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Carbon Nanotube Buckypaper Permeability and Prepreg Process Study

Bryant Marshall Click
THE FLORIDA STATE UNIVERSITY
COLLEGE OF ENGINEERING

CARBON NANOTUBE BUCKYPAPER PERMEABILITY AND PREPREG PROCESS
STUDY

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BRYANT MARSHALL CLICK

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The members of the committee approve the thesis of Bryant Marshall Click defended on July 12, 2010.

__________________________________
Richard Liang
Professor Directing Thesis

__________________________________
Ben Wang
Committee Member

__________________________________
Okenwa Okoli
Committee Member

Approved:
__________________________________
Chuck Zhang, Chair, Industrial and Manufacturing Engineering

__________________________________
Ching-Jen Chen, Dean, Engineering

The Graduate School has verified and approved the above-named committee members.
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ABSTRACT

Carbon nanotubes (CNTs) possess great potential for developing high-performance and multifunctional nanocomposites for a wide variety of applications. As the cost of producing CNT buckypaper, a thin film of CNT networks, continues to decrease while the quality increases, more users and companies are becoming interested in buckypaper for potential applications. Many of these applications, such as electromagnetic interference (EMI) shielding and fire retardant surface skins for fiber-reinforced composites or plastics, may not require buckypaper-based composites to be much stronger compared to fiber-reinforced composites. This means that there is a market for buckypaper even without its theoretical super strength, but desired functionality. There is however a number of challenges with the potential scale-up production of composite parts with affordable buckypaper materials usually made of low cost CNTs, such as multi-walled carbon nanotubes (MWNTs). Such buckypaper is usually very lightweight (10-25 g/m$^2$), thin (10-20 microns), and fragile, hence even small variations and damage in the wet lay-up process can result in large quality variations in the final buckypaper composite. These variations include buckypaper volume fraction, resin rich areas, and contact between BP and other reinforcement materials etc. Thus, keeping the consistency of the resulting microstructure and quality of buckypaper composites is a very challenging issue.

The objective of this project is to study nanostructure-permeability relationships of different types of buckypaper materials, and explore effective prepreg processes to make buckypaper composites with greatly increased consistency, quality, CNT weight fraction and uniformity in the resulting products. The experimental results show that buckypapers have very low permeability, about 8-12 orders lower than those of carbon fiber preform cases, and also sensitive to liquid polarity due to their nanoscale porosity and large surface area. Both solution and resin film transfer prepregging processes were studied to pre-impregnate buckypaper to achieve 50 wt. % CNT concentration. The late one showed better quality in the resultant nanocomposites, but difficult for high viscosity resins. Three case studies were also conducted to demonstrate quality and property consistency of buckypaper composites.
1. INTRODUCTION

1.1. Buckypaper

Carbon nanotubes are cylindrical tubes of pure carbon \(\frac{1}{50,000}\) the size of a human hair. Carbon nanotubes exhibit incredible mechanical, electrical and thermal properties, but have not been fully exploited due to the high cost of manufacturing, and the difficulty involved in handling the CNTs [1][2]. Buckypaper (BP) is a thin sheet formed from a network of carbon nanotubes, as shown in Figure 1.

![Figure 1: SEM images of carbon nanotubes](image1)

Originally, buckypaper was fabricated as a way to transform carbon nanotubes into a macroscopic material, which is good for performing physical property tests [3]. Buckypaper is being researched by many groups and shows promise as a platform material for aerospace vehicles, body armor, and next-generation electronic displays [4-6].

In 2000, BP was introduced to High Performance Materials Institute (HPMI) by researchers at Rice University. The importance of examining nanotube properties for bulk materials applications was recognized, and HPMI began a comprehensive research program to fabricate and investigate the properties of BP and applications in composites.

Since the program started in 2000 the research team has been steadily producing higher quality buckypaper at a faster rate and macroscopic size. Currently HPMI
routinely produces 8” x 8” sheets of buckypaper in less than 2 hours [7]. This increase in production drives down cost and increases the amount of buckypaper which can be studied, further accelerating the research progress for composite application studies.

1.2. Carbon Fiber Prepreg

Prepreg is fiber reinforcement which has been previously impregnated with a fixed amount of matrix material (resin) [8][9]. The matrix material is partially cured during the prepreg process to its B-stage. In the B-stage, the resin contains hardener and is allowed to partially cure in order to raise the viscosity [10]. The curing reaction is then stopped by freezing the prepreg until it is ready for further processing. The prepreg can then be removed from refrigeration and used to fabricate composite parts without the need for mixing and applying liquid resin. Figure 2 shows uncured epoxy, carbon fiber prepreg and a composite panel fabricated from carbon fiber prepreg.

![Figure 2: Examples of carbon fiber/epoxy prepreg, pre-cure (A) and cured panel (B)"

1.3. Advantages of Prepreg

Carbon fiber prepreg has become an accepted industry standard for high quality composite applications because of the advantages it offers over traditional wet lay-up. High quality composites made of prepreg materials offer a number of advantages, compared to the metals that they are typically targeted to replace including higher specific stiffness and specific strength, greater corrosion resistance and faster...
manufacturing due to increases in part integration capability. Increasing manufacturing
rates has a butterfly effect that creates cost saving in several areas of production. The use
of prepreg allows the user to accurately control fiber volume fraction and composite
composition. Prepreg is offered in different sized rolls and is covered on both sides with
a suitable release film. Peeling away the release film reveals the prepreg fibers which
retain a desirable amount of tack. The tack of the prepreg allows for pre-cut pieces to be
securely attached to the composite lay-up similar to placing pieces of double stick tape on
top of each other. The tack is also low enough to allow poorly laid pieces of prepreg to
be pulled up and re-laid without damaging the prepreg fibers. Composite products made
with prepreg materials can provide a higher fiber volume fraction (usually > 55 v. %)
than products made by other processes, such as filament winding or pultrusion. Prepregs
also are available in an extensive range of resin and fiber combinations, enabling the user
to maximize performance [11]. Many industries have invested in technologies such as
automated tape lay-up (ATL) and automated tape placement (ATP) which are used
exclusively with prepregs to further increase the rate of production and mass produce
composite components. In ATL processes, automated computers control machines that
cut and place prepreg tapes in the desired orientations for the given part, with little to no
human interaction. These automated processes also pre-determine the cuts for prepreg
component pieces with different sizes and orientations to optimize material usage and
reduce waste. These processes also achieve production rates several orders higher,
compared to hand lay-up processes.

