakes and theoretically should hinder the conductivity from particle to particle. However, the layer is small enough that researchers have shown that conductivity can be attained with a known monolayer of lubricant remaining on the silver flakes.\textsuperscript{27} Fundamentally, the conductivity across the conductive composite is dominated by the two parameters that describe the contact resistance at the junction of the silver particles (flakes); constriction resistance, $R_{cr}$, and tunneling resistance, $R_t$.\textsuperscript{28} The following expressing describes the relationship:

$$R_c = R_{cr} + R_i$$
$$R_c = \rho_i/d + \rho_t/a$$

where $R_c$ is the total contact resistance, $\rho_i$ is the intrinsic particle resistivity, $\rho_t$ is the tunneling resistivity, $d$ is the diameter of the particle to particle contact, and $a$ is the area of particle to particle contact. The tunneling resistance, $\rho_t$ is a function of the film thickness or in this case the thickness of the insulation barrier between the conductive particles.

Based on the expression for $R_c$, minimizing this distance between silver flake particles, which reduces the $\rho_t$, and maximizing the contact area will reduce the contact resistance, $R_c$, between each silver particle. The entire SFE composite can be likened to a series of resistors where each particle-particle contact point is characterized by $R_c$. Consequently, reducing the $R_c$, as well as reducing the number of contact points will improve the conductivity of the SFE. Though the conductivity is attained without the lubricant removal, intuitively lubricant removal will enhance the conductivity of the SFE by reducing the thickness of the insulation barrier and increasing the area of contact between particles. It is believed that the lubricant exists on the silver surface in the form
of a salt requiring energy to remove it from the surface. Some organic acids have shown
to effectively remove portions of the lubricant from the silver increasing the conductivity
of the composite. These organic acids can be added to the epoxy formulation to assist
in the removal of the lubricant during the curing process. Lubricant removal can also be
assisted by solubility of the resins and it can be accelerated by curing temperatures during
processing of the SFE.

Inherently Conductive Polymers (ICPs)

In 1977 a new discovery, inherently-conductive polymers (ICPs), emerged
delivering greatly enhanced electrical conductivity in a polymer. With an appropriate
dopant, that introduces charges along a conjugated, electron-rich polymer backbone, a
polymer’s conductivity could soar to values as high as 10 S/cm, far exceeding the typical
insulating properties of a polymer. When MacDiarmid and Heeger embarked on the
discovery at the University of Pennsylvania, they reported that polyacetylene underwent a
change in electrical conductivity by 11 orders of magnitude after the introduction of the
dopant, I2 vapor. After the discovery of an inherently conductive polyacetylene,
numerous compounds with an conjugated structure were doped resulting in significant
gains in electrical conductivity taking insulating polymers to the semiconducting regime.
Since their discovery, the most extensively-studied ICPs have been polyacetylene, amine-
based polyaniline and polypyrrole, polythiophene, and polyphenylenes. The basic
structures of these materials are shown in Figure 2.5. Many of the developed ICPs exist
as extensions of these base structures possessing substituents and other modifications to
tune the basic properties.
With the discovery of ICPs, a host of new applications emerge. Numerous electronic applications exist that require static dissipation from polymer compounds. Though carbon-filled composites are suitable solutions, ICPs possess electrical properties in the antistatic regime offering an alternative solution. Electrodes used in LCD displays require the unique combination of electrical conductivity and transparency of which indium tin oxide (ITO) is the primary solution. Some families of ICPs possess transparency and conductivity properties that have stimulated investigation as possible alternatives to ITO.\textsuperscript{32} Since ITO is a brittle material, the use of ICPs as a transparent electrode opens the possibility of flexible displays that can be rolled or folded. ICPs are also under investigation for hole-injection layers in future LCD display applications.\textsuperscript{33}
In addition to conductivity properties, ICPs exhibit other interesting properties that can be harnessed for practical applications. ICPs can absorb and emit characteristic wavelengths of radiation acting as either sensors or light emitting diodes. ICPs respond to voltage and change color and physical characteristics depending on the bias making transistor and battery applications possible. Color change characteristics also make ICPs candidates for sensor applications.\textsuperscript{34} Finally, improvements in corrosion resistance have been reported on various metals including copper-finished printed circuit boards.\textsuperscript{35}

Commercialization of ICPs has not proliferated as originally expected. Though ICPs deliver pronounced conductivity improvements over insulting polymers, low cost carbon-filled composites are capable of delivering comparable electrical conductivity.\textsuperscript{36} Industries will not switch to ICP composites for antistatic and shielding applications without a technical advantage or cost incentive. Greatly improved conductivity would need to be demonstrated with ICP systems. Some applications requiring both antistatic properties and transparency are attainable with ICPs vs opaque carbon-filled composites.

Processing is another major concern. ICPs do not exhibit some of the hallmark properties of standard polymers such as melt flow and solubility in common solvents erecting a barrier to molding and solvent processing of ICP systems. Oxidative stability concerns have always manifested with ICPs resulting from poor thermal stability of the necessary dopants and poor oxidative stability of the highly conjugated backbones.\textsuperscript{37} Finally, ICPs are more expensive than other comparable conductive solutions such as conductive carbon particles and fibers.

Polyaniline (PANI) has emerged as one of the most promising ICPs for commercialization. PANI is relatively easy to manufacture, and the cost of doped and
undoped-PANI is considerably cheaper than other ICPs. PANI exists in 3 different oxidation states, and the chemical structures of each are shown in Figure 2.5. Penigraniline base is the reduced state, leucoemeraldine base is the oxidized state, and emeraldine base is a mixture of both penigraniline base and leucoemeraldine base constituents. The conductivity boost in PANI occurs when the emeraldine form is doped by oxidation with a protonic acid dopant. Like polyacetylene, after doping PANI undergoes a significant conductivity increase of 11-12 orders of magnitude.38

Figure 2.6. Structures of polyaniline in various states: (a) leucoemeraldine base, (b) penigraniline base, (c) emeraldine base.

When PANI is oxidized with an effective dopant, it is postulated that protonation occurs on the quinoid nitrogens where a π electron is elevated to a level between the
valence band and the conduction band and is termed a polaron.\textsuperscript{39,40} The ensuing positive charge is stabilized by a local structural distortion in the polymer. Because of close proximity of the positive charges, a rearrangement occurs where the positive-charged polaron attracts an electron from a neighboring benzene ring creating a new positive charge.\textsuperscript{41} Now, the distance between positive charges is increased minimizing repulsion, and a more stable benzoid structure manifests. The new structure is called a bipolaron. Some common dopants utilized to oxidize the emeraldine base are camphor sulfonic acid, p-toluene sulfonic acid, and dodecybenenesulfonic acid. The doping and transformation of emeraldine base to a polaron and subsequently to a bipolaron is shown in Figure 2.7.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.7.png}
\caption{Emeraldine salt form of PANI doped with a protonic acid: (a) polaron formation (b) bipolaron formation.}
\end{figure}

In addition to low cost and production ease, another alluring property of PANI is thermal stability. PANI exhibits better thermal stability compared to other ICPs.\textsuperscript{42} Simple thermal gravimetric scans have revealed that PANI doped with
dodecybenzenesulfonic acid (DBSA), undergoes a significant weight loss beginning at about 280 °C. The percentage of weight loss is in proportion to the amount of DBSA in the DBSA-PANI material. Therefore, the initial thermal instability is a result of DBSA dopant volatilization. Undoped-PANI exhibits significantly better thermal stability where decomposition doesn’t occur until temperatures above 400 °C.

Because of the inability to solvent process, mold, or form the PANI, researchers have demonstrated that large scale commercialization of PANI is most likely to occur when blending PANI with low cost polymers with good physical properties. Additional benefits of blending PANI with polymers include improved temperature resistance, transparency enhancement, and a means to overcome the poor physical properties of PANI. Because the solubility parameter of PANI is significantly higher than most polymers, it has been shown that PANI can be integrated into other polymers by dispersion methods where doped-PANI is dispersed as fine particles below 20 µ. The doped-PANI exists as small aggregates or domains in the host polymer, and they are not solubilized in the host polymer. By varying the level of doped-PANI in the host polymer, the doped-PANI levels can be characterized by a percolation curve. The percolation threshold and peak conductivity level will be dependent on the physical characteristics of the doped-PANI. The peak conductivity of the composite can typically attain a conductivity value of few orders of magnitude below the conductivity of doped-PANI.

ICPs in Epoxy Materials

In addition to integrating doped-PANI into high molecular weight polymers, the conductivity and physical properties of doped-PANI in epoxies have been investigated.
In work performed by Tsotra, it was shown that the conductivity of a standard epoxy system can be greatly enhanced with incorporation of doped-PANI.\textsuperscript{47,48} The PANI was doped with dodecybenzenesulfonic acid. A large improvement in electrical conductivity was observed where the composite was tested at $10^{-5}$ S/cm, which was approximately 10 orders of magnitude better than the epoxy without doped-PANI. The research concluded that an acid environment was essential to maintain the oxidized state of the doped-PANI, and consequently afford the exceptional electrical conductivity boost. In epoxy chemistries with a high pH (>9.5), doped-PANI addition produced no detectable improvement in electrical conductivity maintaining high electrical insulation.

Other reports of doped-PANI in epoxy systems have shown promise for applications requiring moderate conductivity delivering conductivities as high as $10^{-2}$ S/cm.\textsuperscript{49,50} In addition, a patent has been filed for the use of undoped-PANI (emeraldine base without dopant) in epoxy systems, where the doping occurs from a protonic acid that is released during the curing process.\textsuperscript{51} In all of the applications with epoxies, a percolation behavior is observed in the same manner that is observed when doped-PANI is added to high molecular weight polymers. With epoxies, however, the benefit of integrating the doped-PANI into a blend of low viscosity monomers creates a reasonable method for processing ICPs, as opposed to processing by molding or solvent evaporation techniques typically employed for high molecular weight polymers.

With the addition of PANI-based ICPs, a range of electrical conductivities for a conductive composite can be produced. For the aforementioned reasons, many industrial applications can benefit from highly-conductive composites compared to using highly-conductive metals. Enhanced conductivity of the conductive composites can allow
penetration into new markets where only metals have exhibited the essential electrical conductivity. The range of conductivities for insulators, semiconductors, and conductors is shown in Table 2.1.

Table 2.1. Electrical conductivities of insulators and conductors. 

