Improvement of Microtome Cutting Process of Carbon Nanotube Composite Sample Preparation for TEM Analysis

Sarah Trayner
IMPROVEMENT OF MICROTOME CUTTING PROCESS OF CARBON NANOTUBE
COMPOSITE SAMPLE PREPARATION FOR TEM ANALYSIS

By

SARAH TRAYNER

A Thesis submitted to the
Material Science and Engineering Program
in partial fulfillment of the
requirements for the degree of
Master of Science

Degree Awarded:
Spring Semester, 2014
Sarah Trayner defended this thesis on April 11, 2014.
The members of the supervisory committee were:

   Richard Liang
   Professor Directing Thesis

   Okenwa Okoli
   Committee Member

   Mei Zhang
   Committee Member

The Graduate School has verified and approved the above-named committee members, and certifies that the thesis has been approved in accordance with university requirements.
This thesis is dedicated to my mother and sister for their love, endless support, and inspiration.
ACKNOWLEDGMENTS

I would like to thank my advisor Dr. Liang for the continuous support of my M.S. study and research. His motivation, immense knowledge, and guidance have provided me with a unique skill set to excel in any endeavor. Also, I would like to thank the rest of my thesis commit: Dr. Okenwa Okoli and Dr. Mei Zhang for encouraging me to think “outside of the box.”
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ABSTRACT

As research progresses towards nanoscale materials, there has become a need for a more efficient and effective way to obtain ultra-thin samples for imaging under transmission electron microscope (TEM) for atomic resolution analysis. There are various methods used to obtain thin samples (<50 nm in thickness). However, most of the resultant TEM images of soft materials, such as CNT/epoxy composites, are of poor quality due to the sample cutting difficulties. Such poor quality samples are characterized by uneven sample thicknesses, objective overlapping, overall darkness due to large thickness, and defects such as cutting scratches.

This research is a continuous effort to study and improve the ultra-microtome cutting technique to provide an effective and reliable approach of obtaining an ultra-thin (25-50 nm) cross section of a CNT/polymer composite for high resolution TEM analysis. Improvements were achieved by studying the relationships between the chosen cutting parameters, sample characteristics and TEM image quality. From this information, a cutting protocol was established so that ultra-thin sample slices can be achieved by different microtome operators for high resolution TEM analysis. In addition, a custom tool was created to aid in the sample collection process.

In this research, three composite samples were studied for both microtome cutting and TEM analysis: 1) Unidirectional (UD) IM7/BMI composite; 2) Single-layer CNT buckypaper (BP)/epoxy nanocomposite; 3) 3-layer CNT BP/BMI nanocomposite. The resultant TEM images revealed a clear microstructure consisting of amorphous resin and graphite crystalline packing. UD IM7/BMI composite TEM results did not reveal an interfacial region resulting in a need for even thinner sliced cross sections. TEM results for the single-layer CNT BP/epoxy nanocomposite revealed the alignment direction of the nanotubes and numerous stacks of CNT bundles. In addition, there was visible flattening of CNT packing into dumbbell shapes similar to results obtain by Alan Windle. TEM results for the 3-layer CNT BP/BMI nanocomposite revealed uniformly cut resin. However, when the diamond knife reached graphite crystalline regions, the nanotube either became deformed into a cone-like structure, was cut at a thicker thickness than the resin, or folded over onto itself. This is most likely a result of the nanotubes high mechanical properties in response to the stress of cutting.

Key words: TEM, ultra microtome, nanocomposites, carbon nanotube
CHAPTER ONE

INTRODUCTION

One of the most powerful microscopic tools used today is the transmission electron microscope, or TEM. The TEM utilizes a process in which electromagnetic lenses focus emitted electrons into a thin beam, which in turn passes through the sample being observed [1-3]. The interaction that takes place between the sample and the energetic electrons results in a high resolution, black and white image which can provide topographical, morphological, compositional, and crystalline information of samples [4]. In addition, the TEM has a maximum potential spatial resolution down to 1 Å or lower which makes it possible to study interface and material on a molecular level.

This research is a continuous effort to improve the ultra-microtome cutting technique in order to obtain ultra-thin (25 nm or less) sample slices of CNT/polymer nanocomposites for TEM analysis. Ultra-thin sample slices are obtained by using a diamond knife to create a micro crack that progressively propagates into the sample based on the areas of least resistance [1,5,6]. This process can be utilized at room temperature or cryogenic temperatures producing slices ranging from 5 nm to 500 nm. Because of the desired thickness control of 25 nm, this appears to be a promising method for TEM sample preparation.
CHAPTER TWO

PROBLEM STATEMENT

2.1 TEM Image Quality Classifications

High quality TEM images are electron beam transparent, have uniform thickness, limited defects and/or artifacts, and the microstructure of the sample can be clearly identified [3,8]. Obtaining these optimal attributes can be challenging because most techniques, both physical and ion abrasive, can cause various damages to the sample which could substantially reduce the quality of the image. Figures 1-3 are examples used to discuss the TEM image quality and used as the baseline images for qualitative quality comparison in this study.

![High quality TEM image of MWNT](image)

Fig. 1. High quality TEM image of MWNT [9].

Figure 1 illustrates a high quality TEM image of a multi-walled carbon nanotube (MWNT). In this image, the microstructure is clearly visible in that the individual walls can be counted and the amorphous regions can be identified. This is also true for Figures 2 and 3.
Fig. 2. Baseline TEM images. (a) Pristine CNT [10]. (b) NH$_2$-CNT [10].

Fig. 3. Baseline TEM image of DWNT [9].

On the other hand, poor quality TEM images are characterized by uneven sample thicknesses, inability to distinguish the interface due to overlapping, defects from chemical methods, and/or artifacts from cutting methods [3]. Figure 4 illustrates a poor quality image of a
carbon fiber/resin composite. In this image, there appears to be uneven thicknesses characterized by highly pronounced dark and light areas. In addition, the sample lacks transparency and the microstructure cannot be distinguished.

