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Epoxy/PCL/CNF Nanocomposite

Towards Electrically Triggered Self-Healing and Reversible Adhesion

A Capstone Project Submitted in Partial Fulfillment of the
Requirements of the Renée Crown University Honors Program at
Syracuse University

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May/2011

Honors Capstone Project in Chemical Engineering

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Abstract:

In this report, we summarize the results of research related to development of an electrically-triggered reversible-adhesive material. The material is made of an epoxy comprised of diglcidyl ether of bisphenol-A (DGEBA) and 4,4'-diaminodiphenylsulfone (DDS). By combining the epoxy with PCL a “bricks and mortar” morphology is created with reversible adhesion properties. A phenomenon known as differential expansive bleeding (DEB) is the driving force of the self-healing and reversible-adhesion. The epoxy/PCL was embedded within electrically conductive carbon nanofibers (CNF) created from electrospun poly(acrylonitrile) (PAN). The material's high conductivity allowed convenient heating with a power source. Initial tests revealed a lack of adhesion development, counter to our expectation. After the tests failed to create adhesion, the morphology of the sample was scrutinized. Experiments showed that the morphology of the epoxy/PCL within the fibers is distinct from the morphology in the bulk phase. Correlated with this microstructural difference was a lack of DEB, despite epoxy/PCL phase separation. It is argued that this lack of DEB is related to the much finer scale of phase separation, kinetically hampering PCL flow.

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Acknowledgements:

I would like to start off by thanking my mentor, Dr. Patrick Mather. Without his guidance and expertise, none of this would have been possible. I would also like to thank the entire Syracuse Biomaterials Institute for their help in the laboratory. I will always appreciate their patience and the influence they had on me. Lastly, I would like to thank Dr. George Martin for his direction as I wrote my report.

Advice to Future Honors Students:

Future engineering honors students,

The honors program has many benefits that you will experience shortly after joining. The early registration and the free coffee and popcorn are great, but the best part about the program is the capstone project. The capstone project is your chance to experiment on your own terms. You can literally do anything your heart desires as long as it falls within your major. Had I not joined the honors program I never would have gotten as involved with my research as I am today. Research teaches you so much more than you will ever learn in the classroom.

The honors program is not an easy undertaking for an engineer. Many of the extra classes you are required to take do not fit into your major's curriculum. However, these classes are very fun and introduce you to concepts you would never learn if you stuck with the traditional engineering courses! The honors department is also lenient with engineers; they understand that we have very demanding majors. As long as you stay focused and keep in touch with the honors department as you advance through college, you should have no problem completing all of the honors requirements.

Research Motivation:

Over the past few years the use of polymers has become a mainstay in societies. New technologies allow for polymers to have countless uses today, many of which are now considered "smart polymers." Memory foam, drug delivery systems and airplane wings are just a few of the many applications that smart polymers play in everyday lives. These smart polymers have the ability to be used in areas where traditional metals and polymers cannot. For example, smart polymers have the potential to change their shape,[1, 2] adhere to objects,[3, 4] and even recover from damage.[5] With these properties, it is clear that smart polymers are paving the way towards the future.

With the introduction of self healing polymers,[5] it became possible to heal fractures and cracks within the samples of polymers, drastically increasing the functionality. However, the current way to trigger the self healing of polymers is not very efficient. The only procedure in use is to thermally heat the polymer, by means of an oven or heat gun. With advances in micro–technology, it is now possible to create carbon nanofibers, which are very conductive and allow for the creation and transfer of heat through Joule heating.[1, 5] This method of heating could be very useful in transforming the thermally triggered self-healing polymers into electrically triggered ones.

The same theory applies to polymers that have reversible-adhesive properties. Reversible-adhesive polymers have the ability to bond to substrates when heated, and then de-bond when reheated. Reversible adhesive polymers also require thermal heating to trigger. Using the conductivity of the carbon nanofibers mentioned above, it is conceivable that electrically triggered reversible adhesion in these polymers is possible.

Reversible Adhesion Overview:

Polymerization Induced Phase Separation (PIPS) is the phenomena that allows for the creation of a reversible adhesive polymer.[6] It was found that using diglycidyl ether of bisphenol A (DGEBA) in combination with poly(ε-caprolactone) (PCL) and 4,4'-diaminodiphenylsulfone (DDS) forms a "bricks and mortar" morphology.[5] This morphology consists of spheres of epoxy (DGEBA and DDS) held together by a matrix of PCL. The epoxy imparts its flexural stiffness to the sample while the PCL acts as the reversible adhesive agent. When the samples are combined, they form a yellow viscous mixture that is readily cured at 280 °C in the oven. This mixture is referred to as epoxy/PCL.[6] Once the sample is fully cured, it undergoes differential expansive bleeding when heated, the driving force behind the reversible adhesion and the self-healing. The bleeding effect is the PCL in the "mortar" melting and undergoing thermal expansion since the coefficient for thermal expansion is greater for the PCL than it is for the epoxy. This causes the PCL to "bleed" onto the surface of the sample. If the sample is fractured, the PCL will "bleed" into the fracture and fill it in, thus eliminating the crack. If the sample is put into contact with a substrate while bleeding, it will bond to the substrate upon cooling, thus demonstrating the adhesive property of the sample.

To achieve the electrically triggered reversible adhesion, the thermally triggered reversible adhesive material needed to be altered so that it would be optimally conductive. Optimal conductivity allows current flow and associated Joule heating. To increase the conductivity of the material, carbon nanofibers were chosen.[1] The conductive nanofibers could be embedded with the epoxy/PCL mixture to obtain an electrically triggered sample. Therefore, when the sample is connected to a power source, the epoxy/PCL in between the nanofibers would heat and cause the differential expansive bleeding.

Experimental:

Materials: Diglycidyl ether of bisphenol-A (DGEBA) is the epoxy monomer for the system. The DGEBA has an equivalent weight of 172~176. The curing agent is 4,4'-diaminodiphenylsulfone. The amine protons of the DGEBA react with the epoxide groups of the DDS. Since there are four amine protons on DGEBA and two epoxide groups on DDS a 2:1 molar ratio should be maintained. The mortar portion of the bricks and mortar morphology is made up of poly(ε-caprolactone) (PCL) with a molecular weight of 65,000 g/mol. Poly(acrylonitrile) (PAN) with a molecular weight of 150,000 g/mol was mixed with dimethyformamide (DMF) as the first step in creating the carbon nanofibers. All of the chemicals used were purchased from Sigma-Aldrich.

Epoxy Synthesis: DGEBA and PCL were measured in a glass beaker at a 80/20 weight percent and then added to a one-necked round bottom flask. The flask was submerged up to the level of the liquid in an oil bath at 120 °C. A mechanical stirrer (Arrow 6000) was used to stir the sample while it was heated in the oil bath. The stirrer used a small crescent-shaped Teflon tip attached to the rod to mix DGEBA and PCL. After one hour of stirring, the solution was transparent and homogeneous. At this time the oil bath temperature was increased to 140 °C and DDS was added. If DGEBA and PCL are not at 140 °C, then the only some DDS will melt and form a homogeneous mixture. This would leave particles of DDS suspended in the epoxy/PCL, which is undesirable. The addition of DDS changed the color of the solution to a light yellow. The stirring continued for another 10 minutes, until DDS had fully dissolved within DGEBA and PCL and then the temperature of the oil bath was decreased back to 120 °C. Finally, the mechanical stirrer was removed and a rubber stopper was placed in the neck of the flask. After the mixing was completed there were many air bubbled suspended in the solution. A needle attached to a vacuum was pushed through the stopper and vacuum was drawn. After approximately one hour, all of the air bubbles were removed from the solution. It was then poured out of the flask and into a jar and stored in the refrigerator for further use. All tests conducted were done with the epoxy/PCL(20), where the 20 denotes the 20 weight percent of PCL. For simplicity, the epoxy/PCL(20) will be referred to as epoxy/PCL. The apparatus used is shown in Figure A.1 in Appendix A1.

Carbon Nanofiber Synthesis: The carbon nanofiber mats were created by electrospinning and heating poly(acrylonitrile) (PAN). The electrospinning solution was created by adding 1 g of PAN to 10 mL of dimethyformamide (DMF) in a small glass vial. A magnetic stirrer was added to the vial, which was then sealed and placed on a heated stirrer. The hot plate was set to 95 °C and the stirrer was set to 600 rpm. After 3.5 hours the PAN was fully dissolved in the DMF. Nine milliliters of the sample was then placed in a glass syringe to be electrospun. The distance from the tip of the syringe needle to the 5cm diameter drum was 9.5 cm. The drum was rotated at 400 rpm. The applied voltage difference was 12.5 kV. The volumetric flow rate of the solution was 1 mL/h. The sample was spun for 9 hours until all of the solution was electrospun. The experimental set up for the electrospinning can be seen in Figure A.2 of appendix A1. Electrospinning the PAN created PAN fiber mat. This PAN mat was then stabilized and pyrolized to synthesize the carbon nanofibers. The stabilization heating step consisted of ramping the temperature to 280 °C at 2 °C/min and then holding the temperature at 280 °C for 3 hours in the convection oven. The second heating step, pyrolization, heated the stabilized fibers to 1000 °C at 2 °C/min and then held the temperature of 1000 °C for 1 hour.