<table>
<thead>
<tr>
<th>Material</th>
<th>Log Conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cured Epoxy</td>
<td>-15</td>
</tr>
<tr>
<td>Diamond</td>
<td>-14</td>
</tr>
<tr>
<td>Glass</td>
<td>-10</td>
</tr>
<tr>
<td>Undoped-PANI</td>
<td>-10</td>
</tr>
<tr>
<td>Silicon</td>
<td>-5</td>
</tr>
<tr>
<td>Doped-PANI</td>
<td>1</td>
</tr>
<tr>
<td>Best ICP – Ideal Conditions</td>
<td>4</td>
</tr>
<tr>
<td>Nanotubes/Nanofibers</td>
<td>4</td>
</tr>
<tr>
<td>Silver-Filled Epoxy</td>
<td>4</td>
</tr>
<tr>
<td>Solder</td>
<td>5</td>
</tr>
<tr>
<td>Silver</td>
<td>6</td>
</tr>
</tbody>
</table>
CHAPTER III
EXPERIMENTAL

Preparation of Materials

Two base silver-filled epoxy (SFE) formulations were prepared. Bisphenol-F diglycidyl ether (830-LVP from Dainippon Inc.), 3,4-epoxycyclohexymethyl 3’,4’ epoxy cyclohexanecarboxylate (UVR-6105 from Dow Chemical), and 1,3-bis(glycidoxypropyl) tetramethyldisiloxane (SIB-1115.0 from Gelest) were used as the difunctional epoxy monomers. PC-2506 (from Polyset) based on iodonium hexafluoroantimonate was utilized as an acid-generating catalyst. The PC-2506 salt was dissolved in $\gamma$-butyrolactone solvent (BLO Aldrich) in a 1:1 (w/w) ratio. Dipropylene glycol was also added to the liquids portion of the formulation. The chemical structures of these monomers, catalyst, and solvent are shown in Figure 3.1.

A silver flake, SF#85-HV (from Ferro), which is treated with isostearic acid as a lubricant, was the primary conductor for the experiments. SF#85-HV has an average particle size of 8 $\mu$m, and because of its high aspect ratio and packing density, the silver provides excellent conductivity in most epoxy systems. Although SF#85-HV was the primary conductor in the two formulations, other conductors were substituted for SF#85-HV for one of the experiments. The PANI-based materials and carbon nanofibers were added to augment the conductivity provided by the primary conductor. Doped-PANI, undoped-PANI, and the nanofibers are referred to as conductive additives.
Figure 3.1. Structures of raw materials used in the two epoxy formulations: (a) PC-2506, (b) UVR-6105, (c) γ-butyrolactone (BLO), (d) SIB-1115.0, (e) 830-LVP.

The materials preparation occurred in two steps; liquids and silver. First, the liquids were processed. This included the epoxy monomers, catalyst-solvent blend, and the dipropylene glycol. The PANI was also included in the liquids processing step. For one experiment, carbon nanofibers were incorporated in the liquid step, as well. The second step involved the incorporation of the silver flake, SF#85-HV, into the prepared liquids. It was incorporated at 76% by weight in formulation #1 and 84% by weight in formulation #2.
To begin the liquid preparation, the PC-2506/BLO was added to an amber glass 16 oz. jar. The lid was tightly closed and electrical tape was applied around the lid. The mixture was then rolled on a jar roller for 4 h at 60 °C creating a miscible catalyst solution. The epoxy monomers were added to an 8 oz. polypropylene jar in the proper proportions. A stainless steel disperser blade, that was 2 inches in diameter, homogenized the mixture for 5 min. Next, the PC-2506/BLO was added to the jar and mixed for 15 min. A typical batch size for the liquids was about 50 g.

For the silver integration step about 7-10 g of the liquid blend was added to a 2 oz. polypropylene jar. The appropriate amount of silver was added to the jar and the silver-liquid blend was mixed for 2 min with a stainless steel, flat bottom spatula. Care is taken to ensure that the sides and bottom of the container are scraped free on any silver flake. The mixing step was followed by a degassing step to remove the air. The degassing was performed in a Pyrex bell jar and the air bubbles were removed with a vacuum pump. A stir rod was fitted in a rubber stopper to agitate the mixture during the air removal process to assist in breaking the surface bubbles. After mixing the composition was mixed and degassed for 2 min at > 28.0 in of Hg. The mixing/degassing process was repeated to ensure that the liquids effectively wet the surface of the silver.

Of the two base formulations, Formulation #1 was used in the first found of experiments where various conductive additives were incorporated at varying levels. Formulation #2 was used for the second round of experiments where only undoped-PANI was tested at various levels. Some variations of formulation #2 were presented where other silvers replaced SF#85-HV as the primary conductor. In addition, some modifications of the cure kinetics were conducted by adding copper napthanate to
formulation #2. Copper napthanate addition has a profound impact on the cure speed of the system. Both base formulations are shown in Table 3.1 before any modification with conductive additives.

Table 3.1. Two silver-filled formulations used for conductive additive modification.

<table>
<thead>
<tr>
<th></th>
<th>Formulation #1</th>
<th>Formulation #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>830-LVP</td>
<td>80.0</td>
<td>88.0</td>
</tr>
<tr>
<td>UVR-6105</td>
<td></td>
<td>12.0</td>
</tr>
<tr>
<td>SIB-1115</td>
<td>20.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Dipropylene glycol</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>PC-2506/BLO</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>% silver (by wt.)</td>
<td>76%</td>
<td>84%</td>
</tr>
</tbody>
</table>

ICPs based on PANI and carbon nanofibers were the conductive additives that were evaluated, and they are listed in Table 3.2. Two types of PANI were tested initially. Undoped-PANI (Panipol PA) and doped-PANI (Panipol F) were both used in a powder form as supplied by Panipol Corp. in Porvoo, Finland. The doped-PANI is a mixture of emeraldine-base PANI and DBSA as a dopant. The undoped-PANI is in its emeraldine-base form. The carbon nanofibers were supplied by Zyvex as a predispersed blend at 10% loading in a bisphenol F epoxy similar to 830-LVP. Both PANI materials were also incorporated as preblends into the base resin chemistry. A concentrated blend of 10% PANI and 90% by weight epoxy monomer (830-LVP for formulation #1 and UVR-6105 for formulation #2) was prepared by mixing the two components on a magnetic stirring hot plate. The mixture was mixed in a 500 mL beaker at 60 °C for 2 h on a magnetic stirring hot plate. The preblend defragmented the PANI into a finely dispersed mixture.
Table 3.2. Conductive additives tested in first round of experiments.

<table>
<thead>
<tr>
<th>Conductive Additives</th>
<th>Product Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Doped-PANI</td>
<td>Panipol F</td>
</tr>
<tr>
<td>Undoped-PANI</td>
<td>Panipol PA</td>
</tr>
<tr>
<td>Carbon Nanofibers</td>
<td>Nanosolve 10% CNF by weight</td>
</tr>
</tbody>
</table>

Though most conductivity models are based on volume loading and not weight loading of the conductive media, weight loading is reported throughout the experimentation. Volume loading can easily be calculated to determine congruence with conductivity models. Since the same chemistry and silver is used in a formulation, the small additions of PANI do not significantly affect the density of the SFE. Therefore, the volume loading and weight loading is kept constant for each set of experiments.

In all of the experiments the loading of silver is substantially high and the percolation threshold is comfortably exceeded. Therefore, a contiguous conductive network of silver flake is assured in each case. Modification by PANI or carbon fibers enhanced, inhibited, or did not affect the percolated network attained by the silver flake. Therefore, the conductive additives of doped-PANI, undoped-PANI, and nanofibers do not create a percolation network. For each controlled experiment, the percentage of silver is kept constant for the entire composition, and the introduction of PANI or nanofiber replaces the electrically-insulating polymer, the epoxy constituent including the epoxy, catalyst, and solvents. The ratios within the epoxy polymer constituent are kept constant when modifying with conductive additive, but the amount of epoxy constituent is reduced to account for the addition of conductive additive. As a result the affect of
Conductive additive is observed with a fixed silver loading level. In the first experiment, levels of both PANIs and nanofibers were tested from 0% to 8% by weight of the epoxy, while keeping the silver loading constant at 76% by weight. In the second round of experiments the levels of undoped-PANI were tested from 0% to 7% by weight of the epoxy, and the loading of silver was fixed at 84% by weight. The modifications to both formulation #1 and formulation #2 are shown graphically in Figure 3.2.

Figure 3.2. Graphic depicting weight percentages of silver and conductive additive employed: (a) formulation #1, (b) formulation #1 with conductive additive, (c) formulation #2, (d) formulation #2 with conductive additive.
At times it will be necessary to isolate and test only the polymer constituent of both formulation #1 and formulation #2. This includes the epoxy components (epoxy monomers, catalyst, solvent, etc.) and the varying level of conductive additive (undoped-PANI or doped-PANI). The epoxy polymer portion will be designated, $Epoxy+PANI$. The actual amount of PANI in the $Epoxy+PANI$ constituent can vary from 0 to 8% by weight depending on the experiment. At times it will be necessary to discriminate between the polymer constituents, $Epoxy+PANI$, and the complete silver-filled composition. The complete composition is generated by simply adding the primary conductor, SF#85-HV in most cases, to the $Epoxy+PANI$ epoxy polymer constituent. The complete composition with silver will be designated $Epoxy+PANI+Ag$. The purpose of isolating only $Epoxy+PANI$ was to characterize the polymer matrix independent of the high loading of silver.

Electrical Conductivity Testing

Electrical conductivity of the $Epoxy+PANI+Ag$ composite was tested by applying the material as a thin film to a glass slide. Two strips of Scotch tape were applied along the length of the glass slide with an even gap of 0.250 in between the two pieces. Adhesive was applied to the end of the glass slide, and an additional glass slide was used to draw an even application of material in the gap between the two pieces of tape. The tape was removed from the glass slide, and the samples were cured in an air circulating oven at 175°C. The slides were removed and cooled for 30 min to ambient temperature, and the conductivity was tested with a Keithley 2750 two-point probe resistance meter. Three slides for each material were tested and the resistance reading was measured 3
times for each slide and averaged. Averages of 3 readings were taken for the width and the thickness of each slide. The thickness was measured with a Mititoya thickness gage and the width of the strip was measured with Mititoya calipers. The conductivity, \( \sigma \), in S/cm was calculated with the following equation:

\[
\sigma = \frac{L}{\Omega \cdot wt}
\]

where \( L \) is the length of the specimen, \( w \) is the width of the specimen, \( t \) is the thickness of the specimen, and \( \Omega \) is the resistance of the specimen in ohms. The dimensions of the specimen are calculated in centimeters.