Fig. 4. Varied thicknesses of carbon fiber/resin composite sample.
CHAPTER THREE

MOTIVATION

The motivation of this research is to investigate the molecular structure including the graphene packing/crystalline microstructure, the edge interaction with the resin, and the interphase region of nanotube/polymer composites by obtaining ultra-thin cross sections (25-50 nm) for TEM analysis. In literature, there are various methods used to obtain thin samples for TEM analysis [12-20], however, most of the resulting TEM images are of poor quality. Poor quality TEM images appear dark, have uneven sample thicknesses, overlapping, as well as defects. In addition, most of the methods used to obtain ultra-thin samples are not usually repeatable. This research will focus on studying and optimizing the ultra-microtome cutting technique in order to provide a repeatable means of obtaining ultra-thin cross sections that result in high quality TEM images, specific for CNT/epoxy and carbon fiber/epoxy composites. Improvements will be achieved by studying the relationships between the chosen cutting parameters and sample materials. In addition, the resulting high quality TEM images will allow us to extract more information on a molecular level of the nanotube/polymer composite interface.
CHAPTER FOUR

RESEARCH OBJECTIVES

In this research, the molecular structures of the following composites will be investigated: unidirectional (UD) IM7/BMI composites, carbon nanotube (CNT) buckypaper (BP)/epoxy nanocomposites, and CNT BP/BMI nanocomposites. In addition, these select composites will be cut using the ultra-microtome in order to obtain 25 nm or less thick cuts and then analyzed under the TEM. The TEM images will provide us necessary knowledge on the nature of the microstructure including the graphene packing/crystalline structure, the edge interaction with resin, and the interfacial bonding between the two constituents. The major objectives include:

- Study the effects of material types and characteristics on parameter selection of ultra-microtome process
- Improve ultra-microtome cutting technique
  - Compare to baseline images
  - Develop microtome cutting procedure for room temperature and cryogenic temperatures (ensure repeatability)
- Identify fiber/resin interface thickness, fiber structures, & load transfer evidence for respective samples
  - UD IM7/BMI composites, Aligned single-layer CNT buckypaper (BP)/epoxy nanocomposites, and Aligned 3-layer CNT BP/BMI nanocomposites

Completion of this research will advance the knowledge and understanding on how to obtain ultra-thin (≤ 25 nm) slices for TEM investigation. In addition, from the TEM images, we will be able to observe the interaction (nanotube with nanotube and nanotube with resin) on a molecular level.
CHAPTER FIVE

LITERATURE REVIEW

TEM samples can be prepared by both physical and ion abrasion methods in which the end goal is to obtain a uniformly thin sample with less defects and artifacts. Physical methods involve cutting by means of inducing fracture or using ultra-sonication and ion abrasion methods using active ionic particles to thin the sample [11]. Table 1 provides a summary of the physical and ion abrasion methods used for TEM sample preparation.

Table 1: Summary of TEM sample preparation techniques

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>Advantage</th>
<th>Disadvantage</th>
<th>Ref. #</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ultramicrotome cutting</td>
<td>Cuts thin samples using diamond knife</td>
<td>Cuts ultra-thin (5-100 nm) sample slices, ability to cut at different temperatures, cross sectional and longitudinal cuts</td>
<td>Tearing, or crushing can occur, trial and error, highly trained operator, expensive machinery</td>
<td>1,3,5,6,11</td>
</tr>
<tr>
<td>Ultrasoundation</td>
<td>Scraping nanotubes from substrate surface and sonicating</td>
<td>Simple sample preparation</td>
<td>Mechanical defects, structural damage, no thickness control</td>
<td>9,12,13</td>
</tr>
<tr>
<td>Ball milling</td>
<td>Grinds materials into fine powder</td>
<td>Produces fine nm size particles, uniform dispersions, can induce chemical reactions</td>
<td>Microstructure damage, surface contamination, no control on particle morphology</td>
<td>8,9,11,14</td>
</tr>
<tr>
<td><strong>Ion Abrasion</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ion beam thinning</td>
<td>Ion beam thins sample down to electron transparency</td>
<td>No mechanical damage</td>
<td>Thermal and surface damage, artifacts, redeposition, non-selective</td>
<td>8,11,15,16</td>
</tr>
<tr>
<td>Focused ion beam thinning (FIB)</td>
<td>Focused ion beam thins sample down to electron transparency</td>
<td>Highly anisotropic, independent of material composition, ability to etch ultra-thin samples</td>
<td>High ion damage, thermal damage, residue, redeposition</td>
<td>8,11,17,18</td>
</tr>
</tbody>
</table>
5.1 Physical Methods

5.1.1 Ultra-microtome Cutting

Cutting using diamond ultra-microtomy has been widely used for obtaining thin samples for TEM analysis. For example, in 1997, Feng and coworkers conducted a study involving cutting cross sectional TEM samples of carbon nanotube bundles [19]. The carbon nanotube bundles were produced using the arc discharge method and then, the large nanotube bundles were picked out with tweezers and parallel embedded in an epoxy mold [19]. After curing, slices with thicknesses as thin as 20-30 nm were cut using an ultra-microtome with a diamond knife. The as-cut slices were thin enough for TEM analysis and were prepared by dropping nanotube/ethanol suspensions on a holey carbon TEM grid [19]. Figure 5 illustrates an image of an elliptical cross section of a carbon nanotube. Even though this image is of poor quality due to the overall darkness, the carbon nanotube microstructure can still be viewed. The microstructure shows that abnormal fringe spacing exists in the lower right part indicated by the curved arrow [19]. In addition, some edge type dislocations are indicated by the white arrow heads [19]. Figure 6 illustrates two more cross...
sectional images of carbon nanotubes. Figure 6a illustrates a collapsed core, while Figure 6b illustrates a collapsed nanotube viewed in the longitudinal direction. These TEM results confirmed that there are many defects in the microstructure of carbon nanotubes including Shockley and Frank type edge dislocations and variable fringe spacing leading to a polyhedral and elliptical shape of nanotubes [19]. In addition, the abnormal structure features are closely related to the non-equilibrium growth of nanotubes in the arc discharge process [19].