Differential Scanning Calorimetry (DSC): DSC was conducted using a TA Q200 DSC on the cured sample of epoxy/PCL to ensure that the epoxy/PCL was blended correctly. When properly blended, only one glass transition temperature, T_g, results. To begin the DSC, 1.5 mg of cured epoxy/PCL was placed into an aluminum pan with a hermetic aluminum lid. The sample was heated to 200 °C and then cooled to -20 °C at 10 °C /min. This was done to erase the thermal history of the sample. Then, it was heated to 200 °C at 10 °C /min. After the heating the sample was cooled again to -20 °C at the same rate as before. This second heating and second cooling are the data that will be used to determine the thermal properties of the sample.

Optical Microscopy(OM): OM was done on the epoxy/PCL. First, a small sample of epoxy/PCL was pressed between a glass slide and a cover slide. Then the Olympus BX51 optical microscope was used to observe the curing of the epoxy/PCL with the INSTEC hot stage furnace. In place of the camera, a UV/vis spectrometer (Ocean Optics S2000 miniature fiber optic spectrometer) was placed on the top of the microscope. The Ocean Optics program was used to record the transmitted light intensity versus wavelength. The wavelength of interest is the visible region from 500 nm to 700 nm. Readings of the dark spectrum and the reference spectrum were taken to determine the transmittance. The INSTEC was set to 180 °C and once the temperature was stabilized, the epoxy/PCL sample was quickly inserted. The sample was cured under the light microscope while the spectrometer recorded the data. The set up for the experiment can be seen in Figure A.3 in Appendix A1. The data used to create the Figure 3 can be found in Table A.1 in Appendix A2.

Small Angle Laser Light Scattering (SALLS): SALLS was done on a sample of the epoxy/PCL. First, a small sample of the epoxy/PCL was placed in between two glass slides. Once the sample had cooled, it was placed in the INSTEC to be heated. The INSTEC was placed above the mirror and below a sheet of white paper. The room lights were turned off and the Uniphase 1135P vertically polarized He-Ne laser (λ=632.8 nm) was turned on. The light scattering was recorded using Camstudio Open Source Version 2.5. After 20 minutes, the light began to scatter as the epoxy spheres began to form. The scattering was recorded for 20 minutes until the pattern was constant. Once the data was finished recording, images were taken from the video every 10 seconds after the scattering occurred. These images were put into the computer software, ImageJ, so that the intensity could be quantified. Once this was finished, it was possible to graph the intensity versus the pixels. Using the calculations shown below these data were converted into an Intensity vs. q graph, where q is the magnitude of the scattering vector. This shows the evolving morphology during the cure over time. The set up for the experiment can be seen in Figure A.4 in Appendix A1. The data used to create the graphs can be found in Table A2 in Appendix A2.

Combination of the epoxy/PCL and CNF: Now that the carbon nanofibers were created an embedding method needed to be determined. The first method that was employed was to submerge 5 carbon nanofiber mats, 1 inch by 1 inch, into the epoxy/PCL mixture at 140 °C. Due to the high viscosity of the epoxy/PCL, the mixture was preheated at 140 °C to have a better chance of infiltrating the carbon nanofibers. This temperature is safely below the curing temperature of the 180 °C. After the nanofibers were submerged for 30 minutes they were quickly stacked and placed on the hot press. The sample was cured at 180 °C under a pressure of 50 psi for three hours. The set up for the experiment can be seen in Figure A.4 in Appendix A1.

A second method of infiltration was also attempted. In this procedure, the epoxy/PCL mixture was placed on top of the carbon nanofibers samples. The epoxy/PCL mixture was preheated to 140 °C so that it would be easier to pour. Once the top of the carbon nanofibers had been coated with the epoxy/PCL, the sample was placed in the vacuum oven at 140 °C for 30 minutes. The vacuum was used to help pull the epoxy/PCL into the nanofibers. After 30 minutes in the vacuum oven the sample was removed from the oven and pressed in between two Teflon coated glass slides. Three binder clips were used to hold the slides together. The sample was cured in the convection oven at 180 °C for three hours.

In a similar manner, the CNFs were preheated to 180 °C for 30 minutes while the epoxy/PCL mixture was heating in the convection oven so that it would become less viscous. Once the epoxy/PCL preheated it was poured on top of the hot CNF. The sample was then placed in between two Teflon-covered glass slides and held together with three binder clips. Then, the sample was placed in the vacuum oven at 180 °C and vacuum was immediately pulled. The sample remained in the vacuum oven at 180 °C and under vacuum for three hours to allow the epoxy/PCL to completely cure.

Scanning Electron Microscopy (SEM): SEM was done on the various samples, prepared as described; using a JEOL JSM-5600 scanning electron microscope to check the morphology of the sample and to make sure the epoxy/PCL was embedded within the nanofibers. The high magnification of the SEM allowed for a very clear view of the morphology. The voids within the nanofibers could be readily seen. Also, the PCL could be distinguished from the epoxy.

Differential Expansive Bleeding (DEB): To test bleeding ability of the samples, the fully cured samples were placed in the INSTEC under the Zeiss Discovery V8 stereo microscope. To better observe the bleeding, the sample was sputter coated with a 50/50 gold/platinum compound. The sample was placed on top of a glass slide and quickly inserted into the INSTEC once the temperature was stable. The sample was then heated in 10 °C increments and the sample was observed every 15 minutes. The sample was heated from room temperature to 200 °C. At the end of the experiment, the sample was quickly removed from the INSTEC to cool.

Electrical Heating Experiment: To test the electrical heating capabilities of the epoxy/CNF composite, it was connected to a DC power source. The samples were 2 cm long and 0.75 cm wide. Each end of the sample was connected to the power source with alligator clips. A thermocouple was taped to the surface of the sample to monitor the temperature of the sample as the voltage was increased on the power source. The voltage range started at 6.5 V and was increased by 0.5V up to 13.5V.

Electrically Triggered Reversible Adhesion: To electrically trigger the adhesive properties, the sample was connected to the DC power source. Once connected, the sample was placed into a custom made bonding device consisting of a spring to allow for a known force. The sample was placed in between an aluminum substrate and a stainless steel substrate, and a force of 2N was applied using the spring. The sample was heated to 130 °C. After 15 minutes at 130 °C, the power supply was turned off and the sample remained in the bonding device for 24 hrs. After 24 hours the spring was removed from the bonding device and the sample was removed from the device.

Results and Discussion:

The morphology of the epoxy/PCL is very important to understand because without the correct morphology the mixture will not undergo PIPS within the carbon nanofibers. The tests done to clarify the morphology were the following: Optical Microscopy (OM), Small Angle Laser Light Scattering (SALLS), and curing under the stereo microscope.

Figure 1 below shows the SALLS data 30 seconds after the start of the scattering and 1 minute after the start of the scattering. The figure shows that the epoxy/PCL goes through two main stages during curing. The first stage is a PIPS event of nucleation and the second is an event of spinoidal decomposition.[6] Figure 2 below shows the intensity versus the magnitude of the scattering vector. This data constantly changes as the morphology changes during the curing process. The data for Figure 2 was calculated using Bragg's relationship, as shown below:[7]

$$2d * sin(\theta) = n * \lambda \qquad (1)$$

where θ is half the scattering angle, n is the order of reflection, d is the standard spacing, and λ is the wavelength. Once the scattering angle was known, it was possible to determined the sample to detector distance, for a diffraction standard whos spacing, d, was known, through the following relation:[7]

$$D = \frac{r}{tan(2\theta)} \qquad (2)$$

where D is the sample-to-deterctor distance and r is the radial postion to a given reflection. Finally, the scattering vector, q, can be calculated from the equation below:[7]

(3)

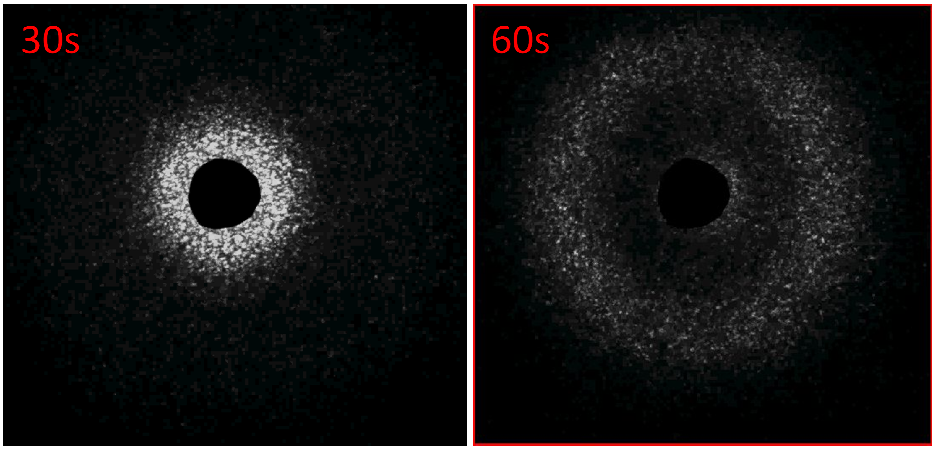

Figure 1: The light scattering observed at 30 seconds and 60 seconds after the scattering began 20 minutes into the heating.