1.4. Prepreg Market Forecast

In 2007, total worldwide prepreg shipments exceeded 125 million lb, up from
about 60 million lb in 2002 and representing $2.2 billion in revenues. On a volume basis,
the global market has doubled in five years, growing at a rate of more than 10 percent per
year since 2002, mainly due to the booming wind energy market, the rapid growth of
composites manufacturing in Asia and a strong aerospace industry in North America and

On a global basis, prepreg market revenue is forecast to grow 13 to 14 percent in
2008 and average almost 12 percent per year during 2008-2013. Global prepreg shipment
values are projected to grow to $4.4 billion in 2013 from $2.6 billion in 2008. This growth depends significantly on the performance of the commercial aerospace, military/defense, general aviation, wind energy and sporting goods industries, which represent 75 to 80 percent of the global market in terms of shipment volume and revenue [11].

As this forecast indicates, many potentially valuable opportunities exist in the global prepreg industry. A number of manufacturers are opening new plants or expanding current facilities due to high demand. This trend is likely to continue as prepregs gain even more acceptance for use in various new aircraft models and emerging applications [11].

1.5. Buckypaper Wet Lay-Up

Buckypaper wet lay-up has been studied first and summarized in the followings. The process began with the gathering of materials and equipment which was used to prepare and fabricate the final composite. First, a scalpel or razor blade was used to cut the desired amount of equally sized buckypaper layers. The buckypaper pieces were cut out while still inside the plastic bag to reduce contamination and provide structural support. After each layer was cut and stored, epoxy resin was prepared by weighing the amounts of EPON 862 epoxy, produced by Hexion, and EPIKURE W curing agent, produced by Hexion, that were required for the resin mixture. Epoxy and curing agent were mixed according to the ratio determined by the manufacturer for optimum performance. At this given ratio the amount of epoxy reactive sites (epoxy groups) equals the amount of curing agent reactive sites (amine groups). The weighed out components were then stirred together for at least 10 minutes, with a glass stirring rod, to ensure that the two components were adequately mixed together. Sometimes the mixed resin was placed in a vacuum to liberate some of the air bubbles which formed while the epoxy and curing agent were mixed. Airtech Advanced Materials Group Release Ease 234TFNP Teflon film was placed as a base for the buckypaper composite lay-up. A hot table could be used to provide the exact amount of heat needed to lower the resin viscosity and reduce resin tack. A small amount of resin (twice the weight of one buckypaper layer) was spread onto the Teflon film and a single layer of buckypaper was
placed on top. A glass stirring rod was then used to uniformly spread the resin under the buckypaper layer and liberate any excess resin. In many cases, especially if a hot table is not used, a small amount of resin would get onto the stirring rod and causes the buckypaper to stick to it. This would tear and damage the buckypaper. Care was taken to ensure that the stirring rod was cleaned after each step during the lay-up process. After the resin under the buckypaper was spread into a thin film beneath the buckypaper, another small amount of resin (twice the weight of one buckypaper layer) was spread onto the top of the buckypaper with a flat piece of plastic. The next layer of buckypaper was placed on top of the spread resin layer and the process repeated until all layers had been added. Each layer had to be very carefully placed because, once a buckypaper layer was placed, and contacted the resin, it was very difficult to move or align without damaging the buckypaper. A thin layer of resin was spread on the top of the buckypaper, resin stack and another Teflon film was placed on top. The buckypaper, resin stack was then placed so that a vacuum bag setup could be built around it. The sample was then vacuum bagged and cured according to the resin curing procedures defined by the manufacturer. The buckypaper wet lay-up was extremely time consuming and could not be used to produce repeatable results in terms of buckypaper weight fraction and part uniformity in these experiments.

1.6. Motivation

As the cost of producing buckypaper continues to decrease while the quality increases, more companies are becoming interested in buckypaper for potential applications. Many of these applications, such as electromagnetic interference (EMI) shielding [12][13], may not require buckypaper to be much stronger than it already is. This means that there is a market for buckypaper even without its theoretical super strength. Currently, there are a number of issues with the actual lay-up and production of composite parts with buckypaper that make it unreliable for industrial use as discussed in Section 1.5. Because buckypaper is so lightweight and fragile, even small variations in the wet lay-up process can result in large variations and defects in the final buckypaper composites. These issues include BP volume fraction consistency, resin rich areas, and contact between BP and other reinforcement materials etc. The consistency of the
resulting microstructure and quality, of BP composites, is a very challenging issue [2]. Figure 3 shows some examples of poor quality BP composites. These images were generated using the A scan feature of the Sonix Ultrasonic C-Scan machine.

Figure 3: C-scan images of defective BP composites. Uneven resin distribution causes wrinkling (A). Curvature from non-uniform resin areas (B).

Based on the trial experiments, eliminating the process of mixing and applying resin used in a wet lay-up would greatly increase the consistency of the quality, CNT weight fraction control and resin uniformity in the resulting buckypaper parts. This can be achieved with a prepreg buckypaper process. By pre-impregnating the buckypaper with a set amount of resin before it reaches the customer, there is less room for variability in the final product. This will make buckypaper more attractive for industrial use. Using prepreg buckypaper in a dry lay-up process reduces waste by removing the need for customers to mix and apply resin on the materials. Because single sheets of buckypaper are very fragile and easy to damage during this process, using a resin reinforced buckypaper prepreg instead of a wet lay-up also reduces the chances that the buckypaper could be damaged during processing. Hence, the study and development of a BP prepreg process are highly desired.
1.7. Problem Statement

There are many disadvantages involved in using a wet lay-up as opposed to a dry lay-up, using prepreg materials [14]. To start with, wet lay-ups are very labor intensive and require time to mix, apply and clean up resin. Resin application can be very difficult, even for an operator who has experience with composite fabrication. Figure 4 shows some of the steps of buckypaper composite fabrication using the hand, wet lay-up method in the initial experiment studies. The pictures show how resin collects in different places around the composite lay-up and adheres to gloves and the stirring rod.

Figure 4: BP wet lay-up experiment: mixing epoxy resin with curing agent (A), applying liquid resin to example composite fiber layers (B), and using a stirring rod to push out excess resin and smooth composite surface (C).

Buckypaper is very thin (10-20um) and fragile and it statically adheres to gloves and tools, making it difficult to position during the lay-up [15]. This is especially true for
larger sheets of buckypaper and makes them difficult to lay flat during an impregnation process. Prepreg buckypaper would be much easier to position since it has a release film backing to provide structure and support. It is very difficult to control the amount of resin used in a wet lay-up as well, especially for very thin composites (less than four layers of BP). Providing a prepreg buckypaper with a pre-determined amount of resin would make the CNT weight fraction much more controllable in the final composite part. It is certainly more efficient to use buckypaper prepreg to scale-up CNT composite production, particularly when using ATP processes. For all of these reasons using prepreg buckypaper in a dry lay-up has much better processability and provides better quality control, than performing a wet lay-up [16].