Wong and coworkers studied the mechanical properties of carbon nanotube reinforced polystyrene rods and CNT reinforced epoxy thin films, as well as, examined the CNT/polymer interface under TEM [20]. In this study, CNT/PS composite rods were tested under a tensile tester and the tensile failure surfaces were then embedded in epoxy to prepare for TEM analysis [20]. Once the embedded epoxy composite cured, samples were cut into 70 nm thin slices at room temperature by a microtome ultra-cut with a cutting speed of 2 mm/s [20]. This ultra-microtome cutting technique was also used to investigate the fracture surface of the CNT/epoxy thin film samples. Figure 7 illustrates TEM images of CNTs embedded in PS or epoxy. In Figure 7a, the dark circular region in the middle is the cross section of the CNT embedded in the PS matrix [20]. The other dark areas are randomly oriented CNTs. This image provides limited information on the

Fig. 6. Cross section of: (a) Nanotube with collapsed core. (b) Collapsed nanotube viewed in longitudinal direction [19].
microstructure of the CNT because of the overall darkness of the image and the uneven cutting patterns. Figure 7b is a slightly better TEM image. This is because the CNT-PS interface is visible and more information can be extracted on the microstructure. Specifically, the change in CNT diameter which promotes mechanical interlocking [20]. Figure 7c shows a TEM image of the CNT/epoxy interface. Non-uniform CNT diameter and bends indicated by the arrows are visible [20]. However, because the image is not cut thin enough, the CNT microstructure is not clear. Finally, Figure 7d illustrates a longitudinal section of CNT. Here we can see epoxy molecules covering the CNT which is known as overlapping [20].

Fig. 7. TEM images of: (a) CNT embedded in PS matrix. (b) CNT/PS interface. (c) Non-uniform CNT diameter and bends (indicated by arrows). (d) Longitudinal section of CNT covered by epoxy molecules [20].
5.1.2 Ultrasonication

Ultra sonication is one of the simplest processes for TEM sample preparation [13]. It consists of scraping grown nanotubes from the surface of a substrate and then dispersing the scraped nanotubes into ethanol, methanol, or acetone by ultrasonic agitations [13]. Finally, the suspension is dropped onto a holey carbon grid. Du and coworkers used this TEM sample preparation technique to investigate the structure of carbon nanotubes [12]. Similar to the previously stated, Du and coworkers sonicated the nickel substrates with CNTs in a small amount of ethanol for 5 minutes after CVD growth and then dropped the suspension onto a copper grid [12]. Figure 8 illustrates a TEM image of a nanotube wall fragment. Here, you can see the 0.34nm spacing of the graphitic layers and in the inset is an enlargement of the marked area which shows defect structure in the CNT wall [12]. This defect could be a result of the chosen TEM sample preparation method.

![Fig. 8. Nanotube wall fragment [12.]](image)

5.1.3 Ball Milling

Recently, Chu and coworkers investigated the interface microstructure and mechanical properties of Cu-Cr composites using the TEM [14]. The TEM sample preparation process involved ball milling the composite into a fine powder, sintering the powder, and then surface grinding to remove the graphitic layer [14]. This is a lengthy process which can damage the
microstructure or lead to surface or interface contamination [9]. Figure 9 shows a TEM image of the CNT/Cu-Cr interface. Here you can distinguish between the matrix, interface, and CNT

![Fig. 9. CNT/Cu-Cr interface [9].]

5.2 Ion Abrasion Methods

5.2.1 Ion Milling

Zheng and coworkers used TEM analysis to study the microstructure of carbon fiber/polycarbosilane-derived SiC composites [15]. In order to prepare the sample for TEM imaging, the samples were polished down to a 40-50 µm thickness and because the samples are weak in the transverse direction, a molybdenum mesh with a hole diameter of 1mm was stuck to both sides of the sample with epoxy resin [15]. This was used to prevent the sample from being damaged during ion milling. Then, the samples were thinned by ion-milling at an angle of 25° for 4 h and then 15° at 5 kV until perforation [15]. In addition, the sample was not rotated during ion milling and the direction of the ion beam was vertical to the alignment of the carbon fiber in the CF/SiC samples to prevent the matrix from separating [15]. Figure 10 illustrates a TEM image of the (002) lattice of M70. Here, we can see the graphene sheets ordered and stacked parallel to the fiber axis [15]. This is a feature of graphite made from mesophase pitch and because of the highly ordered structure of M70, this can explain why M70 has a high elastic modulus of 700 GPa [15].
Figure 11 is a low magnification TEM image that shows the interface of M30/SiC. Here, the interface between M30 and the matrix appears rough and the M30 and matrix bond to each other appears tightly bonded [15].

Also, Suzuki and coworkers studied the microstructure of Pitch based carbon fibers and the interaction of fibers with aluminum coated fibers under TEM [16]. The samples were made thin enough for TEM analysis by using Ar ion etching. Figure 12 illustrates the various interfaces of NS-20/Al, p-55/Al, JIS/Al, and NS-60/Al. The prefix NS represents NS-series coal pitch based
fibers without sizing and JIS represents JIS-series petroleum-pitch-based fibers without sizing [16].

![TEM images](image)

Fig. 12. TEM images of: (a) NS-20/Al interface. (b) P-55/Al interface. (c) JIS-70/Al interface. (d) NS-60/Al interface with up close magnification on bonding of microstructures [16].

These TEM images are good because the interface can be clearly viewed separating the AL from either the NS-20, P-55, JIS-70, or NS-60. Also, in Figure 12d, Suzuki and coworkers provide an up-close image of the interfacial bonding between NS-60 and Al and the different structures that accompany each.

5.2.2 Focused Ion Beam (FIB)

Ke and coworkers studied TEM sample preparation using FIB for carbon nanotube interconnects [17]. TEM samples were prepared by FIB and have been used to obtain lamellae of patterned samples containing CNTs grown inside contact holes [17]. In order to preserve the CNTs and avoid deterioration during milling, a dual cap Pt protection layer and an extensive 5 kV
cleaning procedure was implemented [17]. TEM results show that the inner shell structure of the CNTs were preserved and, as a result, shows that FIB is a useful technique to prepare TEM samples of CNT interconnects [17]. Figure 13 illustrates a lamella containing pieces of CNTs. This image is of poor quality because the image is very dark and there are small areas of dark contrast visible, which could be attributed to small clusters of Pt metal. Also, distinguishing the different microstructures poses a challenge.