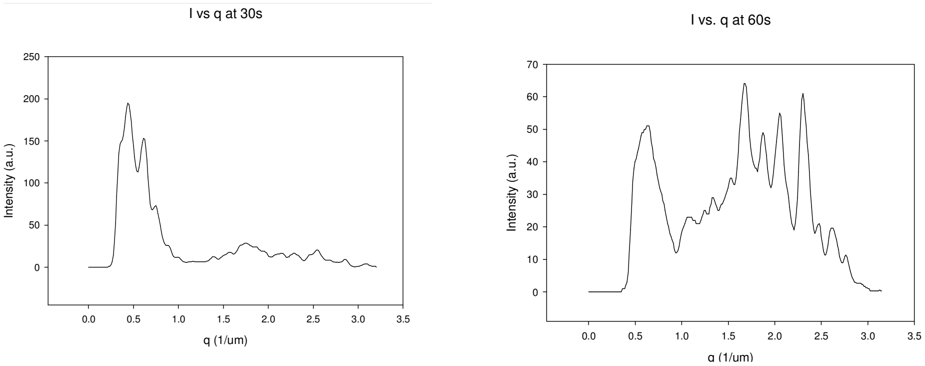

Figure 2: Intensity versus scattering vector for the two images in Figure 1.

A relatively simple and accurate way to monitor the morphology during the curing proesses is through optical microscopy (OM). By observing the light passing through a thin sample of the epoxy/PCL it is easy to determine when the sample undergoes PIPS. A turbididty experiment was carried out to help determine the onset time of the phase separation,[6] also referred to as the cloud point. When the sample begins to cure and the cloud point is reached the light passing through the sample begins to scatter. This is consistent with the SALLS data in that no light is scattered by the sample until the curing begins. This light scattering was recorded using the UV/vis spectrometer and the intensity versus wavelength was recorded. A reading of the dark spectrum and the initial spectrum were also recorded to determine the transmittance. The dark spectrum is the intensity recorded by the spectrometer in the dark and the initial spectrum is the intensity of recorded by the spectrometer before the sample begins to cure. All of the spectra were recorded in the visble light region of 500-700 nm.[6]The following equation shows how the transmittance was calculated.

$$Transmittance\ (\%) = \frac{I(t)-I(d)}{I(0)-I(d)} \tag{4}$$

where I(t) is the integral of the transmittance at a certain time, I(d) is the integral of the dark spectrum, and I(0) is the integral of the initial light spectrum.

Figure 3 below shows the Transmittance vs Time recorded during the cure at 180 °C. It is consistent with the SALLS experiment in that both sets show the nucleation and the spinoidal decomposition. Both of these events are the result of the Ostwald Ripening process,[6] which occurs when the smaller droplets, in this case epoxy spheres, redissolve into the solution to form larger spheres. This phenomenon was not observed when the sample was cured at 160 °C or 200 °C.

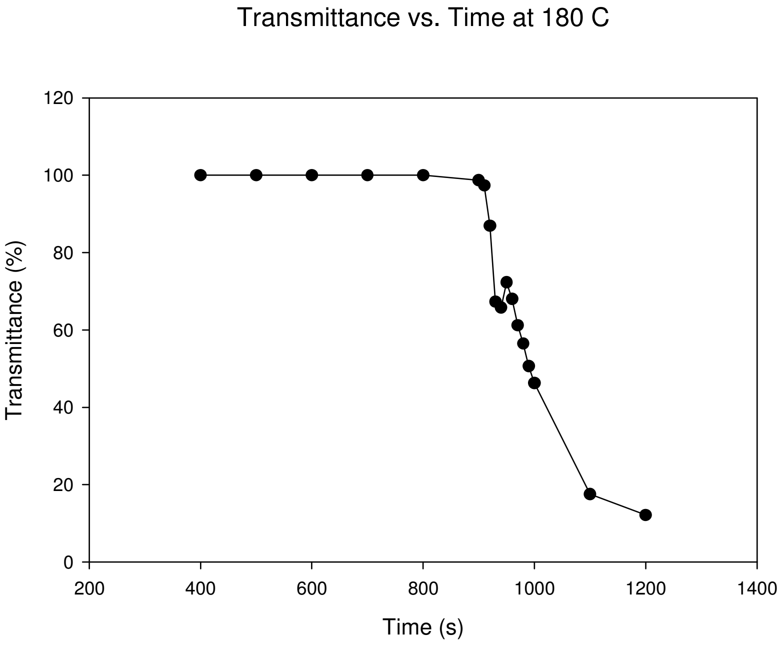

Figure 3: The percent transmittance versus time for the epoxy/PCL curing at 180 °C

Lastly, to determine the morphology of the epoxy/PCL while it cures a sample was cured under the stereo microscope. During the three hour cure, many micrographs of the event were taken. After approximately 5 minutes at 180 °C the epoxy/PCL starts to turn dark. This is when the cross linking between the DGEBA/DDS begins, triggering phase separation. Figure 4 below shows the progression of the cure. At 7 minutes the DGEBA/DDS has started to form small spheres of epoxy. After 13 minutes the DGEBA/DDS spheres were fully formed within the PCL matrix. There was no visible change in the morphology between 20 minutes and 180 minutes.

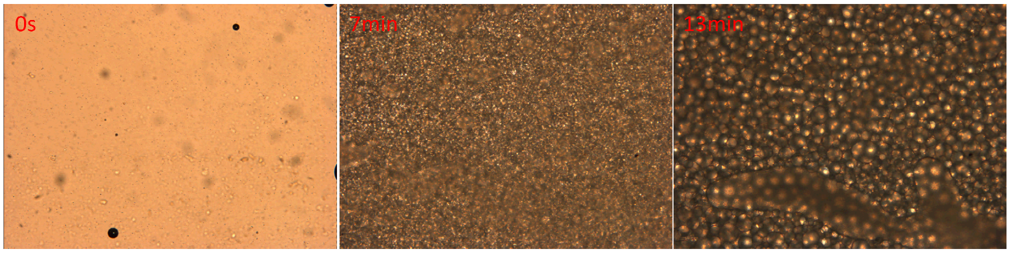

Figure 4: Curing under the light microscope at 0, 7, and 13 minutes.

With the known morphology of the bulk epoxy/PCL, it was time to imbed it within the CNF. After the PAN was stabilized at 280 °C it underwent a dimensional shrinkage and weight loss of 20% and 18%, respectively[1]. During this change a visible color change could be seen. The PAN fibers had darkened and become brown. During the stabilization phase the carbon-nitrogen triple bond is broken and the nitrogen bonds to an adjacent carbon. After the stabilization was completed, the sample underwent carbonization under argon gas at 1000 °C. The dimensions of the sample shrunk by another 11% and it lost 57% more of its mass[1]. Once again a physical color change was observed. This time, the sample changed from brown to black.[5] The chemical structures of the three phases can be seen below in Figure 5 along with SEM images of the fibers from each stage.

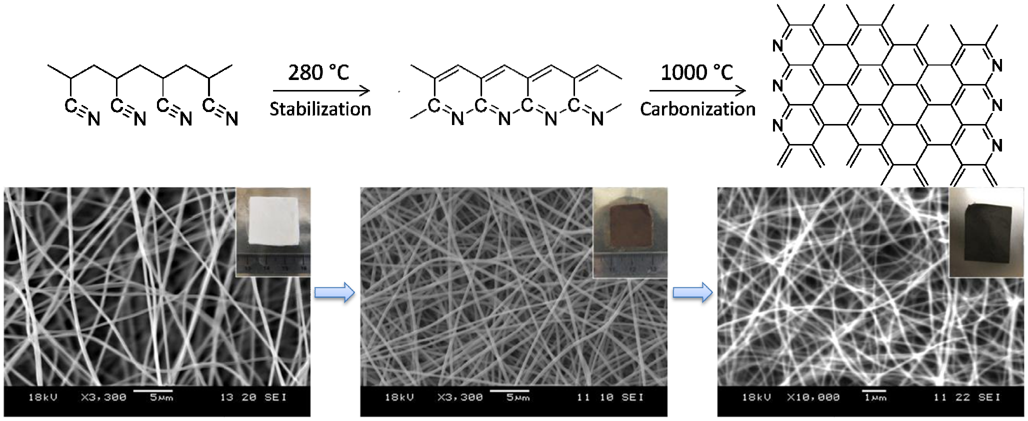

Figure 5: Shows the chemical structure, color, and SEM results of the three stages in making the carbon nanofibers. [1]

Now that the carbon nanofibers had been produced, infiltration into the epoxy/PCL solution could begin. The epoxy/PCL DSC results can be seen below in Figure 6. The image clearly shows the peak at approximately 55 °C, the melting point of the PCL. This shows that the sample undergoes Polymer Induced Phase Separation (PIPS). Had there been no phase separation, there would not be a peak indicating the melting point of the PCL.

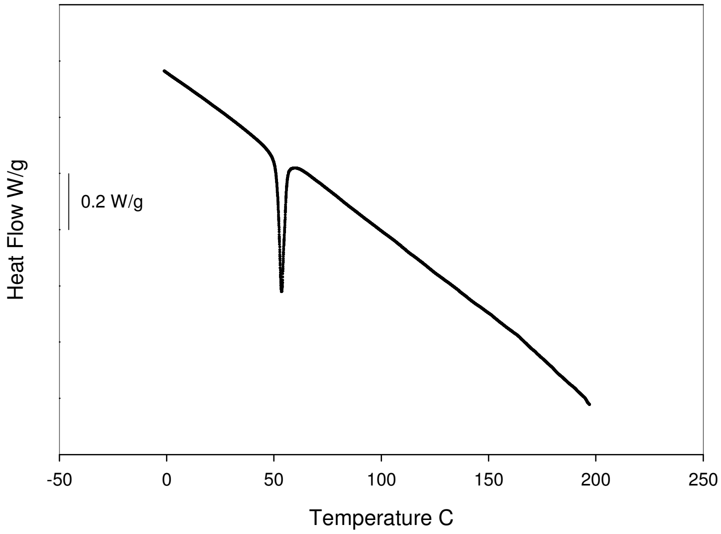

Figure 6: The DCS of the epoxy/PCL sample. This is the second heating of the sample.