The \textit{Epoxy+PANI} constituent was isolated for electrical conductivity testing according to ASTM D157. The bulk electrical conductivity was evaluated for the varying levels of PANI added to the formulation. The liquid compositions were poured into molds formed by two ceramic plates with a metal spacer resulting in a thickness of 1 mm. Vacuum grease was used to insure a tight seal and the ceramic was clamped with large binder clamps. The \textit{Epoxy+PANI} mixture was poured into the top of the mold and cured for 1 h at 175°C. The electrical resistance was measured from a Keithley 6487 with the accompanying Keithley 8009 fixture complying with ASTM D157. Three specimens were made for each sample, and each specimen was tested for resistance 3 times. Therefore, each volume resistivity value is an average of 9 values.

\textbf{Thermal Analysis Characterizations}

An ARES parallel plate rheometer by TA Instruments was used to evaluate the cure characteristics and physical properties of each of the \textit{Epoxy+PANI} constituent. In order to capture the physical properties of the polymer matrix, the samples on the
rheometer did not contain silver thereby isolating only the epoxy with various levels of PANI conductive additive. A small amount of fumed silica (TS-720, Cabot) was added to the formulations to minimize flow and keep the material evenly distributed between the plates. The liquid samples were evaluated at a 2 mm gap between 25 mm diameter aluminum disposable plates. The sample was subjected to a 5°C/min ramp rate to 185 °C and isothermed at 185 °C for 15 min. Then, the sample was cooled to 25 °C at 5°C/min cooling rate.

For each rheology scan, a host of material characteristics can be extracted as the polymer is essentially modeled from the liquid phase, to the gel phase, to the rubbery phase, and finally the glassy phase after cooling of the sample. Figure 3.3 depicts some of the physical property information that can be gathered from a rheometer plot. For evaluating the affect of conductive additives on the epoxy polymer, the gel point (crossover of the $G'/G''$ modulus), crosslink density, and $T_g$ by tan delta were the material properties that were identified and compared.

![Figure 3.3. Rheometer scan and physical property characteristics.](image-url)
The 2950 DMA by TA Instruments was used to measure the cured physical properties of the Epoxy+PANI+Ag composites. The specimens were prepared in a mold that was lined with Teflon tape on an aluminum panel. The sides of the mold were formed with 1 mm thick glass slides that were sprayed with a Teflon release spray. The paste samples were filled into the mold and cured for 1 h at 175°C. After the removal the dimensions were approximately 15 mm x 6 mm x 1 mm. The surface was smoothed with a sanding tool to ensure good dimension. The DMA scans were run from -60 °C to 240 °C at 5 °C/min. A dynamic strain with amplitude of 3 µ was applied at 1 Hz throughout the test. The elastic modulus, $E'$, and the glass transition temperature, $T_g$, were determined by the DMA. The $T_g$ was assigned as the peak of the tan delta curve. The sensitivity of the $T_g$ determination by DMA was considerably better than by ARES rheometer.

A 2010 Differential Scanning Calorimeter (DSC) from TA Instruments was used to obtain additional cure characteristics of the Epoxy+PANI+Ag composition. Scans were run on 30 mg of material in a sealed aluminum pan at 10°C/min. The scans began at 25 °C and continued until 300°C. The onset of exotherm, peak exotherm temperature, and total exotherm in J/g were determined by DSC.
CHAPTER IV
RESULTS AND DISCUSSION

First Round of Experiments: Surveying Conductive Additives

In the first round of experiments, a general survey of conductive additives, both undoped-PANI and doped-PANI were evaluated in formulation #1. As mentioned earlier, carbon nanofibers were also included in the first round of investigation. The largest conductivity enhancement was observed with undoped-PANI, and a second round of investigations was targeted specifically to explore the interactions and effects of undoped-PANI in formulation #2. In addition to electrical conductivity, the physical and electrical properties of the \textit{Epoxy+PANI} constituent and the \textit{Epoxy+PANI+Ag} composite were investigated as a result of various loadings of undoped-PANI.

The relative effectiveness of each conductive additive in formulation #1 (76% by weight SF#85-HV) revealed interesting results that are shown in Table 4.1. Each conductive additive exhibited a notable increase in conductivity relative to the control that did not contain conductive additive. As mentioned earlier, the silver level of 76% by weight is constant in the composition. Interestingly, the conductivity increase with the highest magnitude occurs with undoped-PANI. Table 4.1 shows the peak conductivity for each conductive additive and the amount of conductive additive that was employed to attain the peak conductivity.
Table 4.1. Conductivity of conductive additive modification in formulation #1.

<table>
<thead>
<tr>
<th>Conductive Additive</th>
<th>Conductivity S/cm</th>
<th>% Loading by Weight That Attains Peak Conductivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control, Ag only</td>
<td>6,000</td>
<td>----</td>
</tr>
<tr>
<td>Carbon Nanofibers</td>
<td>7,900</td>
<td>8%</td>
</tr>
<tr>
<td>Undoped PANI</td>
<td>13,900</td>
<td>4%</td>
</tr>
<tr>
<td>Doped PANI</td>
<td>7,600</td>
<td>6%</td>
</tr>
</tbody>
</table>

In formulation #1 the addition of doped-PANI resulted in a marginal improvement in the conductivity of the system. Conductivity as a function of doped-PANI is plotted in Figure 4.1. Conductivity peaked at 6% by weight levels of doped-PANI while decreasing slightly at 8% by weight levels of doped-PANI. In work performed by Tsotra, the conductivity of the acid-cured epoxy continued to increase at levels as high as 10% by weight doped-PANI. With increasing levels of doped-PANI, Tsotra also reported a reduction in $T_g$ and crosslink density, which did not affect the conductivity.

Figure 4.1. Plot of conductivity as a function of doped-PANI levels.
In the case of an epoxy matrix without silver (Epoxy+PANI), the doped PANI is the lone agent in creating a percolation across the epoxy material. In Tstora’s work the conductivity is steadily increasing as 10% by weight loadings are approached. This indicates that the percolation network is still being constructed delivering enhanced conductivity with increasing doped-PANI. In the case of an SFE, the silver has already formed an established percolation network, and the doped-PANI provides enhancements to the previously established network. However, with increasing levels of doped-PANI, reduction of crosslink density reduces the contiguity of the silver flakes. As expressed earlier, cure shrinkage, which can fundamentally be expressed as crosslink density, is an essential variable for the generation of conductivity in a SFE. Decreased crosslink density and less epoxy shrinkage will result in less conductivity of the composite.

Table 4.2. Conductivity and $T_g$ resulting from doped-PANI levels.

<table>
<thead>
<tr>
<th>% doped-PANI</th>
<th>S/cm</th>
<th>$T_g$ (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5200</td>
<td>104.7</td>
</tr>
<tr>
<td>2</td>
<td>5800</td>
<td>107.8</td>
</tr>
<tr>
<td>4</td>
<td>6500</td>
<td>97.7</td>
</tr>
<tr>
<td>6</td>
<td>7600</td>
<td>91.7</td>
</tr>
<tr>
<td>8</td>
<td>6900</td>
<td>63.7</td>
</tr>
</tbody>
</table>

With the ARES rheometer, the $T_g$ of the epoxy with varying levels of doped-PANI blend was determined. The $T_g$ undergoes a significant reduction as can be seen in Table 4.2, which is a result of a decrease in crosslink density. This reduction in $T_g$ was observed in Tsortra’s work and with epoxy modifications with polypyrrole.\textsuperscript{54} Since the epoxy polymerization occurs via a cationic mechanism, propagating electropositive
species will be terminated if a nucleophile such as amine-based PANI is encountered.
Chain termination results in the reduction of crosslink density, and a looser thermoset
network results in a reduction in $T_g$. The mechanism is shown in figure 4.2.

Figure 4.2. Proposed mechanism for termination of cationic polymerization resulting in
reduced crosslink density.

When formulation #1 was modified with various levels of undoped-PANI, the
results were different from the results obtained from doped-PANI. The most prominent
and unexpected observation was that modification with undoped-PANI produced higher
conductivities than modification with doped-PANI. As mentioned earlier, the base
conductivity of doped-PANI is 10 orders of magnitude more conductive than the undoped
form. Also of significance is the peak of the conductivity occurs at about 4% by weight
loading for the undoped-PANI compared to a 6% by weight loading with the doped-
PANI. The plot of conductivity vs % loading by weight undoped-PANI is shown in Figure 4.3.

![Figure 4.3. Plot of conductivity as a function of undoped-PANI levels.](image)

Though higher conductivity is not expected with undoped-PANI, because of the acid producing catalyst that is employed, a protonic acid is made available to dope the undoped-PANI during the cure process. Others have employed protonic acid doping to undoped-PANI, and have observed good electrical conductivity results when undoped-PANI was blended with thermoplastic polymers and thermosetting epoxies.\textsuperscript{55,56} In both cases, a latent acid-generating species is employed that dopes the undoped-PANI during heat processing. Protonic acid doping of undoped-PANI was inspired by the fact that undoped-PANI is easier to process and exhibits better solubility in a host of polymers and solvents, compared to doped-PANI. Therefore, it is entirely plausible for the undoped-PANI to undergo a significant conductivity increase when doped by the protonic acid that is released by the PC-2506 to cure the epoxy.
One notable distinction between the undoped and the doped-PANI is the particle size of the materials. The undoped-PANI exhibits a smaller particle size (mean particle size of 12 µ) than the doped-PANI (mean particle size of 20 µ). To further exaggerate these differences, the doped-PANI formed some small scale agglomerations that could not be defragmented during the dispersion process. Simple Hegman screening revealed particles that were 50-75 µ as opposed to the 20 µ value given by the supplier of Panipol F. It is believed that the agglomeration forms because of the highly polar nature of the doped-PANI.

Because of a significantly smaller particle size, the undoped-PANI exhibits a larger surface area to interact with the epoxy matrix. Percolation theory also indicates that for an irregular particle size with an aspect ratio of ~1, particles with a larger surface area exhibit percolation at lower loadings.\(^57\) Though the primary percolation network is formed by the silver, secondary networks of PANI will be dependent on the particle size of the PANI particle with the smaller particle favoring the formation of contiguous, secondary networks. Furthermore, the larger particle size of the doped-PANI may also interfere with the contiguity of the silver flakes creating barriers to silver particle contact.