![Fig. 13. Lamellae containing pieces of CNTs [17].](image)

A more recent study conducted in 2010, Naito and coworkers used the focused ion beam (FIB) milling technique to thin down their samples of carbon nanotubes grafted onto PAN and pitch based carbon fibers [18]. This process consisted of grafting the carbon fibers with CNTs and then molding the sample in room temperature curing epoxy resin [18]. Finally, the samples were cut to <100 nm thin sections using a focused ion beam [18]. Figure 14 illustrates the TEM image results. Figure 14a depicts a longitudinal view of the T1000GB PAN CF, while Figure 14b depicts the cross section view. From these two images, we can see that PAN-based CF shows a parallel arrangement of only small polycarbon layers [18]. Also, these images have a variety of disclinations (line defect) which is a result of a rotational symmetry violation. Also, on another
note, these images are of poor quality because they are unclear, show wrinkled layer packages, defects, and exhibit overlapping. Figure 14 illustrates the longitudinal view and cross section view of K13D pitch CF, respectively. Here, parallel layers as in the graphite lattice can be found [18]. These images also appear to be covered with catalyst and are of a larger catalyst [18].

Fig. 14. TEM images of (a) Longitudinal view of T1000GB PAN CF. (b) Cross section view of T100GB PAN CF. (c) Longitudinal view of K13D Pitch CF. (d) Cross section view of K13D Pitch CF [18].
CHAPTER SIX

TECHNICAL APPROACH

6.1 Ultra-microtome Cutting Technique

This research focuses on improving the ultra-microtome cutting process for TEM sample preparation. The study includes an understanding on the overall cutting process, setup procedures, sample preparation, and improvement of sectioning processes. Finally, a protocol of CNT composite sample preparation will be proposed.

The ultra-microtome is a valuable tool used to produce ultrathin slices (25-100 nm) by creating a micro-crack that progressively propagates into the sample [1,5,6]. This micro-crack occurs based on areas of least resistance in which the fracture is initiated by the edge of a freshly cut glass or diamond knife [8]. The ultra-microtome can be operated at both room and cryogenic temperatures. Selection of the specific setup should be based on the hardness and plasticity of the samples. The samples must be hard enough to produce a fracture without crushing and plastic enough to ensure that the fracture spreads without breaking the sample into small fragments [21-23]. For example, if the sample material is too soft, the material can be made harder by cutting it at cryogenic temperatures. On the other hand, if the sample is sufficiently hard, cutting at room temperature would be adequate. Also, if the sample is in powder form or cannot be firmly mounted, the sample can be embedded in an amorphous resin [23].

Basic setup for the ultra-microtome consists of a specimen holder assembly and a knife support system. Figure 15 illustrates the specimen holder assembly which includes the cutting

![Fig.15. Specimen holder assembly [8].](image-url)
knife (either glass or diamond), sample, specimen holder, and goniometer. The goniometer is crucial in that it allows for rotation and tilt of the sample. The knife support system consists of a knife clamp, support clamp adjustment, and knife tilt adjustment which can be viewed in Figure 16. In the cutting process, the sample is firmly attached to the arm, which can move either manually or automatically in a “D-shaped” trajectory. When cutting, the straight-line movement occurs in front of the knife and has a lateral clearance, while the rounded or retracting motion occurs after the sample has been cut. At each passage, the arm undergoes an automatic piezoelectric advance which can be programmed between 30-200 nm. In addition, two advancement ranges are possible, either between 30-100 nm, with increments of 2 nm, or between 150 nm and 2 µm with increments of 10 nm.

The major parts of this research include:

1. Develop setups for ultra-microtome room temperature and cryogenic temperatures cutting of CF and CNT composites
2. Study and develop process procedures for ultra-microtome room temperature and cryogenic sectioning
3. Investigate sample preparations and cutting parameters to obtain high quality TEM images utilizing above procedures
6.1.1 Setup Procedure for Room Temperature and Cryogenic Temperatures

When preparing to cut a sample, the respective process procedure should be followed as shown in Figure 17.

Room Temperature Setup

1. Locate armrest, knife support, and segment arc
2. Slide armrest onto Ultracut UC6 microtome machine
3. Guide segment arc into specimen arm of Ultracut UC6
   - Tighten screw located on specimen arm
4. Slide knife support onto knife stage
   - Lock into place by turning lever clockwise on knife stage
5. Check that segment arc and knife support are not touching

Cryogenic Setup

1. Locate and mount the EM FC6 cryogenic setup to the Ultracut UC6 as shown in Figure 18:
2. Use 3 mm Allen key to turn hand wheel of Ultracut UC6 to move specimen arm to highest position
3. Guide cryo specimen arm into specimen arm of Ultracut UC6

Fig.17. Room temperature setup: (A) Specimen holder. (B) Diamond knife. (C) Water pump mechanism.
• Use 3 mm Allen key to lock cryo specimen arm in place
• Check that gap between cryo specimen arm and cryochamber is parallel with a distance of 0.5 to 1 mm

4. Lock FC6 cryochamber to chassis of Ultracut UC6 by turning the lever counterclockwise
5. Lock knife plate of FC6 cryochamber to the knife stage of Ultracut UC6 by turning lever clockwise
6. Turn hand wheel to check that no contact is made between cryo specimen arm and cryochamber
7. Connect the LN2 pump
   • Connect LN2 hose with threaded connection to FC6 cryochamber and to the pump
   • Fill dewar with LN2 using safety gloves and eyewear
   • Slowly lower pump into dewar. Hold pump until boiling subsides and then continue to lower.
8. Check that all connections are made and plugged into wall outlet

Fig. 18. Cryogenic setup: (A) Dewar. (B) Liquid nitrogen pump. (C) Control unit. (D) Cryogenic chamber. (E) Ultra-microtome.
6.1.2 Sample Preparation

Prior to cutting the sample, the sample must be trimmed by machining into a pyramidal shape. The pyramidal shape consists of a very small surface area at one end with the larger end placed into the specimen holder. Also, both ends must be parallel to one another [25]. The pyramidal shape, also known as the sample block, is illustrated in Figure 19.