The carbon nanofibers were submerged into the preheated epoxy/PCL and placed onto the heated press according to the procedure described in the experimental section. At the end of the three hour curing process the press was opened; it was discovered that the individual CNF mats had moved around. Furthermore, the epoxy/PCL was spread over the sample and beyond its borders. This result gave the appearance that it was easier for the epoxy/PCL to be pushed along the nanofibers than it was to infiltrate them. This led to one large flat piece of epoxy/PCL/CNF. The sample (Sample #1) was slightly thicker in the center because of slight overlap from the nanofibers layers. Ideally, the sample would have had a uniform thickness that had the same area as one piece. SEM was taken on this sample and can be seen below in Figure 7. At low magnifications, the sample in Figure 7 appears to be woven. This is an artifact, however, because the reason for the woven look is the nylon release layer that was used to ensure that the epoxy/PCL did not stick to the press. The woven pattern was pressed into the epoxy/PCL. At higher magnifications the SEM confirmed that the epoxy/PCL only partially infiltrated the nanofibers. Figure 7 clearly shows that there are voids in between individual fibers. Preferably, these voids should have been filled in with the epoxy/PCL. This sample was not tested for bleeding or conductivity because of the incorrect morphology.

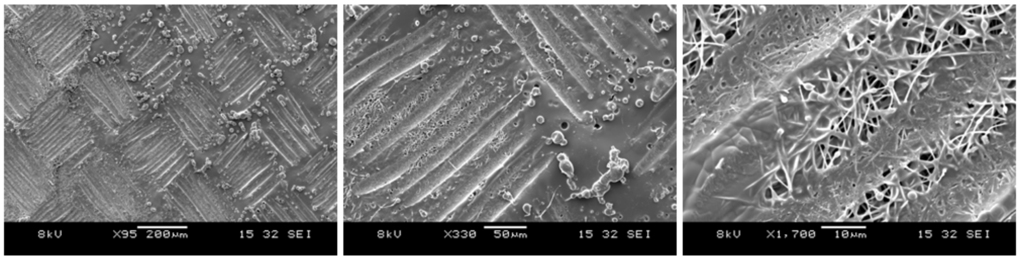

Figure 7: Shows the SEM after the first method of the infiltration was attempted.

The second method of infiltration produced much better results than the first. Preheating the epoxy/PCL mixture and pouring it on top of the preheated carbon nanofibers in the vacuum oven produced a better result. After 30 minutes in the vacuum oven it appeared that the epoxy/PCL had started to infiltrate and spread onto the two nanofibers samples. This was obvious because of the appearance of bubbles on the surface. The bubbles are the air being pulled out of the CNF from the vacuum. The void left by the air was then filled with the epoxy/PCL. The composite was now much more brittle than before. This is due to the cured epoxy/PCL on and within the fibers. Figure 8 shows the SEM images of the sample. The images show that the epoxy/PCL is within the fibers and covering them with excess epoxy. Ideally, there should be no excess epoxy on the top of the fibers. The epoxy/PCL appears to have the correct morphology within the fibers. There are spheres of epoxy held together in a matrix of PCL. Individual nanofibers can also be seen.

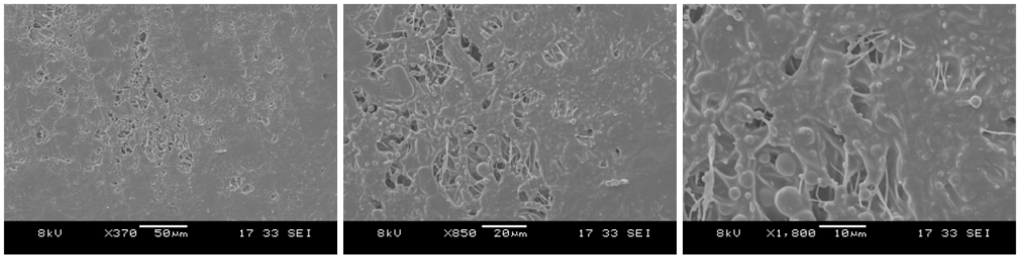

Figure 8: Shows the SEM after the second method of the infiltration was attempted.

Knowing that the sample had the correct morphology, the sample was tested thermally. The sample was heated from 80 °C to 180 °C under the stereo microscope to test for bleeding. The sample did not bleed, however, after the sample was allowed to cool to room temperature, the sample stuck to the glass slide. This showed that the sample did have adhesive properties. To further categorize the morphology of the sample a small piece was broken off of the sample and submerged in chloroform. The chloroform dissolved the PCL from the epoxy/PCL/CNF and another SEM was taken. The SEM showed that the epoxy/PCL was not coated evenly on the sample. Figure 9 shows that the right side of the sample contained the PCL and epoxy, while the left side contained only the PCL. It also showed the spheres of epoxy. The cause of the unevenness of the coating was due to the infiltration method. If the sample was poured more evenly, then the sample would have been more evenly coated.

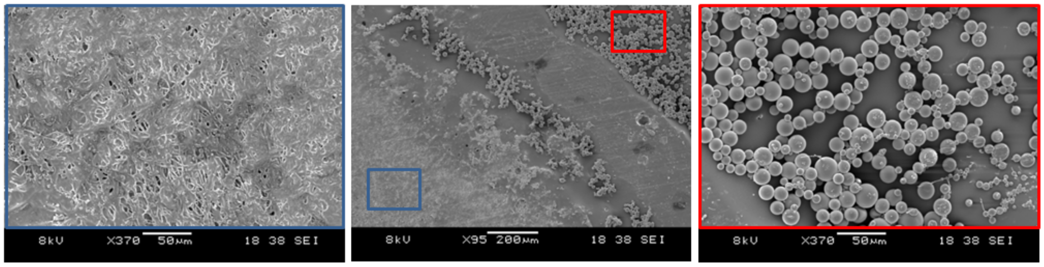

Figure 9: Shows the SEM on the second method after the solvent extraction. The figures on the left and right of the center picture are the magnified sections of the respective sections.

The solvent-extracted sample was compared to a solvent-extracted sample of pure epoxy/PCL. When comparing the solvent-extracted sample, Figure 9, to the solvent extracted pure sample, Figure 10, similarities can be seen. The spheres of epoxy are approximately the same size. This implies that the epoxy/PCL mixture within the nanofibers should have the same properties as the pure epoxy/PCL.

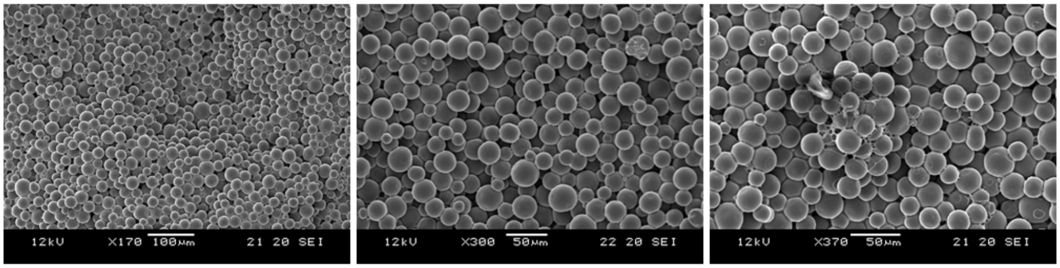

Figure 10: Shows the pure epoxy/PCL mixture after curing and solvent extraction.

To create a more uniformly coated sample a third method of infiltration was used. The preheating of the carbon nanofibers allowed the epoxy/PCL to penetrate deeper within the CNFs. The morphology of the sample was observed using SEM. A razor was used to create a crack on a small section of the sample and then the sample was fractured along the crack. The sample was examined from its side so that the cross section could be observed. Figure 11 below shows the results of the SEM. The SEM showed that the epoxy/PCL was imbedded within the fibers. It also shows a of the CNF mat layers in the composite. The epoxy/PCL is within the layers of the composite.

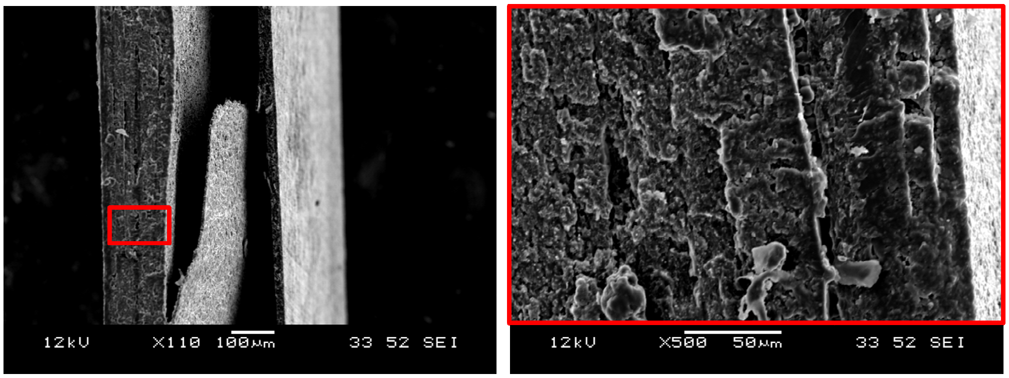

Figure 11: The epoxy/PCL between the layers of the fractured sample.