1.8. Research Objectives

1.8.1. Buckypaper Permeability

In order to determine the optimum parameters for buckypaper prepreg fabrication, it is important to investigate the buckypaper permeability. Permeability is defined as the ability of a porous material to transmit fluids as defined in Darcy’s Law (reference?), which has been widely studied in RTM and VARTM processes. In this study, the permeability is tested by pulling a test liquid through the BP layer, using a vacuum chamber, and measuring the flow rate. With a known vacuum pressure, sample dimensions, fluid viscosity and flow rate, the permeability is calculated using Darcy’s law. Permeability is considered a key parameter for buckypaper. Knowing the permeability of the buckypaper will give insight into how long it will take different liquid resins to infuse into the buckypaper network during buckypaper impregnation.

1.8.2. Buckypaper Porosity

Porosity is defined as the amount of void spaces in a material. The porosity of buckypaper can be measured using the BET method and SEM images. However, the measured porosity of the buckypaper is not directly related to the permeability, and cannot be used to verify the results of permeability testing. In many cases a highly porous material also has a high permeability. However, sometimes a highly porous
material has very low permeability. This is because the pores or free spaces must also be inter-connected in order for a highly porous material to also have a high permeability. The purpose of studying buckypaper porosity is to understand the permeability-porosity relationships of different type of buckypaper materials, including SWNT, MWNT and mixed buckypaper sheets.

1.8.3. Resin Characteristics

Investigation into the rheological properties of each type of resin is important for establishing key factors in the BP impregnation process. Liquid resin viscosity must be low in order to impregnate a material with low permeability. There are two common ways of lowering resin viscosity. One is to utilize heat, which also speeds up the curing reaction. The other is dissolving resin into solution using solvents. In some cases this solution method degrades resin properties due to the existing of residue solvents.

1.8.4. Study of Prepreg Manufacturing Processes

There are two main processes for producing prepreg, which are the solution method and film transfer method.

In the solvent method, as shown in Figure 5, liquid resin is thinned down with a solvent and fiber tows are passed through a resin bath to realize a controlled fiber/resin impregnation. Later coated fibers are dried to eliminate the solvent in a drying tower to fabricate the prepreg [8].
In the film transfer method, as shown in Figure 6, a silicon release paper is coated, normally with resin film on both sides; dry fiber is brought together with this double-sided film to produce a three part laminate. This is passed through heated compaction rollers that press the viscous resin into the fibers to wet them out. The laminated prepreg is then passed over cooling rollers and then onto large rolls for storage and delivery. Hence, this approach is a two step process [8].
Both processes were investigated and attempted in order to determine which one was the best for making BP prepreg.

1.8.5. Study and Control of Buckypaper Composite Quality

Both C-Scan and SEM techniques were used to check and analyze the quality of the resulting prepreg buckypaper prepreg and their composites.

1.8.6. Case Studies

After the process is determined for creating quality buckypaper prepreg, CNT composite parts were fabricated using buckypaper prepregs to study and demonstrate their quality and properties. Three case studies were conducted:

1) Thin panels
2) Battery shells
3) Buckypaper/carbon fiber panel
1.8.7. Protocol Development for BP Prepreg Fabrication

At the conclusion of this study it is necessary to recommend a series of directions for BP prepreg preparation methods to ensure quality and promote scale-up applications of buckypaper composites.

1.9. Research Flow Chart

The planned research tasks are summarized in the Figure 7.

---

**Figure 7: Research tasks**
2. LITERATURE REVIEW

2.1. Permeability of Fiber Preform

Proper flow of resin through fiber network or lay-ups is critical in producing relatively void-free parts and good fiber wet-out (17). In thermoset resins, curing may take place simultaneously with resin flow, and if the resin viscosity rises too rapidly due to curing, its flow may be inhibited, causing voids and poor interlaminar adhesion (18). Resin flow through fiber network has been modeled using Darcy’s equation, which was derived for flow of Newtonian fluids through a porous medium (19). This equation relates the volumetric resin flow rate \( q \) to the pressure gradient that causes the flow to occur as shown in the following.

For one-dimensional flow along the x direction,

\[
q = -\frac{\rho_o}{\eta} \frac{dp}{dx}
\]  \hspace{1cm} (1)

where

\( q \) = volumetric flow rate per unit area \( (m^3/s) \) in the x direction

\( \rho_o \) = permeability \( (m^2) \)

\( \eta \) = viscosity \( (N\cdot s/m^2) \)

\( \frac{dp}{dx} \) = pressure gradient \( (N/m) \), which is negative in the direction of flow (the positive x direction)

The permeability can be determined based on Darcy’s law. The permeability is also determined by the following equation known as the Carmen-Kozney equation:

\[
K = \frac{d_f^2}{16k} \left(1 - \frac{v_f}{v_f^*}\right)^3
\]  \hspace{1cm} (2)

where

\( d_f \) = fiber diameter

\( v_f \) = fiber volume fraction

\( k \) = Kozney constant.

Although simplistic, these equations have been used by many investigators in modeling resin flow from prepregs in vacuum bag molding process and mold filling in resin transfer molding (20)(21). Typically permeability decreases as fiber volume
fraction increases, because the fibers are more densely packed and inhibit liquid resin flow.

2.2. Permeability of Liquid Flow Analysis Techniques

Fluid flow through a porous membrane is tested using the following setup and based on Darcy’s law. Darcy’s law can be expressed as a simple proportional relationship between the instantaneous discharge rate through a porous medium, the viscosity of the fluid and the pressure drop over a given distance,

\[
Q = \frac{-\kappa A (P_b - P_a)}{\mu L}
\]  

(3)

The total discharge, \(Q\) (units of volume per time, e.g., m³/s) is equal to the product of the permeability (\(\kappa\) units of area, e.g. m²) of the medium, the cross-sectional area (\(A\)) to flow, and the pressure drop (\(P_b - P_a\)), all divided by the dynamic viscosity \(\mu\) (in SI units e.g. kg/(m·s) or Pa·s), and the length \(L\) the pressure drop is taking place over.

2.3. Resin Gelation Analysis

Gelation occurs when the molecular weight of the cross-link tends to infinity and the material becomes insoluble and non-fusible and therefore non-processable (22). Gelation is an irreversible process and if it reaches a certain level (>5% degree of curing) prior to composite lay-up it will create a product with poor quality. Many methods for determining gelation time have been used. The most widely used methods to determine the conversion level (degree of curing) make use of Dynamic Mechanical Thermal Analysis (DMTA), Thermo Mechanical Analysis (TMA) and Differential Scanning Calorimetry (DSC) (23). Each method determines the degree of gelation by different means. The DMTA graphs the storage modulus as the sample is cured isothermally over time, as shown in Figure 8. The shear storage modulus increases during the curing process and then stabilizes when curing is complete. The degree of mechanical conversion is determined on the basis of this increase using equation 4.

\[
\alpha_{\text{DMTA}} = \frac{E'_{f} - E'_0}{E'_{\infty} - E'_0}
\]  

(4)
Where $E'_t$, $E'_o$, and $E'_\infty$ represent the storage modulus at time $t$, the storage modulus before curing and the storage modulus after curing respectively.