Without silver providing the primary percolation network in formulation #1, the doped-PANI would unlikely deliver good conductivity to the epoxy composition alone. Since the particles are so large, it’s unlikely that a percolation network is formed at the modest loadings employed in the study. In order to facilitate percolation with doped-PANI, Tsotra incorporated doped-PANI in a system that was dispersed in toluene.\(^53\) The pre-dispersion created doped-PANI particles of about 5µ in diameter enabling percolation at reasonable loadings of about 2% by weight.
Of the numerous publications on the solubility of PANI (doped and undoped), there are widespread disagreements on their solubility parameters. Assuredly, there is a solubility parameter difference between undoped-PANI and doped-PANI. Most empirical and theoretical work estimates the solubility parameter at around 22 MPa$^{1/2}$ for the emeraldine base (undoped-PANI). The solubility parameter of doped-PANI (doped with DBSA) was estimated theoretically from input solubility parameters for emeraldine base and DBSA. The resulting, theoretical solubility parameter of 20.8 MPa$^{1/2}$ for the doped-PANI is lower than the solubility parameter of undoped-PANI. However, Wessling observed that the solubility parameter of doped-PANI is greater than 35 MPa$^{1/2}$, which is well beyond the solubility parameter of common organic solvents making it virtually impossible to solubilize doped-PANI. Observations corroborate the high solubility parameter reported by Wessling in that doped-PANI is considered by many to be intractable and unable to be molded or made soluble in organic solvents. In any case, the doping of PANI alters the solubility to such an extent that common solvent are unable to solubilize the doped-PANI. Certainly, if doped-PANI is insoluble in organic solvents, doped-PANI will also resist dissolution in epoxy resins most notable the SFE resin mixture. Consequently, the poor solubility and large particle size of the doped-PANI are likely explanations for the poor interaction with the model epoxy resin and the resulting minimal conductivity improvement observed with the doped-PANI.

Since undoped-PANI exhibits a smaller particle size and enhanced interaction with the model epoxy SFE relative to the doped-PANI, the physical property differences observed between doped and undoped PANI can be explained. Though the $T_g$ of the doped-PANI at 8% by weight levels exhibited a value of 63°C, all levels greater than 2%
by weight for the undoped-PANI appeared soft and liquid-like. Because the characteristics were viscous and not elastic, a $T_g$ could not be measured by the rheometer of any composition with more than 2% by weight undoped-PANI. The $T_g$ and conductivity results for undoped-PANI in formulation #1 are shown in Table 4.3. Because undoped-PANI exhibits a higher surface area and enhanced solubility with epoxy, the interaction and retardation of a propagating positive species will be more preponderant. Consequently, the absolution of the $T_g$ is evidence of the disruption of crosslinking with increasing levels of undoped-PANI.

Table 4.3. Conductivity and $T_g$ resulting from undoped-PANI levels.

<table>
<thead>
<tr>
<th>% undoped-PANI</th>
<th>S/cm</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6,000</td>
<td>104.7</td>
</tr>
<tr>
<td>2</td>
<td>6,200</td>
<td>91.3</td>
</tr>
<tr>
<td>4</td>
<td>13,900</td>
<td>---</td>
</tr>
<tr>
<td>6</td>
<td>11,100</td>
<td>---</td>
</tr>
<tr>
<td>8</td>
<td>11,000</td>
<td>---</td>
</tr>
</tbody>
</table>

The carbon nanofibers demonstrated a similar conductivity boost as the doped-PANI in formulation #1. The peak conductivities for doped-PANI and the nanofibers exhibited values of 7,900 S/cm and 7,600 S/cm respectively. The nanofiber-modified systems were subjected to a subsequent post-cure heat treatment. An additional cure step at 175 °C for 1 h was followed by a post-cure at 225 °C for 1 h. An increase in conductivity was expected and observed with the high temperature post bake because of additional crosslinking or perhaps the removal of residual, volatile lubricants on the surface of silver. However, when the sample without nanofibers was post-cured, the conductivity was higher than the conductivity of any system with nanofibers that was
cured at 175 °C. In other words, the small benefit obtained with the nanofiber addition can be eclipsed with a post-cure. Furthermore, the sample without nanofibers cured at 225 °C exhibited the same or better conductivity of any system with nanofibers that was cured at 225°C. In other words, the nanofibers addition did not show a benefit when the systems were post-cured; the benefit was only observed with the 175 °C cure. The results of the nanofiber addition are shown in Figure 4.4.

Figure 4.4. Plot of conductivity as a function of nanofiber levels cured for 1 h at 175 °C and with a subsequent post-cure for an additional 1 h at 175 °C + 1 h 225 °C.

Post-cure at high temperatures will advance the epoxy reaction closer to its theoretical completion resulting in a marginal increase in crosslink density. The increased crosslink density enhances the conductivity after the postcures. The nanofiber is another conductive medium in the system that provides a small improvement in conductivity and can be employed if high temperature processing does not occur. The nanofibers are most likely providing a means of assisting electron transfer across the gap between adjacent silver particles. Apparently, the additional crosslinking after post-cure promotes the silver particles contiguity with a better result than the nanofibers at the
175 °C. The resulting increase in conductivity by means of nanofiber addition to an SFE can be considered relatively small and insignificant.

Post-cure treatments were also performed on both PANI systems. As mentioned, doped-PANI systems have exhibited inadequate heat stability because of the poor heat stability of the dopants employed in the PANI systems. The post-cure was performed to provide insight into the temperature stability of these systems. A plot of the conductivities of the doped-PANI in formulation #1 with the 1h at 175 °C cure and the post-cure is shown in Figure 4.5.

![Figure 4.5. Plot of conductivity as a function of doped-PANI levels cured for 1 h at 175 °C and with a subsequent post-cure for an additional 1 h at 175 °C + 1 h 225 °C.](image)

Unlike the behavior observed with the nanofibers, for each loading of doped-PANI the high temperature post-cure did not cause the control (material without conductive additive) to exceed the conductivity of systems with conductive additive (doped-PANI in this case). The magnitude of conductivity increase is larger with the subsequent post cure elucidating that the affect of doped-PANI is magnified at high
temperature post-cures. Additionally, from the curve shown in figure 4.5, the slope of the post-cured systems is steeper indicating that the increase in conductivity with successive levels of undoped-PANI is larger. Interestingly, when the post-cure is employed the conductivity does not undergo a decrease at 8% by weight loading. Instead, the conductivity increases in linear fashion throughout the entire range of doped-PANI levels. The drop in conductivity at 8% undoped-PANI under standard cure conditions is likely due to a reduction in crosslink density. Therefore, the monotonic increase at 8% by weight undoped-PANI with the post-cure most likely increases crosslink density effectively increasing conductivity.

For undoped-PANI, the conductivity trend for the post-cured samples matched the trend of the samples cured for 1 h at 175 °C. These results are shown in Figure 4.6. For all levels of undoped-PANI, the post-cure conductivity was higher except for the 8% by weight, where the conductivity of the post-cured samples matched the conductivity of the samples cured at 175 °C. The post cure may have instigated additional cure as well as volatilized residual organics and lubricants that could interfere with silver particle intimacy producing improved conductivity. Conclusively, the conductivity gains observed with both forms of PANI in formulation #1 were significantly larger than the marginal gains observed with carbon nanofibers. Other electrical attributes, such as interfacial electrical conductivity, could be improved by the presence of nanofibers. However, since bulk electrical properties are the focus of the study, maximizing and exploring the gains with undoped-PANI is the primary goal of the second round of experimentation.
Second Round of Experiments: Exploring Undoped-PANI

In order to elucidate the effects of undoped-PANI, undoped-PANI modifications were conducted with formulation #2 and a full characterization of the physical and electrical properties was performed. Undoped-PANI was added in increments of 1% instead of 2% by weight in the first round of experiments to resolve finer details in the conductivity response. Formulation #2 was introduced in the second round of experiments to deliver an increased crosslink density. This was accomplished by replacing bisphenol F epoxy monomer, 830-LVP, with cycloaliphatic epoxy monomer, UVR-6105. A comparison of the structures of both epoxy monomers was shown in Figure 3.1. The theoretical molecular weights of the UVR-6105 and the 830-LVP are 252 g/mol and 312 g/mol respectively. Assuming reactivity at the 2 epoxy functional groups, the molecular weight between epoxy crosslinks is shorter for the UVR-6105 increasing the crosslink density and the shrinkage during cure. Most importantly, the increased crosslink density afforded by the UVR-6105 can offset the PANI nucleophilic
termination of the propagating positive species. Ideally, the increased crosslink density should permit higher loadings of undoped-PANI suspending crosslink density and $T_g$ reductions until higher levels of undoped-PANI.

In addition to the resin change, the silver loading of SF#85-HV was increased from 76% to 84% by weight in formulation #2. Improvements in conductivity were expected with the increase in silver loading. However, comparing the two formulations without any undoped-PANI addition, the 84% by weight silver loading in formulation #2 delivered only a modest 8% increase in conductivity. Figure 4.7 depicts this marginal conductivity boost from 6,000 S/cm to 6,500 S/cm. With this substantial increase in silver, a larger increase in the base conductivity might be anticipated. However, the percolation threshold is substantially exceeded at 76% by weight and the conductivity response becomes asymptotic with increasing silver loading. In other words, the major “step” in conductivity has been surpassed and the significant conductivity gains with increasing silver loading has diminished.

Though without undoped-PANI additions only a small deviation in conductivity was observed, the addition of undoped-PANI resolved a significant conductivity response between the two formulations. With formulation #1 at 76% by weight silver, a peak conductivity of 13,900 S/cm was observed, while with formulation #2 at 84% by weight silver, the peak conductivity inflated to 35,600 S/cm. The peak conductivity for formulation #1 and formulation #2 was observed at 4% and 3% by weight levels of undoped-PANI respectively. The results summarized in Table 4.4 demonstrate a significantly larger conductivity increase accommodating undoped-PANI addition to formulation #2.
Table 4.4. Comparison of conductivity gains in both formulations #1 and #2.

<table>
<thead>
<tr>
<th>% Ag loading</th>
<th>Conductivity w/ no PANI (S/cm)</th>
<th>Peak Conductivity w/ PANI (S/cm)</th>
<th>% Conductivity Increase with PANI</th>
</tr>
</thead>
<tbody>
<tr>
<td>76% (Formulation#1)</td>
<td>6,000</td>
<td>13,900</td>
<td>130%</td>
</tr>
<tr>
<td>84% (Formulation#2)</td>
<td>6,500</td>
<td>34,600</td>
<td>430%</td>
</tr>
</tbody>
</table>

Interestingly, formulation #2 with undoped-PANI is a factor of 2.5 times more conductive (at 3% by weight undoped-PANI) than formulation#1 with undoped-PANI (at 4% by weight). In comparison, without any undoped-PANI formulation #2 only delivered an 8% (factor of 1.08 more conductive) increase relative to formulation #1. Both the increase in silver loading and the increased crosslink density are plausible reasons for the decisive conductivity benefit in formulation #2. Figure 4.7 depicts the significantly better conductivity of formulation #2 with undoped-PANI, and the marginally better conductivity of formulation #2 without undoped-PANI addition.