The epoxy/PCL within the CNF should have the same properties as the neat epoxy/PCL. To confirm this differential scanning calorimetry (DSC) was done for the epoxy/PCL/CNF and for the pure epoxy/PCL. Figure 12 shows that the melting, crystallization, and glass transition temperatures of the epoxy/PCL/CNF sample was approximately the same as the pure epoxy/PCL. Most importantly, the melting point at approximately 50 °C shows that the sample does undergo PIPS. This implies that the sample should also undergo differential expansive bleeding within the CNF.

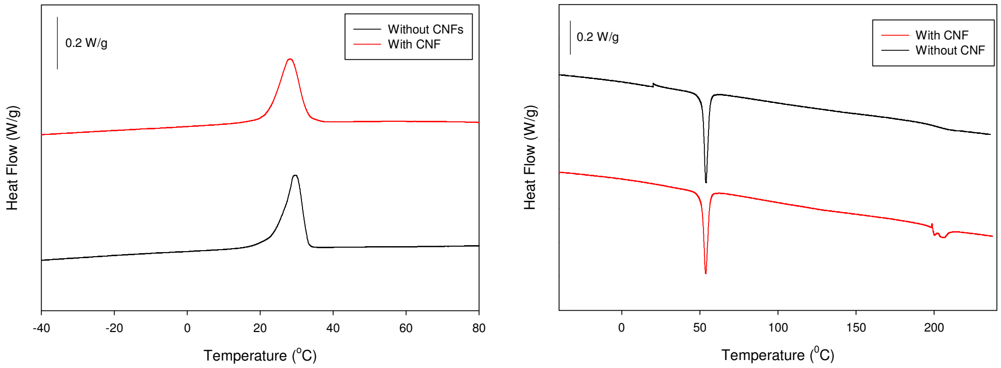

Figure 12: The results from the DCS show the crystallization temperature, melting point, and glass transition temperature of the second sample.

A multi-meter was used to calculate the electrical resistance of the sample. With the known resistance, the resistivity can be calculated by the following equation:

$$\rho = \frac{RA}{L} \tag{5}$$

where ρ is the resistivity, R is the resistance, A is the cross sectional area, and L is the length of the sample. Figure 13 shows the multi meter leads on the sample to test the resistance.

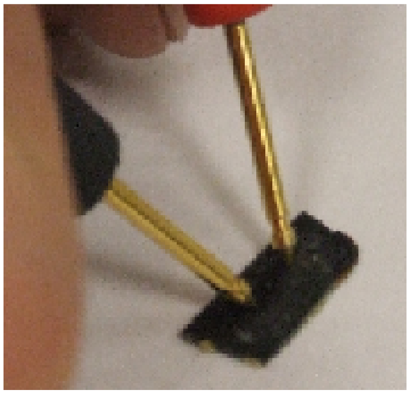

Figure 13: The resistance was calculated for the sample using a multi-meter

The resistance measurement was a very crude and the resistance varied depending on the position. An approximate value of 300 Ω was used because it was the average of the recorded resistances. From equation 5, the resistivity was calculated to be 0.1231 Ω-m. This low resistivity means a high conductivity. A test was done to determine how hot the sample could be at different currents. To do this a power source was attached to the sample as shown in Figure 14.

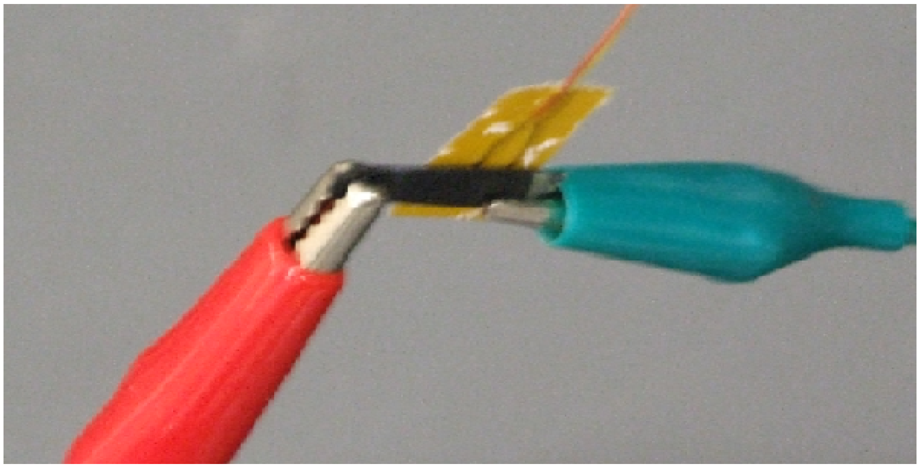

Figure 14: The alligator clips are attached to the sample and the power source. A thermocouple is taped to the top of the sample to observe the temperature as it is heated.

The voltage was held at different levels which changed the magnitude of current that flowed through the sample, according to Ohm's Law. The temperature was monitored using thermocouple tape connected to a computer. Figure 15 shows the results of the tests. The test showed that the sample was able to get very hot relatively easily. A constant temperature of 100 °C was achieved by setting the power source to 8.5 V. This temperature should cause the PCL within the sample to melt. When the voltage was increased to 9.5 V the temperature never leveled off. After a few minutes of heating, the sample ignited.

This is believed to have occurred because the melted PCL decreased the resistance of the sample. The decrease in resistance caused the current to increase in an unbound manner and led to ignition.

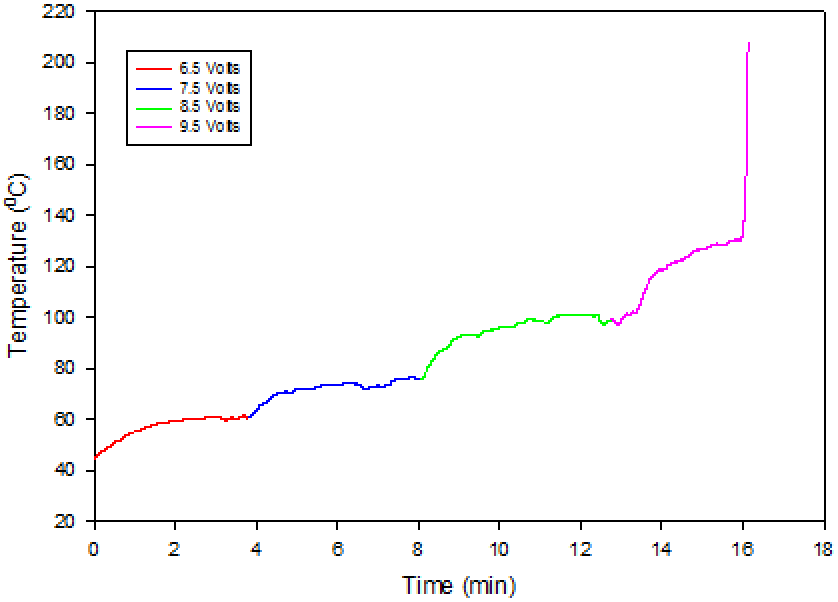

Figure 15: The temperature that the sample reached at each voltage is shown.

A final experiment was performed to test the electrically triggered adhesive abilities of the sample. Figure 16 shows the assembly used to adhere two blocks of metal to the sample.[4]

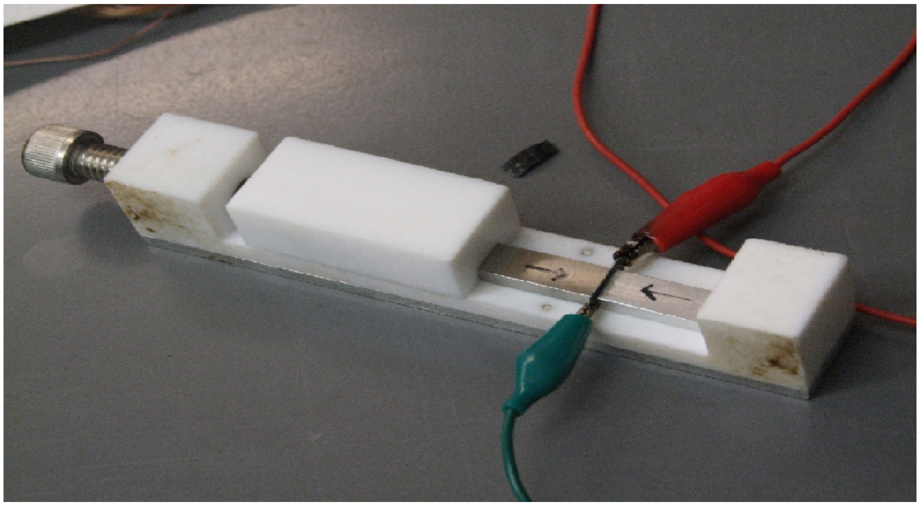

Figure 16: Shows the assembly used to adhere aluminum and stainless steel to the sample.