In addition, the cutting edge must be the appropriate surface size to ensure that the desired thickness is achieved. Table 2 illustrates the thickness guidelines.

<table>
<thead>
<tr>
<th>Section thickness</th>
<th>Cutting surface size</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 µm</td>
<td>A few millimeters</td>
</tr>
<tr>
<td>100 nm</td>
<td>1 mm</td>
</tr>
<tr>
<td>80 nm</td>
<td>0.8 mm</td>
</tr>
<tr>
<td>70 nm</td>
<td>0.5 mm</td>
</tr>
<tr>
<td>60 nm</td>
<td>0.3 mm</td>
</tr>
<tr>
<td>50 nm</td>
<td>0.2 mm</td>
</tr>
</tbody>
</table>

Next, the assembly is mounted onto the microtome, against the knife and is gently moved as close to the sample as possible. When cutting ultra-thin sections, the knife is fixed, and the specimen is advanced automatically using a very low cutting speed (1-4 mm/s) [8,25].
6.1.3 Process Procedure for Sectioning

Although the ultra-microtome has a section thickness control, the true thickness of the sections should be determined from their interference colors [25]. When white light is reflected from the bottom and top of the section, the light will be differentially slowed down depending on the thickness of the section [25]. As a result, the phase of the light will change and these emerging wavelengths will interfere with those reflected from the water’s surface [25]. This gives the sections a particular color [25]. Figure 20 illustrates the interference card that should be used to check the section’s thickness. Next, the sectioning process for both room temperature and cryogenic temperature sectioning will be discussed.

![Interference card showing color spectrum.](image.png)

**Room Temperature Sectioning**

1. Insert sample into specimen holder
2. Insert specimen holder into segment arc and tighten screw located on specimen arm
3. Place and tighten glass knife onto knife support
4. Slide knife support onto knife stage
5. Adjust knife support so glass knife is directly in front of sample slightly touching [8,10,23]
6. Lock knife support by turning lever clockwise located on knife stage [8]
7. Begin trimming manually until glassy surface is achieved
8. Interchange glass knife with boat diamond knife
9. Fill water up to edge of boat diamond knife creating a meniscus [25]
10. Fix diamond boat knife and approach sample through automatic movements
11. Begin sectioning
12. Locate cat whisker and perfect loop
   - Use cat whisker to slide cut section off of diamond knife edge
   - Pick up cut section using perfect loop or slide cut section onto perfect loop using cat whisker
   - Place sample onto copper grid
      ~or~
   - After cut section is picked up, place in glass vial filled with DI water and sonicate for 10 min
   - Use perfect loop to pick up cut section in glass vial
   - Place onto copper grid
13. Check under ultra-microtome microscope and SEM
14. View and analyze under TEM

**Cryogenic Sectioning**

1. Insert cryo specimen holder into specimen arm
   - Lock cryo specimen holder using torque limited screw using 3 mm Allen key
   - Lock cryo holder in the 0° position
2. Lock cryo holder in the 0° position
3. Insert knives into the knife holder
   - Set desired angle (typically 6°) [8,9,25]
• Insert appropriate knives either diamond trimming tool and diamond cryo knife or glass knife and diamond cryo knife (diamond knife can be either 35° or 45°) [8,9]
• Lock knife by turning lock screw clockwise located next to diamond knives
4. Insert knife holder
• Attach knife holder to knife plate by locating pin on knife plate and then place on corresponding hole in knife holder
• Knife holder is held in position by a magnet
5. Cool cryochamber to desired temperature
6. Insert specimen into cryo specimen holder
• Lock specimen in place using 3 mm Allen key [8]
7. Rotate knife holder into trimming position
8. Start trimming
9. Unlock and rotate knife holder into sectioning position
• Lock in place using 3 mm Allen key
10. Begin sectioning
• Ultra-thin sections: knife is fixed, approach specimen through automatic advancements [21,25]
• Thin sections: move knife as close as possible to sample without touching [21,25]
11. Locate perfect loop and dip in DI water and then, pick up copper grid
12. Hold perfect loop (with attached copper grid) in one hand and cat whisker in other hand
• Use cat whisker to collect cut sample from edge of diamond knife
• Place cut sample onto copper grid attached to perfect loop
• Place perfect loop (with attached copper grip) on filter paper
13. Check sample under ultra-microtome microscope and scanning electron microscope (SEM)
14. View under transmission electron microscope (TEM)
CHAPTER SEVEN

TECHNICAL CHALLENGES

Major technical challenges involved when utilizing the ultra-microtome to cut cross sectional and longitudinal cuts. These challenges include:

1. Inadequate sample preparation prior to ultra-microtome cutting
2. Ineffective transportation of the cut sample to the TEM grid
3. Inability to accurately employ the appropriate parameters based on the materials properties

The first challenge is inadequate sample preparation which arises if the sample has not been machined into the necessary pyramidal shape. This is because the shape/dimensions of the cutting edge directly affect the thickness of the cut. Hence, if the cutting edge is not small enough, an ultra-thin cut cannot be obtained. On the other hand, if the cutting edge is too small, the edges can form a sharp point which can result in vibrational phenomena [5,8]. Vibrational phenomena adversely affect the quality of the cut which makes it difficult to obtain an ultra-thin cut free of defects [4,5].

The second challenge is in regard to the nanometer size of the cut sample. As previously stated, the goal of this research is to create a repeatable cutting protocol, as well as, to cut an ultra-thin sample slice approximately 25 nm thick. Due to its nanometer size, transportation of the cut sample to the copper grid becomes challenging because the cut sample is not visible to the naked eye. As a result, other options must be utilized in order to make sure that the cut sample is successfully transported to the copper grid. These options include: initially checking the copper grid under the Leica microscope to ensure integrity, using the correct copper grid to ensure that the mesh size is appropriate for the sample size, creating a custom tool to aid in transfer of cut sample to grid, and checking that the sample has been transported onto the copper grid using the Leica microscope and scanning electron microscope, or SEM.