![Figure 8: Storage modulus, $E'$, and loss tangent, $\tan \delta$, versus time for the powder coating cured isothermally at 125 °C by DMTA (24)](image)

The TMA graphs dimensional changes during curing, as shown in Figure 9. Because resin shrinks during curing the rate of shrinkage can be related to the degree of curing. This relationship is shown in equation 5.

$$\alpha_{TMA} = \frac{L_t - L_o}{L_\infty - L_o}$$  \hspace{1cm} (5)

Where $L_t$, $L_o$, and $L_\infty$ represent the sample thickness at time $t$, before curing, and after curing respectively.
The conversion level in gelation of the powder coating was determined using the DSC, as shown in Figure 10. The DSC graphs the residual heat of the sample to determine the degree of gelation. Curing is a chemical reaction and residual heat is given off during the reaction. By testing the exothermal heat released in total curing and the exothermal heat released in partial curing, the degree of curing can be determined using equation (6) and plotted to determine a degree of curing model (24)(25).

$$\alpha_{\text{DSC}} = \frac{\Delta H_T}{\Delta H_{\text{dyn}}}$$  \hspace{1cm} (6)
2.4. BP Permeability

Previous investigation has determined that the nanoscale pore structure of BP leads to the increased difficulty of resin impregnation [3]. Due to the extremely high fluid flow resistance, BP can only be infused with resin through its thickness or z direction. The average value of the z direction permeability for BP was tested to be $2 \times 10^{-19}$ m$^2$. Compared to glass fiber mats ($V_f = 60\%$), BP has a permeability which is 8-10 orders lower [3].
3. BUCKYPAPER AND RESIN CHARACTERIZATION

3.1. Permeability of BP

The permeability test setup, as shown in Figure 11, was used to test the permeability of single-walled (SWNT), multi-walled (MWNT) and their mixture buckypaper samples. Buckypaper samples which consisted of three parts MWNT and one part SWNT were also tested and are referred to as mixed buckypaper. Each type of buckypaper was made with the same equipment and identical filter papers. The samples were tested using three different fluids; acetone, water and silicone oil. These fluids were chosen to account for a large range of viscosities and different polarity. The viscosity of acetone is very low whereas the viscosity of silicone oil is relatively high and closer to the viscosity of the candidate liquid resins.

Figure 11: Vacuum chamber and reservoir used to test BP permeability
Circular samples for each type of buckypaper were cut from 8”x 8” sheets with a razor blade and stencil. Each circular sample measured 40mm in diameter in order to fit the test apparatus. Each sample was tested for holes and defects by holding it in front of a light source, as seen in Figure 12.

![Figure 12: Defect-free sample (A) and defective sample (B) by visual checks](image)

Many samples contained only one tiny pinhole however, if any light could be seen coming through the sample it was discarded. Initially, larger samples, measuring 80mm in diameter, were used but almost always contained defects and cracked when exposed to vacuum pressure. The circular samples were placed on top of a 40mm Millipore filter with 0.45um pores. The filters were used to support the buckypaper and prevent cracking around the edges of the sample. Because the permeability of the filters is much greater than the permeability of the buckypaper it was assumed that the filters had no effect on the buckypaper permeability. The circular samples were gently flattened by hand onto the filters and placed onto the vacuum chamber. The upper portion of the apparatus was then placed on top of the vacuum chamber pinning the sample between the two magnetic parts and forming a seal at the edges of the buckypaper. Test fluid was poured carefully into the fluid reservoir as to not damage the samples. The vacuum was applied and the fluid was allowed to wet and go through the buckypaper. Any sample that allowed more than one drop of fluid at a time, to flow through it, was considered defective and was discarded. After the fluid appeared to be moving through the sample, the time was recorded for how long (seconds) it took 20 drops (1 mL) to fall from the spout in the
vacuum chamber. This process was done 5 consecutive times recording the time after every 20 drops. The 5 recordings were averaged and checked for consistency. Due to time constraints and varying vacuum pressure, observations were recorded for the time between every 4 drops of D.I. water and every single drop of silicone oil. The values which steadily increased or decreased were noted but not discarded. This test was completed three times for each type of buckypaper with each type of fluid for a total of 27 tests. The results are shown below in Tables 1-3 and Figures 13-16 for SWNT, MWNT and mixed buckypaper samples respectively.

Table 1: SWNT Buckypaper Permeability Measurements

<table>
<thead>
<tr>
<th>Test Fluids</th>
<th>Flow Rate (sec/mL)</th>
<th>Pressure (in Hg)</th>
<th>Permeability ( \times 10^{-20} \text{ m}^2 )</th>
<th>Average Permeability ( \times 10^{-20} \text{ m}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>194</td>
<td>14</td>
<td>1.38</td>
<td>1.41</td>
</tr>
<tr>
<td>Acetone</td>
<td>192</td>
<td>14</td>
<td>1.39</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>185</td>
<td>14</td>
<td>1.45</td>
<td></td>
</tr>
<tr>
<td>DI Water</td>
<td>1170</td>
<td>14</td>
<td>7.17</td>
<td>0.64</td>
</tr>
<tr>
<td>DI Water</td>
<td>1325</td>
<td>14</td>
<td>6.33</td>
<td></td>
</tr>
<tr>
<td>DI Water</td>
<td>1440</td>
<td>14</td>
<td>5.83</td>
<td></td>
</tr>
<tr>
<td>Silicone Oil</td>
<td>30360</td>
<td>19</td>
<td>1.12</td>
<td>1.13</td>
</tr>
<tr>
<td>Silicone Oil</td>
<td>37840</td>
<td>15</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td>Silicone Oil</td>
<td>29400</td>
<td>19</td>
<td>1.15</td>
<td></td>
</tr>
</tbody>
</table>
The SWNT buckypaper has the lowest permeability at around 1.41E-20 m$^2$. The SWNT buckypaper was expected to have the lowest permeability because its tubes have smaller diameters and thus smaller pores.

Table 2: MWNT Buckypaper Permeability Measurements

<table>
<thead>
<tr>
<th>Test Fluids</th>
<th>Flow Rate (sec/mL)</th>
<th>Pressure (in Hg)</th>
<th>Permeability (x 10$^{-20}$ m$^2$)</th>
<th>Average Permeability (x 10$^{-20}$ m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>49</td>
<td>19</td>
<td>4.04</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>50</td>
<td>19</td>
<td>3.95</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>51</td>
<td>19</td>
<td>3.88</td>
<td></td>
</tr>
<tr>
<td>DI Water</td>
<td>375</td>
<td>17.5</td>
<td>1.79</td>
<td></td>
</tr>
<tr>
<td>DI Water</td>
<td>490</td>
<td>17.5</td>
<td>1.37</td>
<td></td>
</tr>
<tr>
<td>DI Water</td>
<td>495</td>
<td>17.5</td>
<td>1.35</td>
<td></td>
</tr>
<tr>
<td>Silicone Oil</td>
<td>9880</td>
<td>19</td>
<td>3.44</td>
<td></td>
</tr>
<tr>
<td>Silicone Oil</td>
<td>9460</td>
<td>19</td>
<td>3.59</td>
<td></td>
</tr>
<tr>
<td>Silicone Oil</td>
<td>9340</td>
<td>19</td>
<td>3.64</td>
<td></td>
</tr>
</tbody>
</table>
The MWNT buckypaper has the highest permeability at around 3.96E-20 m². The MWNT buckypaper was expected to have the highest permeability because its MWNT have larger diameters and thus larger pores in their buckypaper samples.