When the sample was connected to the power source which was set to 8.5 V, it was expected that the sample would heat to 100 °C. However, this was not the case. The two pieces of metal acted like fins for the system and dissipated most of the heat that the power source was supplying. To counter this dissipation, the voltage was increased to 13.5 V. At this voltage the sample began to heat and once again once the PCL had melted the current increased and the sample began to smoke. The power source was then turned off and the sample was allowed to cool to room temperature. After cooling the sample was removed from the assembly and it was lifted. The sample did not stick to the aluminum piece of metal at all. However, it did stick to the stainless steel. It was not a very strong bond, and after lifting the sample by the epoxy/PCL/CNF the stainless steel broke off. The reason that the adhesion was not very strong was because the section of the sample that did adhere to the stainless steel was the section that had excess epoxy. Repeating the experiment led to much different results and the sample with less epoxy did not adhere to either substrates.

To determine the reason for the different results, more DEB tests were done on the sample, while making observations with the stereo microscope. Figure 17 below shows another sample of the epoxy/PCL/CNF. The left image shows that most of the fibers are covered with the epoxy/PCL, but that some areas have excess epoxy/PCL.[3] The image on the right shows epoxy/PCL on the fibers and bulk epoxy/PCL without any fibers. The entire coating should have uniform spheres of PCL, like the bulk on the right image. The entire area should bleed when the sample was heated, but it did not.

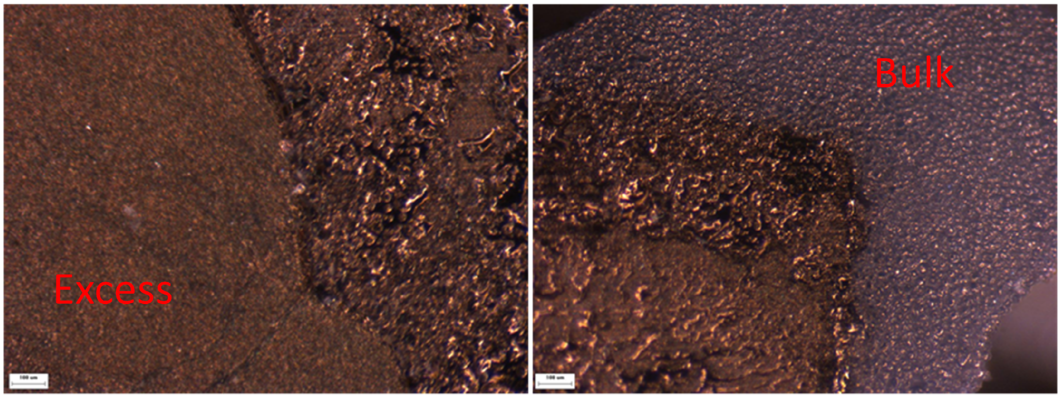

Figure 17: Left: epoxy/PCL in fibers and excess. Right: epoxy/PCL on fibers and bulk epoxy/PCL without fibers

It was postulated that the reason that no DEB was observed is that the carbon nanofibers are selectively wetted by the PCL. This is also due to the fact that there is a much finer scale of phase separation within the fibers. In other words, the morphology of the sample within the fibers is not the same as the bulk morphology of the epoxy/PCL. The PCL in the mixture form spheres and the epoxy is the matrix. This morphology did not undergo DEB when heated.[3] Figure 18 further shows that the morphology of the mixture is not uniform. Close to the fibers many, individual spheres can be seen. The spheres should be dispersed throughout the entire sample, creating an even coating of epoxy/PCL.

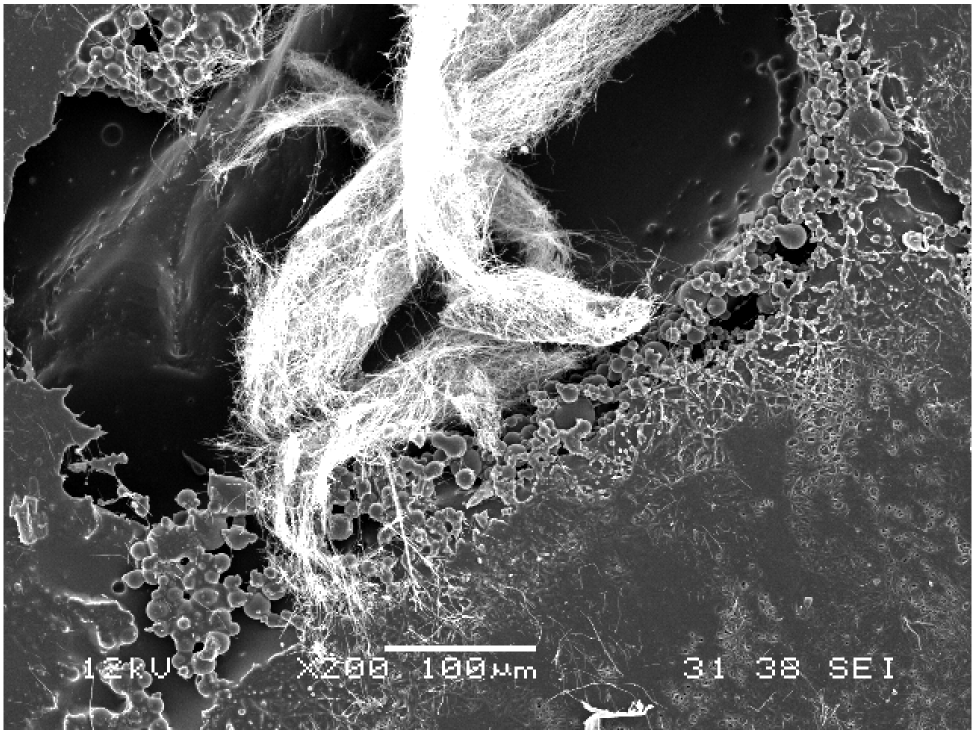

Figure 18: The SEM image showing the differing PCL concentrations near and far from the fibers.

Conclusion:

In this capstone project, the possibility of creating an electrically-triggered reversible-adhesive material was tested using carbon nanofibers and an epoxy/PCL mixture. The phenomena of differential expansive bleeding (DEB)[3-6] and polymerization induced phase separation (PIPS) were examined when the sample of epoxy/PCL was imbedded within a carbon nanofiber matrix. The important results are summarized below.

1) The epoxy/PCL can be successfully imbedded within the carbon nanofibers. To overcome the viscosity of the epoxy/PCL, it was necessary to preheat both samples and then use vacuum to pull the epoxy/PCL into the fiber matrix.
2) The epoxy/PCL within the carbon nanofibers does exhibit polymerization induced phase separation within the carbon nanofibers. The DSC shows that there is a melting point at 55 °C, which is the melting point of the PCL within the sample.
3) The morphology of the epoxy/PCL is not the same as the morphology of the bulk epoxy/PCL. It is postulated that this is due to the selective wetting of the carbon nanofibers by the PCL. This causes excess PCL to accumulate close to the fibers, and reduces the amount of PCL in the voids of the fibers. This morphology consists of PCL spheres within a matrix of epoxy.[6]
4) The adhesion that was observed during certain experiments was due to excess epoxy/PCL on the surface of the sample. When the excess epoxy

was heated it underwent DEB. This small, excess epoxy/PCL on the surface of some samples caused the adhesion.

Future Work:

The next phase of testing should begin with alteration of the composition of the epoxy/PCL mixture. If the PCL selectively wets the carbon nanofibers, as was postulated, then the rest of the epoxy/PCL further from the fibers has less PCL. Increasing the proportion of PCL in the epoxy/PCL could be a successful way to compensate for the selective wetting. The new sample should have stronger adhesion properties and have observable bleeding if the correct epoxy/PCL ratio coats the fibers. Once the reversible adhesion is quantified, self-healing should be attempted. The self-healing part of the experiment will attempt to fix fractures within the sample to restore flexural properties. Tests involving damage sensing can be done by calculating the resistance across the sample. If fractures within the sample change the overall resistance of the sample, then this could be used as a sensor. Additional experimentation should involve removal of the epoxy so that there will only be PCL/CNF. The epoxy was used primarily for structural stability, but the CNF might provide enough stability on its own.

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2. Liu, C.; Qin, H.; Mather, P. T., Review of progress in shape-memory polymers. *Journal of Materials Chemistry* **2007,** 17, (16), 1543-1558.

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4. Luo, X. F.; Lauber, K. E.; Mather, P. T., A thermally responsive, rigid, and reversible adhesive. *Polymer* **2010,** 51, (5), 1169-1175.