Finally, the last major issue is on the ability to choose the appropriate parameters that will produce an optimal ultra-thin cut. The ultra-microtome allows for the manipulation of various parameters that include: temperature, cutting speed, feed, etc., which directly affects the quality of the cut. Because there exist multiple parameters that can be adjusted, research on structure property
relationships is required in order to deduce how varying specific conditions affect the nature of the material to be cut. One of the major factors that affect the quality of the cut is mechanical stresses, such as compression [25]. Compression occurs during cutting and can be reversible depending on the elasticity of the material [8]. It can be reduced by the spreading of water on the surface [8]. However, if the material is hard or brittle, the samples undergoing excessive stresses will break [6]. For example, if the material is too soft or plastic, the sample will crush upon cutting and will not yield a slice. Figure 21 illustrates the compression exerted on the sample and the reaction depending on the hardness [8]. Table 2 includes a list of parameters and ranges that require further investigation. For each sample, the feed will be kept constant at 25 nm.

Fig. 21. Stresses by ductile or brittle material during sectioning.
CHAPTER EIGHT

DEVELOPMENT OF CUSTOMIZED Fixture

8.1 Function of Fixture

The purpose of creating a customized tool is to aid in the sample collection process. Currently, collecting the sample is tedious due to its nanosize nature. In most cases, the 25 nm sample is not successfully transported onto the TEM grid because it is not visible to the naked eye. The goals of the customized tool are to: 1) Decrease the transportation distance from cut sample to TEM grid, and 2) To allow for the ability to transport the cut sample to TEM grid under same optical view.

8.2 Fixture Development

The custom tool design was created using SolidWorks and then produced using a Objet30 3D Printer. The material selected for the custom tool was VeroWhite. Figure 22 illustrates the first design of the custom tool. The overall design consists of a male piece that slides into a female piece. The female piece can stay placed onto the diamond knife from initial sample shaping until the sample surface is ready to be sectioned. When the sample surface is ready for sectioning, a TEM grid is placed onto the end of the male piece and slid into place onto the female piece.

Fig. 22. Initial fixture design.
After testing the initial design on the ultra-microtome, it became apparent that there needs to be a few minor changes made to the design. First, the male piece needs to have some type of grip in order to grasp the male piece and slide it easily onto and off of the female piece. In addition, the female piece needs to have some type of support that wraps around the back of the diamond knife to ensure stability. Figure 23 illustrates the final design with the necessary improvements. Figure 24 is the final fixture in cutting actions.

![Diagram showing grip and support features](image)

Fig. 23. Custom tool development: A) Final fixture design. B) 3D printed fixture assembly.

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Safe for diamond knife</td>
<td>Materials may become brittle at lower temperature</td>
</tr>
<tr>
<td>User friendly</td>
<td>Needs carefully refined guides to slide male piece</td>
</tr>
<tr>
<td></td>
<td>smoothly into female piece</td>
</tr>
<tr>
<td>Sample and grid under same optical view</td>
<td></td>
</tr>
<tr>
<td>Cheap to produce (3D printing)</td>
<td></td>
</tr>
<tr>
<td>Ability to use in RT and cryogenic setups</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 24. Custom tool attached to diamond knife for final sectioning.
CHAPTER NINE
PARAMETER SELECTION

9.1 Cutting Parameters

One of the main goals of this research is to choose the suitable parameters or cutting conditions that minimize the cutting forces, which in turn, minimize the total work done during the cutting process. This will lead to obtaining a high quality, defect free ultra-thin sample slice. Table 4 illustrates the cutting parameters and conditions that were studied for each respective sample. In addition, the cutting sample thickness will be held constant at 25 nm.

Table 4: Parameters to be investigated

<table>
<thead>
<tr>
<th>Sample</th>
<th>Speed (mm/s)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UD IM7/BMI</td>
<td>1</td>
<td>Room temperature (RT), -80</td>
</tr>
<tr>
<td>Single-layer CNT BP/epoxy</td>
<td>1</td>
<td>RT, -80</td>
</tr>
<tr>
<td>3-Layer CNT BP/BMI</td>
<td>1,10</td>
<td>RT, -80</td>
</tr>
</tbody>
</table>

Also, in addition to studying suitable cutting parameters for each sample, choosing the appropriate clearance angle is equally important. The clearance angle will depend on the face of the sample block. Figure 24 provides an illustration of how to choose the appropriate clearance angle. Table 5 summarizes the effects of clearance angle selection.

Fig. 25. Clearance angle effect [29].
Table 5: Effects of clearance angle [29]

<table>
<thead>
<tr>
<th>Clearance Angle Classification</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Too Steep</td>
<td>• Shatter (lines running parallel to knife on sample)</td>
</tr>
<tr>
<td></td>
<td>• Soft section may roll up</td>
</tr>
<tr>
<td></td>
<td>• Knife may dive into sample block</td>
</tr>
<tr>
<td>Too Shallow</td>
<td>• Breakage of sample block</td>
</tr>
<tr>
<td></td>
<td>• Breakage of diamond knife</td>
</tr>
<tr>
<td></td>
<td>• Vibrational effect</td>
</tr>
</tbody>
</table>

The parameters displayed in Table 3 were selected based on the materials mechanical properties and their microstructure features. Table 6 provides the tensile strength and modulus of the component materials that were investigated in this research. The tensile strength and modulus were taken into consideration when selecting the cutting speed and cutting temperature for each material. For example, a low cutting speed of 1 mm/s was selected to cut the UD IM7/BMI composites because of their high mechanical properties. A fast cutting speed is not ideal and could result in damage of the diamond knife or cracking of the sample block.