Table 3: Mixed Buckypaper Permeability Measurements

<table>
<thead>
<tr>
<th>Test Fluids</th>
<th>Flow Rate (sec/mL)</th>
<th>Pressure (in Hg)</th>
<th>Permeability (x 10⁻²⁰ m²)</th>
<th>Average Permeability (x 10⁻²⁰ m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>78</td>
<td>19</td>
<td>2.53</td>
<td>2.55</td>
</tr>
<tr>
<td>Acetone</td>
<td>80</td>
<td>19</td>
<td>2.47</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>75</td>
<td>19</td>
<td>2.63</td>
<td></td>
</tr>
<tr>
<td>DI Water</td>
<td>675</td>
<td>19</td>
<td>9.16</td>
<td>9.16</td>
</tr>
<tr>
<td>DI Water</td>
<td>625</td>
<td>19</td>
<td>9.89</td>
<td>9.89</td>
</tr>
<tr>
<td>DI Water</td>
<td>690</td>
<td>19</td>
<td>8.96</td>
<td>8.96</td>
</tr>
<tr>
<td>Silicone Oil</td>
<td>14880</td>
<td>19</td>
<td>2.28</td>
<td>2.28</td>
</tr>
<tr>
<td>Silicone Oil</td>
<td>15280</td>
<td>19</td>
<td>2.22</td>
<td></td>
</tr>
<tr>
<td>Silicone Oil</td>
<td>14600</td>
<td>19</td>
<td>2.33</td>
<td></td>
</tr>
</tbody>
</table>
The mixed buckypaper permeability is expected to fall somewhere between the permeability of SWNT and MWNT buckypapers. Because the mixed buckypaper is made from a combination of single-walled and multi-walled nanotubes in a ratio of 1:3 respectively, the rule of mixture can be used to predict the mixed buckypaper permeability.

- Mixed Permeability = \( (V_f \text{ of SWNT in buckypaper}) \times (\text{SWNT Permeability}) + (V_f \text{ of MWNT in buckypaper}) \times (\text{MWNT Permeability}) \)

- Mixed Permeability Acetone = 3.32 E-20 m²
- Mixed Permeability D.I. Water = 1.29 E-20 m²
- Mixed Permeability Silicone Oil = 2.96 E-20 m²

The experimental results for mixed buckypaper permeability are lower than the predicted values. This phenomenon will be illustrated and explained later when the pore structure of each buckypaper is compared.

Figure 15: Mixed buckypaper permeability for each test fluid
Figure 16: Comparison of buckypaper permeability for the different type of buckypaper and fluids

For each type of buckypaper tested the permeability is different for each test fluid. This is because each test fluid has different properties and interacts with the buckypaper differently. The results for the permeability tests that use de-ionized water are significantly lower than the other two test fluids. This can be explained by the hydrophobic nature of buckypaper that may inhibit the flow of water molecules through very small pores. Hydrogen bonding may also inhibit the flow of water out of the buckypaper, thus affecting the results of the permeability test. Acetone flows through the buckypapers faster than the other test fluids. It is possible that washing papers with isopropanol paves the way for acetone to flow through the nanotube network. Testing with silicone oil gave similar yet slightly lower permeability results even though silicone oil has a relatively high viscosity. Since the equation (3) used for determining permeability factors in the viscosity of the test fluid, viscosity should not influence the final permeability results. Figures 17 to 19 below show how the contact angle between buckypaper and water is much greater than that of buckypaper with acetone and silicon oil.
Figure 17: Interaction between the different buckypapers and D.I. water

Figure 18: Interaction between the different buckypaper and acetone
3.2. Porosity of BP

Figure 20 shows that SWNT buckypaper has many very small pores, only a few of which have diameters over 10 nm. The densely packed nanotube ropes help explain why the permeability of SWNT buckypaper is so low.
Porosity is the measure of void spaces in a material. Although porosity has an influence on permeability, neither can be used to directly calculate the other. Permeability is determined by the amount of void spaces and how well the void spaces are interconnected. Figures 21-23 compare porosity observations for each of the different buckypaper types to one another.

Figure 21: SEM image of washed, SWNT buckypaper (A) and washed, MWNT buckypaper (B)

Figure 22: SEM image of washed, SWNT buckypaper (A) and washed, mixed buckypaper (B)
The two comparisons shown in Figure 22 and Figure 23 explain why the permeability of mixed buckypaper is closer to that of SWNT buckypaper than the predicted values. It appears that the SWNTs in the mixed buckypaper fill in the larger voids that are contained in the MWNT buckypaper. This is consistent with sorting principles of porosity. Well sorted (grains of approximately all one size) materials have higher porosity than similarly sized poorly sorted materials (where smaller particles fill the gaps between larger particles). Figure 24 illustrates how some smaller grains can effectively fill the pores (where all fluid flow takes place), drastically reducing porosity and hydraulic conductivity, while only being a small fraction of the total volume of the material. MWNT buckypaper clearly has the highest amount of void space and would be the best candidate for initial experiments aimed at impregnating the buckypaper with resin.
3.3. Rheology of Liquid Resins

Rheology is the study of the flow of matter, primarily in the liquid state, but also as 'soft solids' or solids under conditions in which they respond with plastic flow rather than deforming elastically in response to an applied force. Resin rheology curves usually show how the viscosity of each resin decreases as temperature increases. The rheology curves of Epon 862 resin and Hexcel 8552 resin are shown Figures 25 and 26 respectively. The red line in Figure 25 shows that the viscosity of Epon 862 at room temperature is very close to the minimum viscosity of Hexcel 8552 resin. For experiments involving Hexcel 8552 resin the temperature for impregnation must be very close to 150 °C in order to give the resin the lowest viscosity to impregnate the buckypapers.
Figure 25: Rheology curve for Epon 862 resin

Figure 26: Rheology curve for Hexcel 8552 resin
3.4. Prepreg Manufacturing Processes

3.4.1. Solution Method

In the solution method a solvent is mixed with the resin in order to lower the resin viscosity. The BP is then placed into this resin solution. While in the resin solution the BP absorbs both resin and solvent molecules. After the BP is taken out of the solution, it is placed on a heated plate in order to dry. Drying the BP allows the solvent molecules to evaporate while leaving the resin molecules within the BP. The BP is then weighed to determine how much resin has been absorbed by the BP. This process is repeated until the BP reaches a desired resin weight.