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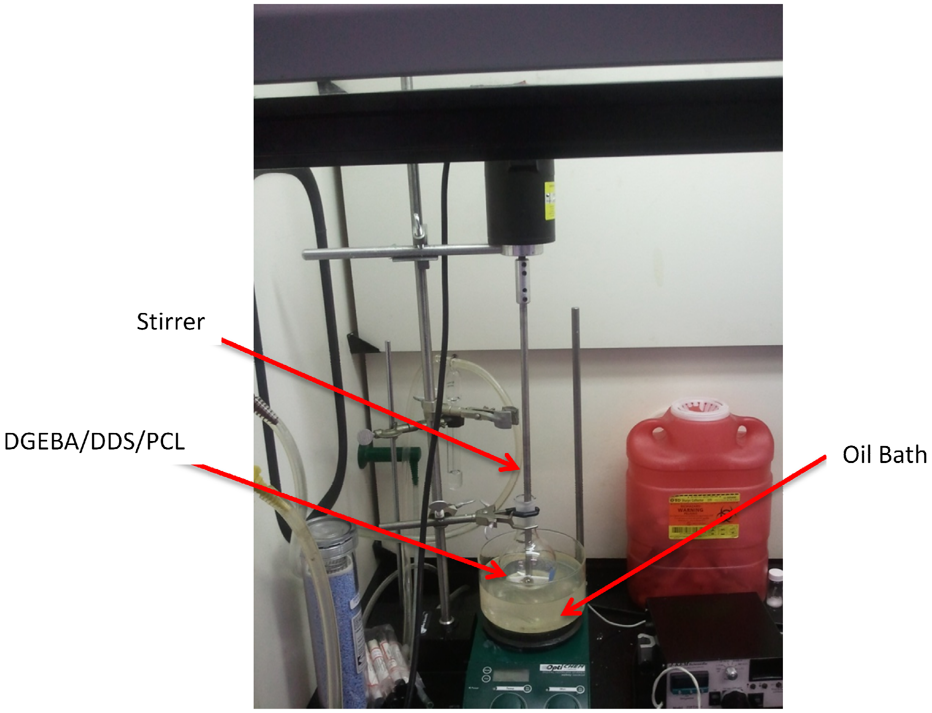
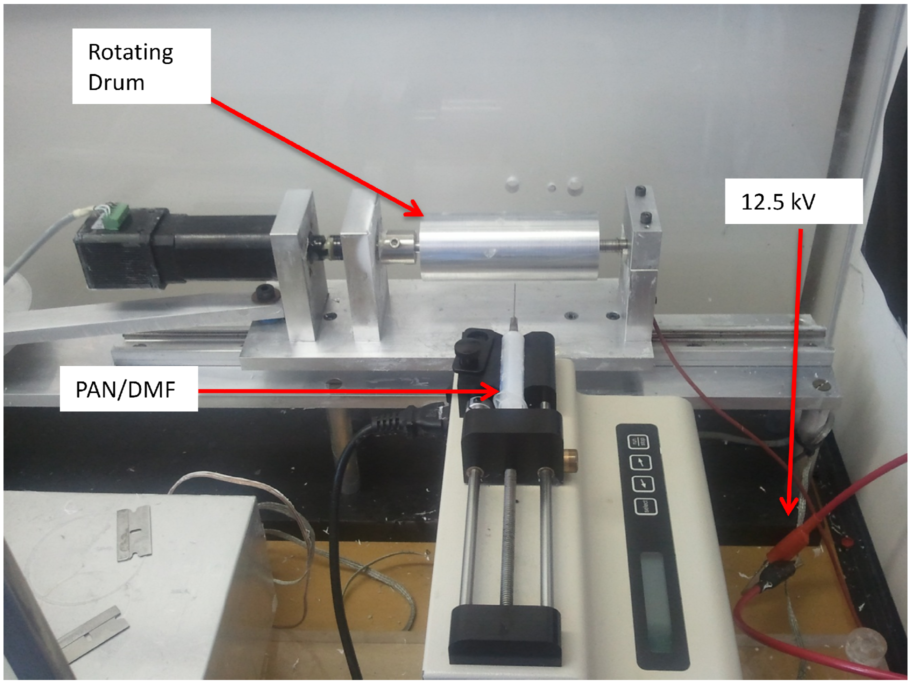
Appendices:

Appendix 1: Experimental Set Ups

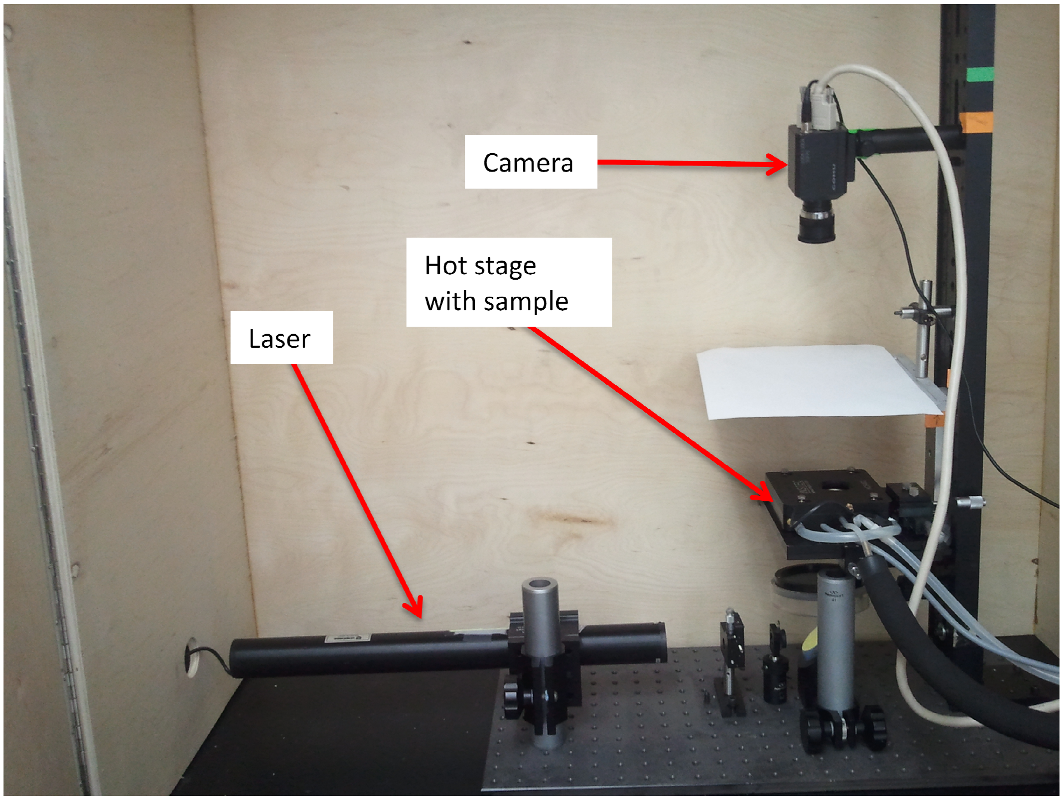
A1: Epoxy Set Up



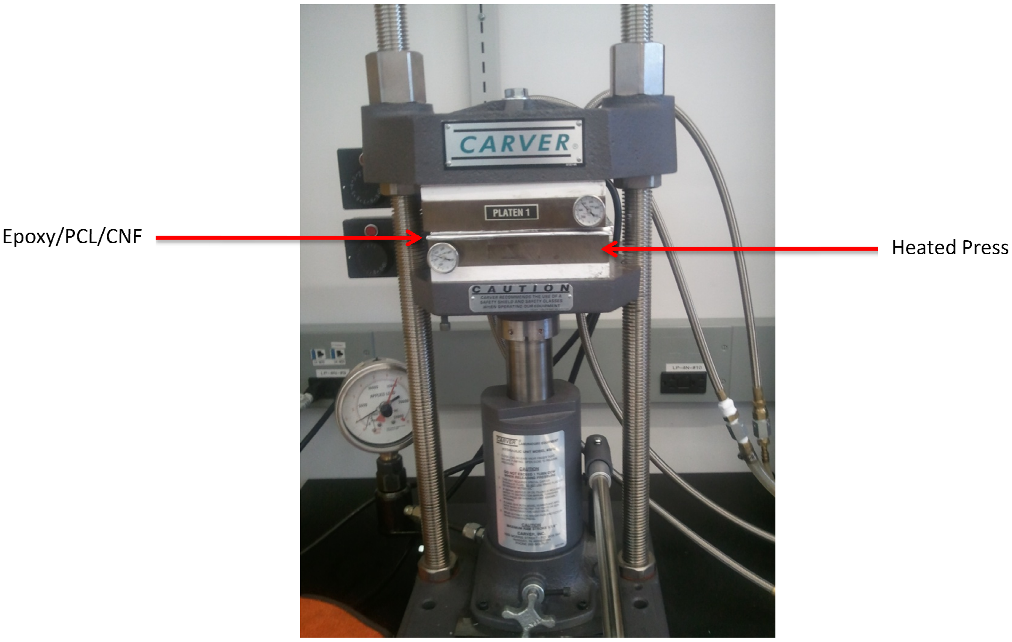
A2: Electrospinning Set Up



A3: SALS set up



A4: OM set up



Appendix A2: Data for Tables

OM Data:

180C				
Time	Integral I(t)	I(t) – I(d)	I(0)- I(d)	Transmittance (%)
Dark	19471.7	0	17290.8	n/a
400	36762.5	17290.8		100
500	36762.5	17290.8		100
600	36762.5	17290.8		100
700	36762.5	17290.8		100
800	36762.5	17290.8		100
900	36534.7	17063.0		98.7
910	36304.2	16832.6		97.3
920	34502.5	15030.9		86.9
930	31105.3	11633.6		67.3
940	30843.4	11371.7		65.8
950	31969.5	12497.8		72.3
960	31230.6	11759.0		68.0
970	30050.5	10578.9		61.2
980	29231.1	9759.5		56.4
990	28222.9	8751.2		50.6
1000	27466.2	7994.5		46.2
1100	22495.1	3023.5		17.5
1200	21568.3	2096.6		12.1

SALS Data:

Calc Parameters	
d (um)	3.33
r (mm)	53
lam (nm)	632.8
n	1
theta (rad)	0.19
2theta (rad)	0.38
Dcalc (mm)	132.45