![Figure 4.7](image-url)  

Figure 4.7. Chart showing significantly larger conductivity increases with the addition of undoped-PANI in the 84% by weight silver-loaded chemistry (formulation #1) vs. the 76% by weight silver-loaded chemistry (formulation #2).
Figure 4.8. Plot of conductivity as a function of doped-PANI levels for formulation #2.

Though the conductivity boost is larger for formulation #2, the plot of conductivity vs. undoped-PANI levels looks similar for both formulations. Figure 4.8 shows the peak conductivity at 3% by weight loading with the overall curve exhibiting a general “bell shape.” Previous discussion with both doped and undoped-PANI results postulated that the decrease in conductivity and the associated “bell-shaped” curve is a result of the decrease in crosslink density with excessive amounts of PANI. Though additional PANI will increase the conductivity of the polymer network, its affect on crosslink density minimizes the pressure on the silver particles affording larger insulating distances and less contact area between silver particles. Since both constriction resistance, $R_{cr}$, and tunneling resistance, $R_{t}$, are related to the contact area between particles, the contact resistance between particles increases with less pressure applied to the particles. The effective conductivity of the composite is decreased as a result of increased contact resistance between silver particles.
Crosslink density was measured for the various loadings of undoped-PANI in formulation #2. As mentioned earlier the crosslink density can be determined with a parallel plate rheometer by evaluating the shear modulus in the rubbery plateau region. Figure 4.10 highlights only the $G'$ and the rubbery modulus region that enables the calculation of $M_c$.

![Rheometer scan](image)

Figure 4.9. Rheometer scan featuring the temperature excursion and the resulting shear modulus, $G'$, during the cure, isotherm, and cooling of the epoxy.

The determination of the $M_c$ can be expressed with the following equation:

$$M_c = 3q \frac{\rho RT}{E_R}$$

Since the elastic modulus, $E$ is related to shear modulus, $G$, by the relation,

$$E' = 2G'(1 + \nu),$$
the crosslink density calculations were performed by combining the expressions and obtaining the new expression for crosslink density:

\[ M_C \equiv 3q \frac{\rho RT}{2G_R(1 + \nu)} \]

As mentioned, only the \textit{Epoxy+PANI} constituent was tested on the rheometer isolating only the physical properties of the polymer. The inclusion of the silver would result in a significantly higher modulus value for the composite and an erroneous calculation of crosslink density. An overlay of the rheometer scans for the \textit{Epoxy+PANI} constituent for varying levels of undoped-PANI is shown in Figure 4.10.

![Figure 4.10. Overlay of shear modulus development for each level of undoped-PANI in formulation #2. Formulations do not contain silver isolating only the polymer properties.](image)

A plot of the conductivity and crosslink density as a function of undoped-PANI was used to examine potential relationships between crosslink density and conductivity. As shown in Figure 4.12, the conductivity peaks at about 3% by weight undoped-PANI,
while it appears that the $M_c$, distance between crosslinks, is essentially constant up to 6% by weight undoped-PANI. Beyond 6% by weight undoped-PANI, the $M_c$ begins an upward trend as the crosslink density is drastically reduced. It appears that there is not a fundamental relationship between the increase in $M_c$ and the decay in electrical conductivity. It is worth noting that since the decay in crosslink density does not manifest until 7% by weight undoped-PANI, this is in sharp contrast to the point of decay in formulation #1 where the material was soft and liquid-like at levels greater than 2% by weight undoped-PANI. This indeed is a result of the increased crosslink density afforded by formulation #2 that suspends the crosslink density reduction until higher levels of undoped-PANI. Therefore, the primary goal of the chemistry change has been attained by permitting higher levels of undoped-PANI before observing the decay of physical properties such as crosslink density and $T_g$.

![Figure 4.11](image_url)

**Figure 4.11.** Plot of conductivity and $M_c$ as a function of undoped-PANI levels.

From the rheometer it appears that the decay in conductivity and the increase in $M_c$ are unrelated, however the DMA was used to further investigate the relationship between the two variables. Unlike the rheometer work that isolated the $Epoxy+PANI$
constituent, the DMA evaluated the \textit{Epoxy+PANI+Ag} composition. Therefore, the DMA provides a physical characterization of the complete silver-polymer composite. Figure 4.12 depicts the elastic modulus, $E'$, modulus and the tan delta by DMA as a function of undoped-PANI in formulation #2.

![DMA plots for formulation #2 (with silver) as a function of undoped-PANI: (a) elastic modulus vs. temperature (b) tan delta vs. temperature.](image)

Figure 4.12. DMA plots for formulation #2 (with silver) as a function of undoped-PANI: (a) elastic modulus vs. temperature (b) tan delta vs. temperature.
The overlay plots in Figure 4.12 reveal a correlation between the physical properties and levels of undoped-PANI. With increasing undoped-PANI, the \( T_g \) shifts to lower temperatures. This is evident by the decrease in the peak tan delta temperature and the decrease in the onset temperature of \( E' \). Another notable trend is the reduction in the \( E' \) at 250 °C with increasing levels of undoped-PANI. The 250 °C \( E' \) was arbitrarily chosen for characterization since 250 °C is comfortably in the rubbery plateau for all of the compositions. Because of the silver in the composition, the rubbery plateau cannot be used to calculate the intrinsic \( M_c \) of the polymer matrix. However the 250 °C plateau modulus is an indicator of the relative \( M_c \) for the various compositions. The \( T_g \) and \( E' \) at 250 °C values are summarized in Table 4.5.

Table 4.5. Conductivity and properties for undoped-PANI levels in formulation #2.

<table>
<thead>
<tr>
<th>% Undoped-PANI by weight</th>
<th>Conductivity (S/cm)</th>
<th>( E' ) at 250°C</th>
<th>Tan Delta</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6,500</td>
<td>894</td>
<td>192.8</td>
</tr>
<tr>
<td>1</td>
<td>7,400</td>
<td>827</td>
<td>195.3</td>
</tr>
<tr>
<td>2</td>
<td>14,900</td>
<td>841</td>
<td>188.6</td>
</tr>
<tr>
<td>3</td>
<td>34,600</td>
<td>675</td>
<td>153.2</td>
</tr>
<tr>
<td>4</td>
<td>19,900</td>
<td>327</td>
<td>94.0</td>
</tr>
<tr>
<td>5</td>
<td>14,400</td>
<td>216</td>
<td>23.2</td>
</tr>
<tr>
<td>6</td>
<td>13,900</td>
<td>255</td>
<td>33.8</td>
</tr>
<tr>
<td>7</td>
<td>7,100</td>
<td>Too soft to measure</td>
<td></td>
</tr>
</tbody>
</table>

Insight into the crosslink density relationship extracted from the DMA data can be utilized to further understand the reduction in electrical conductivity after 3% by weight undoped-PANI levels. There are no significant changes in \( E' \) and \( T_g \) from 0% to 2% by weight levels of undoped-PANI. At 3% by weight undoped-PANI the first significant
change in physical properties occurs where the $T_g$ undergoes a 30 °C plunge, and the modulus at 250 °C decreases by about 160 MPa. With 4% by weight undoped-PANI, the $T_g$ now undergoes an additional $T_g$ drop of about 70°C, and a more sizable reduction in the 250 °C $E’$. Finally, at 7% by weight undoped-PANI the sample was so soft that a DMA measurement could not be taken. When the $E’$ at 250 °C and the conductivity is plotted as a function of undoped-PANI, an interesting relationship is observed in Figure 4.13. The decay in $E’$ at 250 °C undergoes its sharpest decline just beyond the 3% by weight levels of undoped-PANI coinciding with the drop in electrical conductivity of the composites. Because of the dependency of pressure on silver particles, the drop in crosslink density is most likely the reason for the decay in electrical conductivity. Despite the fact that more undoped-PANI, the decrease in crosslink density results in less cure shrinkage, less pressure on the silver particles and less silver flake contiguity. As a result the distance between silver particles and the contact surface area of the silver flake is reduced. Based on the relationship for contact resistance, the electrical conductivity is decreased.

4.13. Plot of conductivity and elastic modulus, $E’$, at 250 °C as a function of undoped-PANI levels in formulation #2.
An obvious discrepancy exists between the Epoxy+PANI results from the rheometer and the Epoxy+PANI+Ag results by DMA. When only the Epoxy+PANI was tested by rheometer, the crosslink density was constant from 0-5% undoped-PANI by weight. Only 7% by weight undoped-PANI revealed an increase in the $M_c$. DMA measurements gave a small decrease in plateau modulus (inversely proportional to $M_c$) at 3% undoped-PANI followed by a steeper drop in the property after 3% by weight. This indicates that the decay in physical properties occurs at lower levels of undoped-PANI for the Epoxy+PANI+Ag DMA samples.

Besides sample geometry, deformation modes, and strains between the two test methods, the most obvious difference is the fact that the DMA samples contained 84% silver and the rheometer testing evaluated only the epoxy polymer network. Since the silver contains aliphatic lubricants it is believed that the removal of the lubricant occurs during the curing process. The removal and subsequent release of the lubricant into the resin matrix adds a plasticizing moiety into the network. Unlike the highly crosslinked network, the lubricant can reduce the crosslink density and $T_g$. Therefore, with the increased plasticity of the lubricant it is plausible that the reduction in crosslink density and $T_g$ occurs at lower levels of undoped-PANI in the Epoxy+PANI+Ag samples. Both the lubricant and the increased levels of undoped-PANI can erode the crosslink density of the network.