3.4.2. Film Transfer Process

In order to produce prepreg with the film transfer method it must first be determined whether or not each type of BP can be wet-out during the impregnation stage of the film transfer process for each type of resin. Using the permeability of the BP and the viscosity of the resin discussed before, the time it takes to wet-out the BP can be calculated based on Darcy’s Law. Using the DSC and curing kinetics, the time for which a resin can be heated to achieve and maintain a certain viscosity, before it exceeds the maximum allowable degree of curing for B-stage (5%), can be calculated. If the time for wet-out exceeds the time for which the resin can be heated, then the film transfer must be reconsidered.
4. PREPREG MANUFACTURING PROCESS EXPERIMENTS

4.1. Solution Method Experiment

The solution method experiment was designed to mimic the solution route prepreg manufacturing process as shown in Figure 5 to make buckypaper prepreg samples. Then, a composite sample was fabricated using 3 layers of prepreg MWNT buckypaper, which were prepared using the solution method. In the experiment, MWNT buckypapers were coated with resin by dipping each piece of buckypaper in a resin solution. Epon 862 resin was selected as the candidate resin for this experiment because it has low viscosity and is easily dissolved into acetone. The resulting composite was then analyzed using C-scan testing, SEM images and DMA tensile testing.

During the solution process, a resin solution was first prepared by mixing acetone and Epon 862 resin together in a ratio of 9:1 respectively. Three buckypaper rectangles measuring 80 mm x 50 mm were cut and weighed to determine the target weight content of each buckypaper in the resultant prepreg samples. The goal was to create composite samples with 50% buckypaper weight fraction. The three prepreg buckypaper samples were then combined to form a three layer buckypaper composite. The composite was cured using the Carver 6” x 6” hot press and in accordance with the cure cycle parameters for Epon 862 resin.

The results from the C-scan test are given below in Figure 27. The images are taken from the same scan and differ only in the contrast of the image in order to highlight different areas.
The C-scan shows several bubbles in the upper portion of the composite and cracks and damage on the lower portion. The bubbles are thought to come from insufficient solvent evaporation before the combination of the prepreg layers. The lack of bubbles in the lower portion of the composite can be attributed to the cracks and damage which were likely created as a route for the trapped air bubbles to escape. This conclusion is supported by the presence of several tiny bubbles which can be seen around the cracked areas. The presence of excess resin, around the edges of the composite, shows that while lowering the viscosity of the resin to facilitate resin flow into the buckypaper layers, also increases the resin flow out of the buckypaper stack. The images taken from the SEM show that resin has not completely penetrated into CNT networks in the buckypaper. Figure 28 shows two SEM images of the surface of the buckypaper prepreg.
The tensile test results using DMA also confirm the poor quality of the composite. Each mechanical property is compared to thickness, as shown in Figures 29 to 31, to highlight how resin rich influences the properties of the composite panel. Because each tested sample contained three layers of buckypaper, and each buckypaper is assumed to have relatively uniform thickness, hence the thicker samples contain more resin. The resin rich samples have relatively low tensile modulus and large strain to failure.

Table 4: Tensile Test Results for Solution Method Composite

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
<th>Young's Modulus (GPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.63</td>
<td>0.05</td>
<td>8.22</td>
<td>44.38</td>
<td>58.48</td>
</tr>
<tr>
<td>2</td>
<td>4.8</td>
<td>0.05</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>3</td>
<td>5.31</td>
<td>0.05</td>
<td>7.64</td>
<td>67.71</td>
<td>97.92</td>
</tr>
<tr>
<td>4</td>
<td>3.03</td>
<td>0.04</td>
<td>8.37</td>
<td>22.48</td>
<td>34.15</td>
</tr>
<tr>
<td>5</td>
<td>2.48</td>
<td>0.04</td>
<td>11.54</td>
<td>61.58</td>
<td>60.22</td>
</tr>
<tr>
<td>6</td>
<td>3.07</td>
<td>0.04</td>
<td>9.27</td>
<td>60.44</td>
<td>75.63</td>
</tr>
<tr>
<td>7</td>
<td>2.64</td>
<td>0.05</td>
<td>8.65</td>
<td>42.24</td>
<td>51.71</td>
</tr>
<tr>
<td>8</td>
<td>2.3</td>
<td>0.03</td>
<td>11.53</td>
<td>41.21</td>
<td>41.71</td>
</tr>
<tr>
<td>9</td>
<td>2.22</td>
<td>0.03</td>
<td>11.57</td>
<td>72.69</td>
<td>65.06</td>
</tr>
</tbody>
</table>
Figure 29: Strain vs. thickness for solution process composite sample

Figure 30: Tensile strength vs. thickness for solution process composite sample
4.2. Film Transfer Method Experiment

The film transfer method experiment was designed to mimic the film transfer route prepreg manufacturing process. A composite was fabricated using 4 layers of MWNT buckypaper prepreg, which were prepared using the film transfer method, to evaluate impregnation quality. MWNT buckypapers were sandwiched between two layers of resin film to form a flexible, tape like prepreg. Hexcel 8552 resin was selected as the candidate resin for this experiment because it has high viscosity and can easily be pressed into a thin resin film. The resulting composite sample was then analyzed using non-destructive C-scan and DMA testing.

Four MWNT buckypaper squares measuring 4” x 4” were cut and weighed. Small pieces of Hexcel 8552 resin weighing from 250 mg – 350 mg were pressed, between two layers of Teflon release film, into resin film and the results are shown in Table 5. Peel off ability describes how the resin behaves when the two pieces of Teflon film, that the resin film is sandwiched between, are pulled apart. Good peel off ability is achieved when all of the resin remains on one of the Teflon films when separated, without wrinkles or stretch marks. Initial resin film press parameters; Time = 60 sec, Temperature 250°F, Pressure 2 MPa.
Table 5: Parameters for Resin Film Fabrication

<table>
<thead>
<tr>
<th>Hexcel 8552 Resin</th>
<th>Weight (mg)</th>
<th>Film Diameter (inches)</th>
<th>Peel Off Ability</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>250</td>
<td>4</td>
<td>Edges not good/weak spot</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>4.5</td>
<td>Good some wrinkling</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>4.5</td>
<td>Same as others</td>
</tr>
</tbody>
</table>

We further improved the resin film press parameters: Time 180 sec, Temperature 275°F, Pressure 2 MPa. The weight of resin was gradually increased until a large enough resin film was produced with 600 mg of Hexcel 8552 resin. Previous experiments have shown that increasing the pressure causes the resin film to become too thin and extremely difficult to separate from the Teflon release film. Eight resin films were prepared using the parameters described above. Peel off ability was improved by putting the resin film samples in the freezer immediately after pressing, and peeling the Teflon films apart immediately after the sample was removed from the freezer. Figure 32 below shows the prepared resin films.