Table 6: Tensile strength and young’s modulus of respective materials [30-35]

<table>
<thead>
<tr>
<th>Materials</th>
<th>Tensile Strength (GPa)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Fiber (IM7)</td>
<td>5</td>
<td>300</td>
</tr>
<tr>
<td>CNTs</td>
<td>11-63</td>
<td>70-100</td>
</tr>
<tr>
<td>3-Layer BP/BMI Nanocomposites</td>
<td>0.877</td>
<td>103.4</td>
</tr>
<tr>
<td>1-Layer BP/BMI Nanocomposites</td>
<td>0.520</td>
<td>95</td>
</tr>
<tr>
<td>Epoxy and BMI resin</td>
<td>0.06 -0.100</td>
<td>3 -4</td>
</tr>
</tbody>
</table>

9.2 Structure-Property Relationships for Respective Materials

Carbon fiber
• Graphitic layers formed by strong covalent bonds along the axis direction[31,33,35]
• Carbon fiber filaments with a diameter of 5-8 micrometers [31,33]
CNT Buckypaper Sheets

- SWNT or MWNTs of cylindrical nanostructure wrapped from graphene sheet/tubule structure [31]
- 1D, perfect nanotube structures resulting in strong/higher properties [31,33]
- Small diameter which means less defects [31]
- Large aspect ratio allows SWNTs to behave like idea 1D quantum wires [31,33]

Epoxy and BMI resin Matrices

- Thermosetting polymers
- Amorphous microstructures
CHAPTER TEN

TEM RESULTS AND DISCUSSION

The purpose for obtaining high quality TEM images is to be able to identify the microstructure and interface at a molecular level solution, as well as to be able to understand the overall structure-property relationship. One of the key areas that requires further investigation is the interphase region. The interphase region is the area between the matrix and the fiber or CNT and defines the integrity of the composite as a whole. Weak interfacial bonding results in a material having poor mechanical properties, whereas strong interfacial bonding results in optimum properties such as high strength and high modulus. By studying the crystalline packing and the interphase interactions (nanotube with nanotube, nanotube with resin, etc.) for each of the respective samples, we can provide more evidences as to what defines a weak or strong interphase. TEM images from different samples and cutting parameters are discussed in the next sections. TEM images were taken using the JEM-ARM200cF (A Sub-angström Cs Corrected Transmission/Scanning Transmission Electron Microscope from JEOL) at 80 kV and ultra-thin specimen samples were obtained using the Leica EM-UC6 (ultra-microtome) with different cutting parameters. The custom tool was used in the sample collection process for the single-layer CNT BP/epoxy nanocomposite and the 3-layer CNT BP/BMI nanocomposite.

10.1 UD IM7/BMI Composite

The UD IM7/BMI composites were prepared using the Buelter Microcut and then shaped to have a 0.1 mm² cutting surface under the ultra-microtome using a glass knife. Also, the glass knife was used to smooth the cutting surface of the sample. Once the cutting surface appeared to have a glassy finish, the glass knife and diamond knife were interchanged. Table 7 illustrates the cutting parameters selected to cut the UD IM7/BMI composite.

Table 7: Parameter selection for UD IM7/BMI composite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Speed (mm/s)</th>
<th>Feed (nm)</th>
<th>Approach Step (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UD IM7/BMI</td>
<td>RT &amp; -80</td>
<td>1</td>
<td>25</td>
<td>0.1</td>
</tr>
</tbody>
</table>
Good sample slices were achieved for the UD IM7/BMI composite sample cut at room temperature (RT). However, sample slices were not able to be achieved at cryogenic temperatures. Cutting at cryogenic temperatures resulted in scratching of the sample block.

TEM images of the room temperature cut sample were taken from low magnification to high magnification. The objective was to view the uniformity of the cut sample crossing large areas. At low magnification, TEM results reveal variations of the sample thickness. This is visible in Figure 26 in which thinner areas are located at the edge of the sample, while thicker areas are located towards the center of the sample. At high magnifications, TEM results reveal a decrease in variation, and an increase in uniformity. Figure 27 illustrates the red region at a higher magnification. Further increasing the magnification results in an area that has a more uniform thickness. This is illustrated in Figure 28.

![Fig.26 Low magnification of UD IM7/BMI composite.](image1)

![Fig.27 Decrease in variation at higher magnification.](image2)
In addition, Figure 28 TEM results reveal a clear microstructure of the IM7 carbon fiber and BMI resin matrix. The UD IM7/BMI composite microstructure consists of both crystalline and amorphous regions. The crystalline regions consist of visible graphite packing structure, while the amorphous regions lack long range order within the fiber. Amorphous region of the resin is clearly distinguished. A drawback to this TEM image is that the interphase is not visible.

Fig. 28 CF composite cut at 25 nm.

10.2 Single-layer CNT BP/Epoxy Nanocomposite

The single-layer CNT BP/epoxy nanocomposite was prepared by soaking the BP CNT sheets in 8552 resin epoxy for 30 minutes and then baking it in the oven at 120°C for 7 hours. The glass transition (Tg) of the CNT BP/epoxy nanocomposite sample was 300°C. Next, the sample was embedded in Armorstar resin and cured at room temperature. After the sample was cured, the cutting surface was shaped to achieve a 0.1 mm cutting surface by both the Buelter Microcut and glass knife. 25 nm samples were collected and placed onto a TEM grid using the custom tool designed in Chapter 8. Cutting parameters are displayed in Table 8.

35
Table 8: Parameter selection for single-layer CNT BP/epoxy nanocomposite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Speed (mm/s)</th>
<th>Feed (nm)</th>
<th>Approach Step (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-layer CNT BP/epoxy</td>
<td>RT &amp; -80</td>
<td>1</td>
<td>25</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Cutting at -80°C resulted in obtaining a cleaner sample slice. TEM images were taken from low magnification to high magnification to view the uniformity of the cut sample. In Figure 29A, the thickness appears to be uniform throughout the cut sample, except for where there is visible nanotube pullout. Figure 29B illustrates a high magnification TEM image of the nanotube pullout region. Upon further increasing the magnification, Figure 30 reveals a clear microstructure including visible nanotube flat packing and defined nanotube boundaries.

Fig.29 TEM images: (A) Low magnification. (B) High magnification.
Figure 30 illustrates another good high magnification TEM image. Figure 31 reveals a distinct interphase region, nanotubes adequately covered by resin epoxy, as well as, the alignment direction of the nanotubes. In addition, flatten CNT packing is visible due to the nanotubes having a large diameter and collapsing. This is similar to Alan Windle’s TEM image illustrating the collapsing of nanotubes into a dumbbell shape found in Figure 32 [36].

Fig.31 NC Nanotube nanocomposite cut at 25 nm.
Fig. 32 Alan Windle’s image of flat packing [36].