Calc Data	30s Trial			
Intensity	Pixels	r (mm)	theta	q (1/um)
0	0	0.00	0.00	0.00
0	1	0.17	0.00	0.01
0	2	0.33	0.00	0.02
0	3	0.50	0.00	0.04
0	4	0.67	0.00	0.05
0	5	0.83	0.00	0.06
0	6	1.00	0.00	0.07
0	7	1.17	0.00	0.09
0	8	1.33	0.01	0.10
0	9	1.50	0.01	0.11
0	10	1.67	0.01	0.12
0	11	1.83	0.01	0.14
0	12	2.00	0.01	0.15
0	13	2.17	0.01	0.16
0	14	2.33	0.01	0.17
0	15	2.50	0.01	0.19
0	16	2.67	0.01	0.20
0	17	2.83	0.01	0.21
1	18	3.00	0.01	0.22
1	19	3.17	0.01	0.24
3	20	3.33	0.01	0.25
6	21	3.50	0.01	0.26
14	22	3.67	0.01	0.27
29	23	3.83	0.01	0.29
53	24	4.00	0.02	0.30
84	25	4.17	0.02	0.31
113	26	4.33	0.02	0.32
135	27	4.50	0.02	0.34
146	28	4.67	0.02	0.35
149	29	4.83	0.02	0.36
151	30	5.00	0.02	0.37
156	31	5.17	0.02	0.39
167	32	5.33	0.02	0.40
179	33	5.50	0.02	0.41
190	34	5.67	0.02	0.42
195	35	5.83	0.02	0.44
193	36	6.00	0.02	0.45
185	37	6.17	0.02	0.46
173	38	6.33	0.02	0.47

Calc Data	60s Trial			
Intensity	Pixels	r (mm)	theta	q (1/um)
0	0	0.00	0.00	0.00
0	1	0.17	0.00	0.01
0	2	0.33	0.00	0.02
0	3	0.50	0.00	0.04
0	4	0.67	0.00	0.05
0	5	0.83	0.00	0.06
0	6	1.00	0.00	0.07
0	7	1.17	0.00	0.09
0	8	1.33	0.01	0.10
0	9	1.50	0.01	0.11
0	10	1.67	0.01	0.12
0	11	1.83	0.01	0.14
0	12	2.00	0.01	0.15
0	13	2.17	0.01	0.16
0	14	2.33	0.01	0.17
0	15	2.50	0.01	0.19
0	16	2.67	0.01	0.20
0	17	2.83	0.01	0.21
0	18	3.00	0.01	0.22
0	19	3.17	0.01	0.24
0	20	3.33	0.01	0.25
0	21	3.50	0.01	0.26
0	22	3.67	0.01	0.27
0	23	3.83	0.01	0.29
0	24	4.00	0.02	0.30
0	25	4.17	0.02	0.31
0	26	4.33	0.02	0.32
0	27	4.50	0.02	0.34
0	28	4.67	0.02	0.35
1	29	4.83	0.02	0.36
1	30	5.00	0.02	0.37
1	31	5.17	0.02	0.39
2	32	5.33	0.02	0.40
3	33	5.50	0.02	0.41
6	34	5.67	0.02	0.42
12	35	5.83	0.02	0.44
19	36	6.00	0.02	0.45
27	37	6.17	0.02	0.46
34	38	6.33	0.02	0.47

Capstone Summary:

New advancements in polymer science have allowed for the creation of “smart polymers.” These polymers have the ability to revolutionize many applications and processes in the world today. This capstone project was focused on creating a nanocomposite material with adhesive properties. There were two requirements of the nanocomposite.

1) The material needed to have reversible adhesive properties so that it could be easily removed from its substrate. This part of the experiment had already been completed.
2) The material needed to be electrically conductive so that the adhesion could be controlled electrically, as opposed to thermally. This part of the experiment is the focus of my capstone project.

Materials were created by combining the epoxy mixture of diglcidyl ether of bisphenol-A (DGEBA) and 4,4’-diaminodiphenylsulfone DDS with the polymer poly(acrylonitrile) (PCL). When the epoxy was correctly mixed with the PCL it underwent polymerization induced phase separation (PIPS). PIPS created a material with a bricks and mortar morphology.[3-6] The morphology consisted of a network of linked spheres of epoxy surrounded in a matrix of PCL. Hence, the two phases were separated. This material had adhesive properties when it was heated due to the phenomena of differential expansive bleeding (DEB). DEB was caused in the material because of thermal expansion. The PCL in the sample expanded much more rapidly than the epoxy when it was heated above its melting point. This expansion caused the PCL to “bleed” onto the surface of the sample. When the melted PCL on the surface of the sample made contact with a substrate it created an adhesive bond. If the sample was cooled below its melting point and was kept in contact with the substrate then the bond would be semi-permanent. However, if the sample was reheated the PCL would melt once again and the substrate could be easily removed from the sample. This was the reversible adhesive property of the material.

Unfortunately, this material was not very electrically conductive, and therefore it was difficult to heat it electrically. To create a more electrically conductive material, carbon nanofibers (CNFs) were synthesized. The carbon fibers were synthesized into a mat consisting of many fibers strung together. The voids within the fibers were filled with the reversible-adhesive epoxy/PCL mixture. The conductive nanofibers would allow for the electric heating of the material and therefore the electrically-triggered reversible-adhesion.

The first task that needed to be accomplished was to synthesize the carbon nanofiber mat. To synthesize the carbon nanofibers PAN was electrospun to create a PAN fiber mat. This PAN fiber mat was heated twice to synthesize the carbon nanofibers. The PAN fibers were first heated to 280 °C, stabilization, and then to 1000 °C, carbonization.[1,5] At the end of the two heating sequences the PAN fibers were chemically altered and were now carbon fibers.

The next task was to determine a method to infiltrate the highly viscous epoxy/PCL into the voids of the carbon nanofibers. The first method that was attempted was the press method. Multiple mats of the carbon nanofibers were submerged in the heated epoxy/PCL. The heating of the epoxy/PCL decreased the viscosity and would allow for the infiltration. After the samples had been submerged within the epoxy/PCL for 30 minutes they were quickly removed, stacked, and placed onto a heated press. The layers were then pressed together at 180 °C for three hours to allow the sample to cure. Unfortunately, this viscosity of the sample was still too great to infiltrate the nanofibers and the experiment failed. A second method was then used that relied on vacuum suction to pull the heated epoxy/PCL into the voids of the fibers. This time, the epoxy/PCL was poured on top of the nanofibers and pressed between two Teflon-covered glass slides. The sample was then into the vacuum oven at 180 °C and vacuum was pulled. The theory was that as the air was pulled out of the nanofibers, the epoxy/PCL would be pulled in. This method of infiltration was a success.

Once the nanocomposite was created, many tests were conducted to ensure that it had the correct properties to allow for the electrically-triggered reversible-adhesion. The first test was differential scanning calorimetry (DSC). This test ensured that the epoxy/PCL had undergone PIPS during the cure. Once the PIPS was confirmed, the DEB needed to be observed. The tests for bleeding consisted of heating the sample under the microscope. The bleeding can be easily seen under the microscope, even at a low magnification. However, no bleeding was ever observed. Occasionally, the sample would stick to the glass slide that it was on. The reason was still unknown at the time, but it turned out that the adhesion to the glass slide was caused by the melting of excess epoxy/PCL on the surface of the sample. Finally, the samples were tested for electrical conductivity. As expected, the carbon nanofibers dramatically increased the conductivity of the sample. Electrical heating tests were conducted and it became simple to heat the sample by adjusting the voltage of the power source. Unfortunately, there was still no observable bleeding.

To determine the reason that no bleeding was observed, many tests were done on bulk epoxy/PCL. Small angle laser light scattering, optical microscopy and curing under the microscope were the three morphology characterization experiments done to determine that the bulk epoxy/PCL had the correct morphology. Once this was determined and no bleeding was observed, it was postulated that the morphology within the carbon nanofiber matrix must be different than the morphology in the bulk phase. It is believed that selective wetting of the PCL on the CNFs is the cause for the change in the morphology. Selective wetting is when one of the components in the mixture favors the carbon nanofibers more than another. In this case, the PCL may selectively wet the carbon nanofibers. This would cause the amount of PCL away from the fibers to decrease. When the ratio of PCL decreases it changes the morphology of the sample. At the decreased ratio the PCL formed the spheres and the epoxy formed the matrix[4]. This combination is still phase separated, but it does not bleed. To achieve the bleeding, a different ratio of PCL in the initial epoxy mixture will need to be utilized.

This project has many useful applications in society. The reversible adhesive is a very efficient way to adhere two substrates repeatedly. The bond that it forms is strong and durable as well. Besides the reversible adhesive properties, the material will also have self-healing properties. In other words, if the sample is fractured during its use, it can fix itself. This is also based on the differential bleeding phenomena. When the PCL bleeds onto the surface it will fill in the fracture and harden. This has the ability to replace the flexural properties of the sample. Other proposed uses of this material are for damage sensing. If the conductivity of the material changes when it is fractured, it is then possible to check for fractures that cannot be seen. For example, if the conductivity of the sample suddenly decreased, that would be an indication that the sample is cracked. It is relatively simple to measure the conductivity of the sample. One practical example would be for airplane. The wings of airplanes are susceptible to microfractures that can be difficult to detect. If the conductivity of the non-fractured wing is known than it would be possible to detect the microfractures simply by checking the conductivity of the wing continuously.