While much of the discussion pertaining to crosslinking and $T_g$ explain the decline in conductivity observed with undoped-PANI above 3% by weight, explanations for the conductivity increase associated with low levels of undoped-PANI is of most interest. Crosslink density explanations have given the framework in which the undoped-PANI
can effectively operate in an SFE, but a more thorough understanding of the conductivity mechanism is advantageous to optimize the effects. Tsotra’s work proved that the introduction of doped-PANI into the epoxy polymer enabled the epoxy to increase in conductivity by 11 orders of magnitude. With small particles percolation resulted at reasonable loadings to create the conductive composite. It’s reasonable to hypothesize that the conductivity increase with undoped-PANI is related to a boost in the electrical conductivity of the \( \text{Epoxy+PANI} \) constituent. To verify, a simple evaluation of the electrical properties of the \( \text{Epoxy+PANI} \) constituent with varying levels of undoped-PANI would reveal any such conductivity increases in polymer alone. Figure 4.14 depicts the conductivity of formulation #2 with and without silver as a function of varying undoped-PANI levels.

![Figure 4.14. Plot of composite conductivity at 84% silver in formulation #2 and intrinsic conductivity of the polymer as a function of undoped-PANI levels.](image)

Interestingly, the first step in electrical improvement of the \( \text{Epoxy+PANI} \) constituent occurs at 3% undoped-PANI by weight coinciding with the maximum
electrical conductivity of the \textit{Epoxy+PANI+Ag} composite. The conductivity benefit for the \textit{Epoxy+PANI} constituent appears to level-off from 3-6\% by weight, until an additional step in conductivity is observed at 7\% by weight undoped-PANI. Though the 3\% by weight step in the \textit{Epoxy+PANI} samples correlates with the maximum electrical conductivity for \textit{Epoxy+PANI+Ag}, 1\% and 2\% by weight levels for the \textit{Epoxy+PANI} samples did not show discreet conductivity increases. Conductivity benefits are observed at 1\% and 2\% by weight in the \textit{Epoxy+PANI+Ag} samples, which cannot apparently be correlated with increases in conductivity in the \textit{Epoxy+PANI} samples. These low levels of undoped-PANI apparently are unable to exceed the percolation threshold in the \textit{Epoxy+PANI} constituent maintaining the same conductivity. However, in the \textit{Epoxy+PANI+Ag} small levels of undoped-PANI (1-2\% by weight) are able to assist in creating secondary conduit between silver particles.

Though \textit{Epoxy+PANI} exhibited conductivity increases at greater than 3\% by weight undoped-PANI, the magnitude of conductivity increase is certainly less than the gains reported by Tsotra with the doped-PANI in epoxy. One of the reasons for relatively low conductivity with varying levels of undoped-PANI in the \textit{Epoxy+PANI} constituent could be related to the efficiency of doping. Doped-PANI is doped with a proven dopant, dodecybenzenesulfonic acid. The acid environment that was proven to offer the best conductivity in Tsotra’s work merely maintained the oxidized, doped state of the PANI. In the second round of experiments the doping is presumed to occur by the protonic acid that is released during the curing process. Many important details such as the molar acid concentrations, diffusion rates, and doping kinetics vs. cure kinetics could account for the lower magnitude of conductivity observed with the \textit{Epoxy+PANI} constituent.
Furthermore, Tsotra’s work utilized a highly dispersed version of doped-PANI with an average particle size of 5 µ. The considerably smaller particle size in contrast to the 20 µ undoped-PANI will enable lower percolation thresholds resulting in higher conductivities.

DSC scans were conducted where the materials were ramped at 10 °C/min and the resulting exotherm from cure was measured. The DSC evaluation was performed on the Epoxy+PANI+Ag compositions. Without undoped-PANI the cure rate is relatively sluggish with a broad exotherm that peaked at about 150 °C. The 1% by weight addition of undoped-PANI resulted in a significant shift of the peak exotherm temperature to approximately 140 °C. Based on the lower peak exotherm and the steepness of the curve, the 1% by weight undoped-PANI system is certainly faster than the system without any PANI. With increasing additions of undoped-PANI at 2% and 3% by weight, the cure speed began to decrease relative to the 1% level of undoped-PANI, but 1%, 2%, & 3% by weight levels each appeared to exhibit faster cure speed compared to material without undoped-PANI. Levels greater than 4% by weight undoped-PANI resulted in significant cure speed reductions where the peak exotherm shifted to higher temperatures than the system without PANI.

The amount of energy from the curing exotherm in J/g significantly decayed with increasing undoped-PANI levels above 4% by weight. Not only is the cure speed reduced at these high levels of undoped-PANI, but the degree of polymeric conversion is also significantly reduced. This result coincides with the observation that the physical properties, namely the $T_g$, of systems with high levels of undoped-PANI significantly decay. The DSC plots are shown in Figure 4.15, while a table of the results is included in Table 4.6.
Figure 4.15. DSC scans of formulation #2 at 84% by weight silver loading as a function of each level of undoped-PANI showing a significant shift in peak exotherm temperature and total energy with increasing levels of undoped-PANI.

Table 4.6. DSC results for formulation #2 with corresponding undoped-PANI levels.

<table>
<thead>
<tr>
<th>% undoped-PANI by Weight</th>
<th>DSC onset (°C)</th>
<th>DSC Peak Exotherm (°C)</th>
<th>Exotherm (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>134</td>
<td>151</td>
<td>82</td>
</tr>
<tr>
<td>1</td>
<td>133</td>
<td>140</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>139</td>
<td>145</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>140</td>
<td>147</td>
<td>67</td>
</tr>
<tr>
<td>4</td>
<td>145</td>
<td>160</td>
<td>38</td>
</tr>
<tr>
<td>5</td>
<td>133</td>
<td>151</td>
<td>17</td>
</tr>
<tr>
<td>6</td>
<td>155</td>
<td>181</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>154</td>
<td>171</td>
<td>6</td>
</tr>
</tbody>
</table>
Lubricant Investigation: Examining Different Silvers

Since silver flake lubricant removal and its affect on conductivity have been studied extensively, undoped-PANI was added to formulation #2 with conductors in place of SF#85-HV silver flake that did not have an insulating organic lubricant. Presumably, a controlled experiment isolating conductors with and without lubricant and with and without undoped-PANI would delineate if the undoped-PANI conductivity benefit was related to the lubricant. An ideal case would involve testing a silver flake similar to SF#85-HV that was free of lubricants, but as mentioned earlier, lubricants are necessary for flake-like silver.

In order to examine the potential interaction of undoped-PANI with lubricants, silver powders with and without lubricant were evaluated. Because of the sphere-like geometry, silver powders typically do not exhibit high conductivities in epoxy systems. However, since silver powders are supplied without lubricant, it does provide an excellent opportunity to examine the affects of the lubricant. One silver powder without lubricant, called P1, and one silver powder with lubricant, called P2, were added independently to formulation #2 as the primary conductor in place of SF#85-HV. Each of these silver powders was tested without PANI and with 2.5% by weight undoped-PANI. Although 3% by weight undoped-PANI provided the maximum gain in conductivity for SF#85-HV in formulation #2, the onset of the decay of the physical properties also began at 3% by weight. Since 2% by weight undoped-PANI also created a large conductivity gain, 2.5% by weight was chosen to provide a solid potential gain in electrical conductivity while minimizing the potential decay in any physical properties.
Since the lubricated silver powder, P2, contains a different lubricant than the lubricant on the SF#85-HV, additional testing was conducted to understand the full effects of lubricant. P2 uses oleic acid as the lubricant, while SF#85-HV utilizes isostearic acid as the lubricant. A large silver flake, that is very similar in characteristics to SF#85-HV, was designated LF2 (large flake #2). LF2 has comparable surface area and particle size to the SF#85-HV, but it utilizes oleic acid as the lubricant. Included in the study was another oleic-based flake, designated SF2 (small flake #2), which has a much smaller particle size than the larger silver flakes and both silver powders. Table 4.7 outlines the differences between the different conductive particles. SEM photographs of the SF#85-HV and the silver particle, P1, are shown in Figure 4.16 demonstrating a distinct difference in the microstructure between the flake and the particle.

<table>
<thead>
<tr>
<th>Conductive Filler</th>
<th>Median Particle Size (µ)</th>
<th>Surface Area (m²/g)</th>
<th>Lubricant</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>3.0</td>
<td>0.4</td>
<td>None</td>
</tr>
<tr>
<td>P2</td>
<td>2.4</td>
<td>0.8</td>
<td>Oleic</td>
</tr>
<tr>
<td>SF2</td>
<td>0.8</td>
<td>1.9</td>
<td>Oleic</td>
</tr>
<tr>
<td>LF2</td>
<td>6.6</td>
<td>0.3</td>
<td>Oleic</td>
</tr>
<tr>
<td>SF# 85-HV</td>
<td>5.8</td>
<td>0.6</td>
<td>Isostearic</td>
</tr>
</tbody>
</table>

Figure 4.16. SEM photographs provided by supplier, Ferro: (a) silver particle designated P1, (b) silver flake SF#85-HV.62
When comparing the two silver powders, P1 and P2, a new observation emerges where the conductivity actually decreases as a result of adding undoped-PANI. In Figure 4.17 the ANOVA plot clearly shows that silver powder without lubricant, P1, undergoes an obvious decrease in conductivity after the addition of undoped-PANI. The statistical significance of the difference is well resolved when examining the t-test results where the circles at the right of the graph do not touch. Though the sample size includes only 3 conductivity slides, the results are in stark contrast to the previous high conductivity gains of 434% observed with lubricant-based silver flakes and undoped-PANI.

![Figure 4.17. Comparison of silver powder without lubricant, P1, in formulation #2 with and without undoped-PANI](image)

When a silver powder with oleic acid lubricant, P2, was tested with and without undoped-PANI, the results were different. Unlike the powder without lubricant a small increase in conductivity is observed with P2. Since only 3 slides were used for each sample set, the distinction in conductivity is actually statistically insignificant where the circles of the t-test intersect each other. Perhaps with a larger sample size, the difference in conductivity will take on statistical significance. Though the conductivity values do
not show a large increase like SF#85-HV silver flake, the results differ depending on whether lubricant is present on the powder. The plot in Figure 4.18 shows the conductivity values for the P2 silver powder.

![Graph showing conductivity values for P2 silver powder with and without undoped-PANI.](image)

Figure 4.18. Comparison of silver powder with oleic lubricant, P2, in formulation #2 with and without undoped-PANI showing an incremental conductivity increase when undoped-PANI is added.