Figure 32: Hexcel 8552 resin films prepared
The buckypaper squares were flattened onto the resin film by hand with relative ease. Another resin film was placed on top of the buckypaper to form a sample of MWNT buckypaper sandwiched between two layers of resin film. The sandwiched samples were pressed at parameters: Time 300 sec, Temperature 275°F, Pressure 1 ton, and placed in the freezer. The top layer of Teflon film was then peeled away to reveal a flexible prepreg buckypaper as shown in Figure 33. The flexibility of the buckypaper prepreg is shown in Figure 34.

Figure 33: Buckypaper prepreg: resin film/buckypaper/resin film sandwich

Figure 34: Flexibility of buckypaper prepreg
The four layers of the buckypaper prepreg were laid-up to create a single four layer composite sample. The lay-up of the resin films was very easy and almost identical to the lay-up of carbon fiber prepreg. The composite was cured in the hot press according to the cure cycle parameters provided for Hexcel 8552 resin. Figures 35 and 36 show the fabricated composites and its C-scan result.

Figure 35: Finished buckypaper prepreg composite

Figure 36: C-scan image of buckypaper prepreg composite
It can be seen that the Hexcel 8552 resin flows out of buckypaper stack rather than actually impregnating the buckypaper sheets. It is due to the permeability of buckypaper being too low for high viscosity resins to impregnate it, compared to carbon fiber pre-forms as discussed before. However, there are also limitations that prevent the use of additional pressure and force to push the resin into the buckypaper, because it causes the buckypaper to tear and deform. Hence, we need to use either stronger buckypaper materials and/or less viscous resins.
5. CASE STUDIES

5.1. Thin Panel of Multiple Buckypaper Layers/Epoxy Composites

In order to demonstrate how buckypaper can be used to shield sensitive electronic equipment we conducted a case study to fabricating extremely thin composite panels with buckypapers. The demonstration required that the composite panels be very light with a high concentration of carbon nanotubes (>30 wt. %). The panels were required to be larger than 8 x 8 inch squares, in order to create a box that could house some electronic equipment.

This case study resulted in producing three composite panels. Two panels were made using Epon862 resin through wet hand layup due the resin low viscosity, and one was made with Hexcel 8552 resin through the film transfer process. Each composite panel on consisted of two BP layers to improve handle ability. There were many challenges which arose in this investigation giving insight into how difficult it is to achieve a controllable and consistent fiber volume fraction when fabricating thin composites.

The most difficult part of this case study was achieving uniform resin distribution with such a limited amount of resin. The amount of resin available was limited due to the goal of producing a composite with a high nanotube volume fraction. It was also very difficult to lay up the large 8” by 8” pieces of BP very flatly on top of one another. Of the three panels produced the highest fiber weight fraction obtained was 38 wt. %. All of the three panels showed poor resin distribution. Among them, the best one is the panel make of the 8552 resin through the film transfer method. The C-scan images in Figures 37 -39 show the resin distribution in composite panels.
Figure 37: Photo of thin panel sample No. I (two layer MWNT buckypaper/EPON 862 nanocomposites), highest $W_e$ of all samples at 38 wt%, which appears to have uniform resin impregnation, surface is uneven and cracked (A); C-scan image showing delamination and resin poor areas as well as curvature from non-uniform resin areas (B).

Figure 38: Photo of thin panel sample No. II (two layer MWNT buckypaper/EPON 862 nanocomposites), $W_{CNT}$ is low at 24%, resin rich areas can be seen (A); C-scan image showing dark and gray areas indicate high density and resin rich areas respectively, while lighter areas represent defects (B).
Figure 39: Photo of thin panel III (A) made with two layer MWNT buckypaper and Hexcel 8552 resin using, film transfer method: Showing visually uniform resin distribution; C-scan image (B) showing uniform resin impregnation compared with other two samples using wet hand layup process; Black dots representing the weights that were used to flatten the sample to be c-scanned
The C-scan results show poor resin distribution and internal defects. Both of these occurrences contribute to poor mechanical properties. The main cause for the poor resin distribution was that either not enough resin was applied to the part to begin with or resins was not able to spreading evenly and penetrated into buckypaper sheet. If more resin had been used it would have had a better chance of uniformly spreading out during the early stages of vacuum bagging. However using more resin would eliminate the chance of producing a part which contained high buckypaper by weight. In conclusion, in order to create buckypaper composite parts with high CNT loading and uniform resin distribution, buckypaper/resin impregnation property need to be further studied. It is important to observe that although the panel made with Hexcel 8552 resin and the film transfer method, exhibits some curvature, but the C-scan of the sample shows significantly better resin distribution.

Dynamic Mechanical Analysis (DMA) is a method commonly used to study and characterize materials. In this test, a sinusoidal stress in applied to measure the strain in materials. The temperature of the sample or the frequency of the stress is often varied, leading to variations in the complex modulus. This can be used to reveal the glass transition temperature (Tg) of the material, as well as to identify transitions corresponding to other molecular motions.

For tensile testing using the DMA, the sample is clamped in a fixture and a force is applied to stretch the sample apart. The force consistently increases until the sample breaks. The force which is required to break the sample characterizes the sample’s tensile strength. The strain and young’s modulus are also obtained during the tensile test. The tensile properties of the two layer buckypaper/EPON composite panel were tested and summarized in Table 6.
Table 6: Tensile Test Results of Buckypaper/EPON 862 Composite Thin Panel

<table>
<thead>
<tr>
<th>Sample</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
<th>YM(GPa)</th>
<th>TS(MPa)</th>
<th>Strain(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.58</td>
<td>0.06</td>
<td>6.68</td>
<td>42.5</td>
<td>0.74</td>
</tr>
<tr>
<td>2</td>
<td>3.2</td>
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<td>4.38</td>
<td>43.54</td>
<td>1.88</td>
</tr>
<tr>
<td>3</td>
<td>3.2</td>
<td>0.09</td>
<td>2.51</td>
<td>51.9</td>
<td>1.72</td>
</tr>
<tr>
<td>4</td>
<td>2.89</td>
<td>0.11</td>
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<td>49.47</td>
<td>1.98</td>
</tr>
<tr>
<td>5</td>
<td>3.17</td>
<td>0.09</td>
<td>3.73</td>
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<td>1.18</td>
</tr>
<tr>
<td>6</td>
<td>3.07</td>
<td>0.09</td>
<td>3.72</td>
<td>22.59</td>
<td>1.47</td>
</tr>
<tr>
<td>7</td>
<td>3.3</td>
<td>0.08</td>
<td>3.12</td>
<td>45.34</td>
<td>1.56</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>3.94</td>
<td>41.49</td>
<td>1.50</td>
</tr>
<tr>
<td>Dynamic Test</td>
<td>Width (mm)</td>
<td>Thickness (mm)</td>
<td>Storage Modulus</td>
<td>Tg (°C)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4.36</td>
<td>0.09</td>
<td>5572 MPa</td>
<td>81.56</td>
<td></td>
</tr>
</tbody>
</table>

The thin panel with the highest buckypaper loading was tested using the DMA to characterize mechanical properties. Results can be seen in Table 6. As expected the tensile strength is considerably low and inconsistent. These tensile strength values are most closely related to the strength of the neat EPON resin, but the Young’s modulus noticeably increased due to high CNT loading.