Another good TEM image of the CNT BP/epoxy nanocomposite is depicted in Figure 33. Figure 33 reveals that the sample was cut with a uniform thickness, which allows the microstructure to be clearly visible. In addition, this TEM image reveals nanotubes covered by resin, a clear boundary of the nanotubes, and nanotube flatten packing and interface zones.

![Fig.33 TEM image showing cut sample with uniform thickness.](image)

**10.3 3-Layer BP/BMI Nanocomposites**

The 3-layer BP/BMI sample consisted of 3 layers of stretched BP and BMI resin matrix [37,38]. The stretch media used was water and the stretch ratio was approximately 30-35% [37].
The process consisted of water stretching, roller pressing, then soaking in BMI [37,38]. Finally, the sample was embedded in Armorstar Resin, cured at room temperature, and shaped to have a 0.1 mm cutting surface using a glass knife. Table 9 illustrates the selected parameters.

Table 9: Parameter selection for 3-layer BP/BMI nanocomposite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Speed (mm/s)</th>
<th>Feed (nm)</th>
<th>Approach Step (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-layer BP/BMI</td>
<td>RT &amp; -80</td>
<td>1</td>
<td>25</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Good TEM images were obtained cutting the sample slices at -80°C. Figure 34 illustrates TEM images taken from low to high magnification in order to view the uniformity of the cut sample. Figure 34A reveals that the cut sample was not placed flat on the TEM copper grid. As a result, some areas appear thicker due to layering or folding of the cut sample slices. As the magnification is increased in Figure 34B, we see that catalysts are located throughout the sample. However, further increasing the magnification, the catalysts may or may not be visible as in the cases of Figures 34C and 34D. Figure 34D is analyzed further in Figure 35.

Fig.34 TEM images of: (A) Uniformly cut sample slice. (B) Numerous catalysts visible. (C) Minimal catalyst visible. (D) No catalysts visible.
Figure 35 reveals a clear identifiable microstructure of the 3-layer BP/BMI sample. Amorphous resin regions can be seen coating the outer edges of the nanotube walls which signifies good adhesion. Also, there is distinct nanotube bundle packing between amorphous resin. Also, this TEM image reveals the deformation of nanotubes into a v, or cone-like shape. This is most likely due to the stress of the nanotube when cutting via ultra-microtome.

![Figure 35 3-Layer BP/BMI with deformed nanotubes cut at -80°C.](image)

Figure 36 reveals a uniformly cut sample slice with a distinct pattern of alternating amorphous resin and graphite crystalline packing cut at -80°C. In addition, nanotube bundles are visible in the crystalline regions with minimal overlapping of the amorphous resin. The transition region between the amorphous resin and graphite crystalline region is referred to as the interfacial zone. To obtain more information on this region, thinner sample slices are required (< 25 nm).
Figure 36 Alternating amorphous and crystalline regions cut at -80°C.

Figure 37 illustrates another good TEM image of the 3-layer BP/BMI composite cut at -80°C. Here, the nanotube bundles, amorphous regions, and catalysts are clearly identifiable. The catalysts are signified by surrounding areas of crystalline packing.

Fig.37 Numerous catalysts visible in amorphous regions.
TEM results also reveal a difference in the thickness of the resin and nanotube regions when cutting using the diamond knife. Figure 38 shows the regions of amorphous resin as having an even, uniformly cut thickness. However, once the diamond knife reached the highly concentrated nanotube region, the cut became slightly thicker or the nanotube bundles fold over themselves. This is most likely a result of the nanotubes high mechanical properties, which cause it to bend and not break from the stress of cutting.

Fig.38 Nanotube bundles folded over.
CHAPTER ELEVEN

CONCLUSION

From this research, a protocol was setup to ensure that ultra-thin sample slices can be achieved by different microtome operators for high resolution TEM analysis. In addition, a custom fixture was created to solve the sample collection efficiency. Three composite samples were analyzed under TEM: 1) UD IM7/BMI composite; 2) Single-layer CNT BP/epoxy nanocomposite; 3) 3-layer CNT BP/BMI nanocomposite. Good sample slices were achieved for the UD IM7/BMI composite sample cut at room temperature. Sample slices cut at cryogenic temperatures resulting in scratching of the sample and the inability to get a clean sample slice. TEM results revealed an evenly cut sample slice with a clear microstructure consisting of amorphous resin and graphite crystalline packing. However, an interfacial region was not visible resulting in the need for even thinner sliced cross sections. Good sample slices were achieved for the single-layer CNT BP/epoxy nanocomposite cut at -80°C. TEM results revealed visible flattening of CNT packing into dumbbell shapes, as well as, a clear distinction between the amorphous resin, interface, and crystalline packing regions. Cutting at RT resulted in separation or bending of the sample embedded in Armorstar resin. Finally, TEM results for the 3-layer BP/BMI nanocomposite cut at -80°C revealed uniformly cut resin. However, when the diamond knife reached graphite crystalline regions, the nanotube either became deformed into a cone-like structure, was cut at a thicker thickness than the resin, or folded over onto itself. This is most likely a result of the nanotubes high mechanical properties.
CHAPTER TWELVE

FUTURE WORK

One of the major challenges encountered during this research was to make sure that the cut cross section lay completely flat on the TEM grid. Also, that they did not fall on top of each other creating layers. This is illustrated in Figure 34.

![Layering of cut sample slices](image)

**Fig. 39 Layering of cut sample slices.**

One way to remediate this issue is to drop a small amount of IPA onto the TEM grid. This makes the sample less dense and causes the cut sample to adhere better to the TEM grid. However, a limitation is that dropping the IPA onto the TEM grid can cause the cut sample to be pushed off of or moved to the edge of the TEM grid. Another issue is that the cut sample is still not thin enough in order to obtain a clear visual on the molecular microstructure, specifically the interface. More research on parameter selection is required to obtain even thinner sample slices.
REFERENCES


31. Dr. Richard Liang’s notes from Advanced Composites (Spring 2013).


BIOGRAPHICAL SKETCH

Sarah Trayner earned her Bachelor of Science degree in Industrial Engineering with Honors, Cum Laude, from Florida State University in 2012. In 2014, she received her Master of Science degree in Material Science and Engineering from Florida State University.