Though the increase in conductivity of P2 with the addition of undoped-PANI is at best marginal, there are a few reasons why a large conductivity boost is not observed. First, silver powder is typically not chosen as a conductor in thermosetting resins because of the low aspect ratio. Geometrically it is more difficult for the particles to make contact and at normal silver loading the total number of contact points across a composite is relatively large compared to a silver flake with a high aspect ratio. In principle, this means that there are a greater number of high resistance points associated with the contact points between silver powder particles. Then a question arises whether the conductivity benefits with undoped-PANI can overcome an inferior percolation network with silver powder. Second, the oleic-based P2 may not have the same synergistic effect as isostearic-based lubricants such SF#85-HV.
The two oleic-based flakes, SF2 and LF2, represent the extremes of particle size. As mentioned, LF2 is similar in size to SF#85-HV, while SF2 is considerably smaller than the silver powders. The results of SF2 are shown in Figure 4.19 displaying the most prominent conductivity increase of 8 orders of magnitude with the addition of undoped-PANI. Not only is undoped-PANI effective with small silver flake, but the magnitude of conductivity increase eclipses the improvements seen with SF#85-HV, which was 405% at 2.5% by weight undoped-PANI. Conclusively, undoped-PANI can be effective with small silver particles. Also, since SF2 is oleic-based silver, effective conductivity gains with undoped-PANI have been demonstrated with both oleic and isostearic lubricant. Conclusively, the low magnitude gains observed with silver powder, P2, are not a result of the small particle size or the oleic-based lubricant seeing that SF2 is smaller in particle size than P2 and the same oleic lubricant exhibited a superior conductivity boost in SF2 and a marginal boost in P2.

![Figure 4.19](image-url)

Figure 4.19. Comparison of the small silver flake with oleic lubricant, SF1, in formulation #2 with and without undoped-PANI exhibiting the largest observed conductivity increase when undoped-PANI is added.
Now that two completely different results were observed with oleic-based silvers, results from LF2 with oleic acid lubricant will be revealing. The results are shown in Figure 4.20, comparing the effects of undoped-PANI on both large flakes LF2 and SF#85-HV. The addition of undoped-PANI in the LF2 results in a small decrease in conductivity for the oleic-based flake, while the isostearic-based flake, SF#85-HV, experienced the 405% increase in conductivity. Unlike all of the other systems, the conductivity of the oleic-based LF2 is extremely good at nearly 37,000 S/cm without the addition of undoped-PANI. The data in Figure 4.20 clearly shows that the type of lubricant does affect the initial conductivity and can perhaps have an interaction with the addition of undoped-PANI. Though there is no improvement in conductivity with the addition of undoped-PANI in LF2, the initial conductivity without undoped-PANI addition is one of the highest conductivity values observed in the study.

Figure 4.20. Comparison of large silver flakes with lubricant; isostearic-based SF#85-HV exhibits a large improvement in conductivity after undoped-PANI addition, while the oleic-based large flake, LF2 exhibited excellent conductivity before undoped-PANI addition and little change after the undoped-PANI addition.
Now that 3 different oleic-based silvers exhibited different conductivity responses, some trends are apparent. First of all, the initial conductivity without undoped-PANI for all 3 systems is considerably different. Secondly, the scale of conductivity increase is an inverse function of the initial conductivity before undoped-PANI addition. SF2 having the lowest initial conductivity (<1 S/cm) demonstrated the largest change with the addition of undoped-PANI. On the contrary, the LF2 had the highest initial conductivity and exhibited a marginal decrease after addition of undoped-PANI. Finally, the physical attributes of the silvers also follow a trend. The highest surface area conductor, SF2, underwent the largest increase in conductivity, while the smallest surface area conductor, LF2, underwent the marginal conductivity decrease. Therefore, larger surface areas undergo larger conductivity increases with undoped-PANI addition.

Furthermore, it stands to reason that a larger surface area equates to more lubricant on the silver. Thermal gravimetric analysis (TGA) data from the supplier conveys weight loss at 538 °C, an indication of the amount of lubricant present on the silver. Interestingly, though P2 does not have the largest surface area, it does have the most amount of oleic acid on its surface. This implies that perhaps the P2 has more efficient coverage of lubricant or more than a monolayer of lubricant is present on the P2.

Since lubricant removal is essential to maximizing conductivity, more lubricant on the silver will hinder the development of conductivity in a polymer. LF2 with the least amount of lubricant delivered high conductivity without undoped-PANI addition. SF2 having nearly twice the amount of lubricant as LF2 produced very low conductivity initially, but with the addition of undoped-PANI, SF2 attained the same conductivity as LF2 hinting to the possibility of undoped-PANI interactions with the lubricant.
The lack of improvement in the P2 after undoped-PANI could be related to the excessively high level of lubricant on the surface of the silver powder. Though only conjecture at this point, perhaps because of the high level of oleic lubricant, undoped-PANI addition could not overcome the lubricant barrier to conductivity. As mentioned previously, silver powders are not known for the potential for producing high conductivities as the primary conductor in an epoxy. Table 4.8 outlines the trends in initial conductivity, surface area, and weight loss, and how they relate to the change in conductivity. Though difficult to explain all of the results, deductively the lubricant percentage impacts the initial conductivity as well as the potential ultimate conductivity attained with undoped-PANI.

Table 4.8. Conductivity and particle characteristics for oleic-based silvers.

<table>
<thead>
<tr>
<th></th>
<th>Initial Conductivity (S/cm)</th>
<th>Conductivity with PANI (S/cm)</th>
<th>% Change in Conductivity</th>
<th>Surface Area</th>
<th>Weight loss (%), % of lubricant</th>
</tr>
</thead>
<tbody>
<tr>
<td>LF2</td>
<td>36,900</td>
<td>31,100</td>
<td>-16%</td>
<td>0.30</td>
<td>0.36%</td>
</tr>
<tr>
<td>SF2</td>
<td>0.017</td>
<td>29,400</td>
<td>2 x 10^9 %</td>
<td>2.00</td>
<td>0.58%</td>
</tr>
<tr>
<td>P2</td>
<td>2337</td>
<td>3,300</td>
<td>40%</td>
<td>0.75</td>
<td>1.20%</td>
</tr>
</tbody>
</table>

Numerous other lubricant-free conductors were evaluated as primary conductors in place of SF#85-HV in formulation #2. Conductive graphite, carbon nanofibers, and silver nanoparticles represented different sizes and aspect ratios of conductive fillers without lubricant. The general properties of these conductors are outlined in Table 4.9. The loading level of each filler depended on the effect on the viscosity, and the loadings were significantly less than the loading attained with SF#85-HV. This is expected because of the large surface area of these conductors. However, with the large surface
area, a lower percolation threshold is observed. For each conductor when undoped-PANI was added to the system at 2.5% by weight, no statistically significant change in conductivity was observed. Including the P1 silver powder, a total of 4 primary conductors did not show a favorable conductivity response after the addition of undoped-PANI. The common denominator for all of these conductors is the lack of a lubricant coating on the surface implying that the primary conductor must be coated in lubricant in order to observe favorable conductivity interactions with undoped-PANI.

Table 4.9. Conductive additives without lubricant that did not exhibit conductivity improvements after undoped-PANI addition.

<table>
<thead>
<tr>
<th>Conductive Additive</th>
<th>Median Particle Size (µ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver nanoparticle</td>
<td>0.050</td>
</tr>
<tr>
<td>Carbon Black</td>
<td>0.080</td>
</tr>
<tr>
<td>Nanofiber</td>
<td>10.0/0.010</td>
</tr>
<tr>
<td>P1</td>
<td>3.0</td>
</tr>
</tbody>
</table>

After testing the numerous conductors with undoped-PANI, a few generalities persisted. Firstly, only systems that were coated with organic lubricants underwent any significant change in electrical conductivity. Any silver or carbon-based system without lubricant did not change or in some cases decreased in electrical conductivity after the addition of undoped-PANI. Lubricant in some fashion interacts with the undoped-PANI to create the substantial enhancement in electrical conductivity. Second, the magnitude of conductivity increase in lubricated silvers was inversely proportional to the initial conductivity of the system without undoped-PANI. In other words, composites with the lowest initial conductivities had the potential to undergo the largest gains in electrical
conductivity after undoped-PANI modification. Thirdly, both isostearic and oleic lubricant were subject to large gains in conductivity with undoped-PANI under the right conditions. Finally, with the 3 silver flakes, SF#85-HV, SF2, and LF2, there appeared to be a maximum capacity of 30,000 S/cm to 35,000 S/cm that each flake could attain in the epoxy. If the flake generated conductivity near the capacity without undoped-PANI, undoped-PANI addition did not improve the conductivity. When the system was below the capacity, undoped-PANI enabled the system to reach the capacity whether the system was 8 orders of magnitude or 1 order of magnitude below the capacity.

The degree that lubricant removal affects conductivity in a polymer matrix is not completely understood. Theories have been presented that lubricant removal is not necessary for the generation of electrical conductivity in a polymer matrix, and that resin shrinkage and the accommodating pressure on the silver particles is the only prerequisite for conductivity. Others maintain that lubricant removal is the only way to generate conductivity with a silver flake. Lovinger insists that high temperature curing enhances the solubility of the lubricants in the resin chemistry, which removes more lubricant instigating conductivity. It is understood that the lubricant exists as a fatty acid salt on the silver surface, and it will not be removed thermally until temperatures exceed 200°C. However, the lubricant can be removed at significantly lower temperatures in the epoxy chemistry. The lubricant removal can successfully occur during the curing process with high temperatures enhancing solubility of the lubricant in the resin, and with additives that have a strong affinity for silver that can displace the lubricant acid-salt complex.
Cure Speed and Conductivity

The cure speed of formulation #2 was manipulated without undoped-PANI to understand the dependence of conductivity on the gel temperature of the material. The gel temperature was reduced (cure speed increased) by adding copper napthanate. At the gel temperature of the epoxy, the polymer matrix abandons its liquid-like characteristics, and the propensity for solubility in the epoxy begins to diminish. Therefore, a higher gel temperature allows more time at higher temperature for the solubility of lubricants to persist in the host polymer matrix. Figure 4.21 depicts how the conductivity of formulation #2 without undoped-PANI has a strong dependence on the gel temperature.

![Graph showing conductivity as a function of ARES gel time.](image)

Figure 4.21. Conductivity as a function of ARES gel time.