5.2. Battery Shell Study

The goal of the battery shell study was to produce thin cylinder shaped composites measuring 25 mm in diameter and 2 inches in length using CNT buckypaper or thin sheets. The cylinders needed to have a high fiber volume fraction to promote electrical conductivity. The challenges included making a mold to fabricate the BP cylinders in which the cylinders could be removed after final curing. In order to provide consistent geometry and a smooth surface very little space was allowed in the mold for resin to occupy. This meant that the resin layer between the two pieces of BP in the mold must be very thin and would not be liberated during curing.

This challenge was overcome by making BP prepreg with the solution method and use of high strength CNT buckypaper from Nanocomp. The buckypaper prepreg of 50 wt. % CNT concentration was achieved and used to make the parts. Figure 40 shows
the produced battery shells. The results showed that the composite cylinders had 150 um thickness and high electrical conductivities over 800 Siemens/cm. It has the potential to provide lightweight and high conductive solution for battery applications.

Figure 40: Buckypaper composite battery shells: (A) Mold parts for battery shells; (B) BP battery shells made of buckypaper/EPON 862 nanocomposites

The results for mechanical testing were limited by the number of samples available and cost of materials. Two samples were tested using the DMA for storage modulus and Tg. The results are shown below in Table 7. Due to the use of the strong buckypaper and CNT content, the buckypaper composites show substantially improved mechanical properties, compared to the thin panel case study.

Table 7: Storage Modulus and Tg Results of Buckypaper/EPON 862 Shell

<table>
<thead>
<tr>
<th>Sample</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
<th>Storage Modulus (MPa)</th>
<th>Tg(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.75</td>
<td>0.01</td>
<td>85865</td>
<td>158</td>
</tr>
<tr>
<td>2</td>
<td>4.14</td>
<td>0.02</td>
<td>46075</td>
<td>155</td>
</tr>
</tbody>
</table>
5.3. Buckypaper/Carbon Fiber Composites

In this case study, two large (10” x 10”) layers of BP prepreg were placed on each side of an uncured carbon fiber prepreg stack comprised of six prepreg layers to make buckypaper/carbon fiber hybrid composites for improving both mechanical and electrical properties of the base carbon fiber panel. The BP prepreg made with EPON resin and resin solution method and carbon fiber prepreg were cured simultaneously in a mold to create the final composite part. The part was c-scanned and sent to an industrial partner to conduct mechanical tests.

A steel mold was designed and machined for fabricate the part as shown in Figure 41. The mold contained a single rectangular cavity measuring 20.7 inches x 10.43 inches. The depth of the mold was determined by calculating the cured thickness of the six carbon fiber layers that would result in a composite which contained 48% carbon fiber by weight. The depth was calculated to be 0.0898 inches.

The six carbon fiber prepreg layers were cut and laid-up to create a six layer carbon fiber prepreg composite. Four 10”x 10” layers of SWNT buckypaper provided by Nanocomp Technologies were then prepared using Epon 862 and the solution method. The resulting prepreg buckypapers were then placed on each side of the carbon fiber
prepreg stack, creating a carbon fiber composite with two layers of buckypaper prepreg on each side. The entire assembly was vacuum bagged for 1 hour and then placed into the mold for final part curing following curing parameters as shown in Figure 42. Figures 43 and 44 show the panel fabricated the carbon fiber only control sample and buckypaper/carbon fiber composite panels and their C-scan results. The composite samples show good quality.

Figure 42: Cure cycle for buckypaper/carbon fiber part
Figure 43: Finished carbon fiber panel without buckypaper (A) and with two layers of buckypaper on each side (B)

Figure 44: C-scan images of buckypaper/carbon fiber composite panel showing defect-free and uniform impregnation
6. CONCLUSIONS

The objective of this project is to study nanostructure-permeability relationships of different types of buckypaper materials, and explore effective prepreg processes to make buckypaper composites with greatly increased consistency, quality, CNT weight fraction and uniformity in the resulting products. The experimental results show that buckypapers have very low permeability, about 8-12 orders lower than those of carbon fiber preform cases, and also sensitive to liquid polarity due to their nanoscale porosity and large surface area. The average permeability values of SWNT buckypapers are 6.45e-21 m², 1.34e-20 m², and 1.41e-20 m² for water, silicone oil and acetone respectively due to their nanoscale porosity and possible strong interactions with the test fluids. The permeability values of MWNTs are higher than those of SWNT samples. The mixed SWNT/MWNT buckypaper permeability values are fallen between SWNT and MWNT cases, but less than the Rule of Mixture prediction due to dense packing effect of different size particles.

Buckypaper has an extremely low permeability which makes resin impregnation very challenging. Two prepreg methods were attempted to make buckypaper prepreg materials with different resins. Both solution and resin film transfer prepreg processes were studied to pre-impregnate buckypaper to achieve 50 wt. % CNT concentration. The late one showed better quality in the resultant nanocomposites, but difficult for high viscosity resins. Three case studies were conducted to evaluate the feasibility of these methods for actual buckypaper fabrication and quality control. The case of thin composite panels using only two layer buckypapers show that it is difficult to make sizable and good quality part because the buckypaper materials used are very thin and fragile characteristics. For the battery shell and buckypaper/carbon fiber composite case studies, high strength buckypapers were used to enhance processability and performance. The results show that both prepreg methods can achieve much better quality consistency and electrical and mechanical performance. Although this research provided limited successes, many of the lessons learned could be useful for future developments in buckypaper prepreg processes and their applications.
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BIOGRAPHICAL SKETCH

Bryant Click was born in Tallahassee, FL on April 13, 1984. From a very young age he enjoyed building and design. Legos being his favorite childhood toy were the first hint that one day he would be an engineer. Bryant was tested and admitted into the gifted program before he started first grade and excelled in science and math throughout his years of grade school. He attended The Florida State University for his Industrial and Manufacturing Engineering undergrad and continued to pursue his Masters degree in Materials Engineering specializing in composite technology. Bryant has put his academic education to use, working for General Dynamics Land Systems as an Industrial Engineer and HPMI as the senior member of the nanocomposite manufacturing group.