Gel times of the undoped-PANI modified systems were examined to insure that the mechanism for the conductivity boost associated with undoped-PANI was not a result of a shift in the gel time. If the undoped-PANI modification significantly slowed the cure speed shifting the gel time to a higher temperature, then the conductivity increase would
be simply a result of slower cure kinetics and enhanced temperature-related lubricant solubility. A plot of the conductivity and gel temperature vs the level of undoped-PANI is shown Figure 4.22 revealing no relationship between the gel temperature and the conductivity. Shifts to a higher gel temperature do occur at levels greater than 4% by weight, but the conductivity decays at levels greater than 4% by weight. Consequently, the shift in gel temperature is not related to the boost in electrical conductivity. At 3% by weight undoped-PANI, which is the peak in conductivity, the gel temperature is 130°C. This matches the gel temperature for the system without any undoped-PANI. DSC results shown in Table 4.6 also corroborate the gel temperature data. The DSC peak exotherm temperature actually marginally decreases at 1%, 2%, and 3% by weight compared to the system without undoped-PANI addition. The marginally lower peak exotherm represents faster cure kinetics, which would actually oppose improved solubility of the lubricant. Consequently, the conductivity increase is not a function of a decrease in cure speed (increased gel temperature) in the system.

Figure 4.22. Plot of conductivity of formulation #2 and gel temperature as a function of undoped-PANI levels.
It is proposed that the undoped-PANI is effective in improving conductivity by removing lubricant from the silver surface. Though the mechanism cannot be completely explained, it has been established that organic additives with hydroxyl, ester, and ether functionality have been effective at removing lubricant from silver flakes.\textsuperscript{30} Also, as mentioned earlier, moieties with strong affinities for silver can displace lubricant. The evidence for this assertion resides in the fact that the boost in conductivity with undoped-PANI was shown to be highly dependent on the amount of lubricant on the silver. Furthermore, those primary conductors without lubricant did not exhibit a conductivity change with undoped-PANI addition. Finally, though the conductivity is highly dependent on the gel temperature, the gel temperature was not altered with the addition of undoped-PANI.

A final manipulation was performed by adding copper napthanate to the standard formulation #2 with and without undoped-PANI in order to impact the gel temperature. The previous manipulation of the gel temperature was performed on formulation #2 without undoped-PANI. Expectations were that the gel time will be reduced, the solubility of the lubricant in the epoxy will be decreased, the time for undoped-PANI to displace lubricant will be decreased, and the resultant conductivity boost will be minimized or nullified. The important question to answer is whether the undoped-PANI can enhance the conductivity in a system with a lower gel temperature. Figure 4.23 shows a comparison between the low gel temperature (fast-curing) and the higher gel temperature (slow-curing) modifications. With the addition of undoped-PANI to the fast-curing system with copper napthanate, the conductivity decreases instead of undergoing the typical ~405% conductivity increase typically observed in the standard formulation#2.
Figure 4.23. Comparison of slow and fast curing versions of formulation #2 with and without undoped-PANI.

This plot in Figure 4.23 clearly shows the necessity of slower gel temperatures or slower curing kinetics to capture the benefits of adding undoped-PANI. Rapid gel materials do not benefit from the enhanced lubricant solubility of the undoped-PANI, and the time to displace lubricant is greatly minimized. As displayed in Figure 4.23, there is not a statistically significant change in conductivity when adding undoped-PANI to the fast-curing material. In addition to the nullified benefit from the undoped-PANI addition, the faster chemistry also exhibits deficient conductivity comparing the fast and slow chemistry without undoped-PANI. Again less time at higher temperature hinders the ability of the epoxy chemistry (without undoped-PANI) to solubilize lubricant. Table 4.10 summarizes the conductivity and gel time for these materials.
Table 4.10. Modifications of formulation #2 yielding different gel times and conductivities.

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Undoped-PANI</th>
<th>Conductivity (S/cm)</th>
<th>Gel Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast cure/ low gel temp</td>
<td>No</td>
<td>3,700</td>
<td>116°C</td>
</tr>
<tr>
<td>Fast cure/low gel temp</td>
<td>Yes</td>
<td>3,400</td>
<td>115°C</td>
</tr>
<tr>
<td>Slow cure/high gel temp</td>
<td>No</td>
<td>9,300</td>
<td>130°C</td>
</tr>
<tr>
<td>Slow cure/high gel temp</td>
<td>Yes</td>
<td>36,900</td>
<td>131°C</td>
</tr>
</tbody>
</table>

ICPs have been utilized in other metal filler applications. In a LDPE polymer matrix, polypyrrole-coated nickel flake exhibited improved electrical conductivity over uncoated nickel flake. The formation of molecular wires protruding from the flakes and improving contact with molecular wires on adjacent flakes was cited as the reason for improved conductivity.64 This is unlikely the primary reason for improved electrical conductivity of the undoped-PANI in formulation #2. The undoped-PANI could certainly displace the lubricant and adsorb to the surface of the silver. However, if the formation of molecular wires was the primary mechanism, conductivity improvements would have been observed when undoped-PANI was added to a system with a primary conductor that did not possess lubricant. On the contrary, results of conductors without lubricant showed no change in conductivity with undoped-PANI addition.

The conductivity benefit of lubricant removal has been demonstrated by others. On a much smaller scale of improvement, lubricant was removed with a mixture of sulfuric acid and alcohol. A 16% improvement in conductivity resulted and SEM observations conveyed an improvement in the contiguity of the silver where the sheared surface appeared coarser. An additional 13% benefit resulted when a coupling agent was added to improve the dispersion and adhesion of polymer to silver. Again, a coarser
morphology by SEM examination was observed. It is unlikely that the adhesion is improved with the integration of undoped-PANI simply because the benefits of undoped-PANI are only seen on conductors with lubricant. Conductors without lubricant would undergo a conductivity improvement similar to the work with a coupling agent added to the system.

The SEM images in Figure 4.24 depict a material that has 0%, 3% and 6% by weight undoped-PANI in an 84% by weight silver system similar to formulation #2. The silver appears to exhibit a change in appearance with additional levels of undoped-PANI, which is perhaps related to the improved contiguity of the particles as a result of lubricant removal with undoped-PANI.

Figure 4.24. SEMs of 84% by weight silver-filled material with (a) no undoped-PANI, (b), 3% by weight undoped-PANI, (c) 6% by weight undoped-PANI.
Though the empirical evidence suggests a unique interaction with removing lubricant from the silver, any decrease in conductivity with the addition of undoped-PANI appears counter-intuitive. A decrease in conductivity was observed with the addition of undoped-PANI to LF1. Since the undoped-PANI is moderately conductive, and with the silver loadings constant, it seems plausible that undoped-PANI addition could only improve the conductivity of the composite. Because the undoped-PANI aggregates exhibit marginal solubility in the epoxy resin, these domains most likely exist as a fraction of their initial particle size of about 12 µ. Solubility into the epoxy and dispersion may reduce the particle size. Since the domain is comparable in size to a silver flake or silver particle, it is reasonable to assume that the undoped-PANI aggregates interfere with the contiguity of the silver network minimizing the area of contact for the particles. Despite the fact that undoped-PANI removes insulating lubricant, if lubricant is not present or already removed from the silver, large PANI aggregates decrease conductivity by interfering with silver particle contacts. Although PANI may be moderately conductive and doped by the acid catalyst, the conductivity offered by the PANI is several orders of magnitude lower than that of silver. Therefore, if PANI interferes with the contiguity of the silver network and minimizes the contact area of silver particles, the net result on the conductivity will be unfavorable. Overall, if the undoped-PANI is not needed to remove lubricant, there is no benefit in adding undoped-PANI with the intention of increasing conductivity.

Finally, the additional data point of 2.5% by weight undoped-PANI to formulation #2 was added to the previous data where integers from 0% to 7% by weight of undoped-PANI were added to formulation #2. The curve is shown is Figure 4.25
where the 2.5% by weight undoped-PANI data point fits nicely with the rest of the data smoothing the contour of the curve.

Figure 4.25. Plot of conductivity as a function of doped-PANI levels for formulation #2 with an additional data point at 2.5% by weight undoped-PANI.
CHAPTER V
CONCLUSION

The survey of conductive additives to silver-filled epoxy materials began with unexpected results where the undoped form of PANI registered better conductivity increases than doped-PANI and carbon nanofibers. Repeatedly, the less conductive undoped form of PANI emerged with the best electrical conductivity boost in the silver-epoxy composite. An optimal loading of undoped-PANI was identified, and was optimized by increasing the crosslink density of the epoxy matrix.

The importance of maximizing crosslink density was realized seeing that with increasing levels of undoped-PANI the crosslink density, $T_g$, and other physical properties quickly deteriorated limiting the amount of undoped-PANI that could be effectively added. The DMA results showed that the relative crosslink density and $T_g$ began to decay at 3% by weight undoped-PANI levels where maximum conductivity was observed. The decay in electrical conductivity after 3% by weight levels follows the decay in crosslink density, since the conductivity of the composite is proportional to the crosslink density.

Electrical conductivity increases of the $Epoxy+PANI$ constituent were observed with increasing levels of undoped-PANI. This follows from the fact that the acid curing epoxy can protonate and essentially dope the PANI aggregates increasing the electrical conductivity of the otherwise electrically-insulating epoxy matrix. Though increasing the
conductivity of the epoxy matrix was one of the original mechanisms thought to increase the conductivity of the composite, the data suggest that the alternative mechanism of efficient lubricant removal is responsible for the large conductivity gains associated with the addition of undoped-PANI.

Since lubricant on the primary conductor of the composite was a prerequisite for the conductivity boost associated with undoped-PANI addition, it was clear that the efficient lubricant removal was the key to the conductivity boost. Silver flakes have historically been the most effective conductor in polymer composites because of intrinsic high conductivities, conductive oxide layers, and the flake-like, high aspect ratio geometry of the silver. However, a lubricant is necessary for the silver flake to undergo proper dispersion and to prevent cold welding of the silver flakes together. Therefore, efficient lubricant removal during the curing process is vital to the contiguity of the silver flakes. Increased contiguity increases the contact areas between silver particles, reducing the electrical contact resistance between the particles.

The mechanism for the lubricant removal with undoped-PANI is not completely understood. Extensive study will be necessary to determine the degree of solubility of the undoped-PANI in the epoxy, the domain size of undoped-PANI in the epoxy matrix after cure, and the comprehension of the true mechanism of lubricant removal. Reducing the particle size of the undoped-PANI would be an excellent way to increase the interaction of the PANI with the epoxy and create a secondary percolation network throughout the matrix. Smaller particles will also minimize the interference with the larger silver flakes.
The gains in conductivity still do not approach a conductivity equivalent to that of pure silver metal. PANI provides a unique and exciting means to attain an order of magnitude increase in conductivity. Though values of 40,000 S/cm were observed, replacement of conductive metals will not be realized until values of 500,000 S/cm are reached. However, PANI is a new addition to a polymer chemist’s toolbox that can provide the necessary conductivity boost for many niche applications that need marginal conductivity improvements.
REFERENCES


